ADVANCED STATISTICAL MECHANICS

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Advanced Statistical Mechanics (Tuckerman)

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This text was compiled on 03/10/2025

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CHAPTER OVERVIEW

1: Classical mechanics

1.1: The Lagrangian Formulation of Classical Mechanics

In order to begin to make a connection between the microscopic and macroscopic worlds, we need to better understand the microscopic world and the laws that govern it. We will begin placing Newton's laws of motion in a formal framework which will be heavily used in our study of classical statistical mechanics.

First, we begin by restricting our discussion to systems for which the forces are purely *conservative*. Such forces are derivable from a potential energy function $U(r_1, \cdots, r_N)$ by differentiation:

$$F_i = -\frac{\partial U}{\partial r_i}$$

It is clear that such forces cannot contain dissipative or friction terms. An important property of systems whose forces are conservative is that they conserve the total energy

$$E = K + U = \frac{1}{2}\sum_{i=1}^{N} m_i \dot{r}_i^2 + U(r_1, \cdots, r_N)$$

To see this, simply differentiate the energy with respect to time:

$$\begin{aligned}\frac{dE}{dt} &= \sum_{i=1}^{N} m_i \dot{r}_i \cdot \ddot{r}_i + \sum_{i=1}^{N} \frac{\partial U}{\partial r_i} \cdot \dot{r}_i \\ &= \sum_{i=1}^{N} \dot{r}_i \cdot F_i - \sum_{i=1}^{N} F_i \cdot \dot{r}_i \\ &= 0\end{aligned}$$

where, the second line, the facts that $\ddot{r}_i = \frac{F_i}{m_i}$ (Newton's law) and $F_i = -\frac{\partial U}{\partial r_i}$ (conservative force definition) have been used. This is known as the law of *conservation of energy*.

For conservative systems, there is an elegant formulation of classical mechanics known as the *Lagrangian* formulation. The *Lagrangian* function, L, for a system is defined to be the difference between the kinetic and potential energies expressed as a function of positions and velocities. In order to make the nomenclature more compact, we shall introduce a shorthand for the complete set of positions in an N-particle system: $r \equiv r_1, \cdots, r_N$ and for the velocities: $\dot{r} \equiv \dot{r}_1, \cdots, \dot{r}_N$. Then, the Lagrangian is defined as follows:

$$L(r, \dot{r}) = K - U = \sum_{i=1}^{N} \frac{1}{2} m_i \dot{r}_i^2 - U(r_1, \cdots, r_N)$$

In terms of the Lagrangian, the classical equations of motion are given by the so called *Euler-Lagrange* equation:

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{r}_i}\right) - \frac{\partial L}{\partial r_i} = 0$$

The equations that result from application of the Euler-Lagrange equation to a particular Lagrangian are known as the *equations of motion*. The solution of the equations of motion for a given initial condition is known as a *trajectory* of the system. The Euler-Lagrange equation results from what is known as an *action principle*. We shall defer further discussion of the action principle until we study the Feynman path integral formulation of quantum statistical mechanics in terms of which the action principle emerges very naturally. For now, we accept the Euler-Lagrange equation as a definition.

The Euler-Lagrange formulation is completely equivalent to Newton's second law. In order to see this, note that

$$\begin{aligned}\frac{\partial L}{\partial \dot{r}_i} &= m_i \dot{r}_i \\ \frac{\partial L}{\partial r_i} &= -\frac{\partial U}{\partial r_i} = F_i\end{aligned}$$

Therefore,

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{r}_i}\right)-\frac{\partial L}{\partial r_i}=m_i\ddot{r}_i-F_i=0$$

which is just Newton's equation of motion.

An important property of the Lagrangian formulation is that it can be used to obtain the equations of motion of a system in *any set of coordinates*, not just the standard Cartesian coordinates, via the Euler-Lagrange equation (see problem set #1).

1.2: The Hamiltonian formulation of classical mechanics

The Lagrangian formulation of mechanics will be useful later when we study the Feynman path integral. For our purposes now, the Lagrangian formulation is an important springboard from which to develop another useful formulation of classical mechanics known as the *Hamiltonian* formulation. The Hamiltonian of a system is defined to be the sum of the kinetic and potential energies expressed as a function of positions and their *conjugate momenta*. What are conjugate momenta?

Recall from elementary physics that momentum of a particle, P_i, is defined in terms of its velocity $\dot{r}_i$ by

$$p_i = m_i \dot{r}_i$$

In fact, the more general definition of conjugate momentum, valid for any set of coordinates, is given in terms of the **Lagrangian**:

$$p_i = \frac{\partial L}{\partial \dot{r}_i}$$

Note that these two definitions are equivalent for Cartesian variables. In terms of Cartesian momenta, the kinetic energy is given by

$$K = \sum_{i=1}^{N} \frac{P_i^2}{2m_i}$$

Then, the Hamiltonian, which is defined to be the sum, $K + U$, expressed as a function of positions and momenta, will be given by

$$H(p,r) = \sum_{i=1}^{N} \frac{P_i^2}{2m_i} + U(r_1, \cdots, r_N) = H(p,r)$$

where $p \equiv p_1, \cdots, p_N$. In terms of the Hamiltonian, the equations of motion of a system are given by *Hamilton's equations*:

$$\dot{r}_i = \frac{\partial H}{\partial p_i} \dot{p}_i = -\frac{\partial H}{\partial r_i}$$

The solution of Hamilton's equations of motion will yield a trajectory in terms of positions and momenta as functions of time. Again, Hamilton's equations can be easily shown to be equivalent to Newton's equations, and, like the Lagrangian formulation, Hamilton's equations can be used to determine the equations of motion of a system in any set of coordinates.

The Hamiltonian and Lagrangian formulations possess an interesting connection. The Hamiltonian can be directly obtained from the Lagrangian by a transformation known as a *Legendre transform*. We will say more about Legendre transforms in a later lecture. For now, note that the connection is given by

$$H(p,r) = \sum_{i=1}^{N} p_i \cdot \dot{r}_i - L(r, \dot{r})$$

which, when the fact that $\dot{r}_i = \frac{p_i}{m_i}$ is used, becomes

$$\begin{aligned} H(p,r) &= \sum_{i=1}^{N} p_i \cdot \frac{p_i}{m_i} - \sum_{i=1}^{N} \frac{1}{2} m_i \left(\frac{p_i}{m_i} \right)^2 + U(r_1, \cdots, r_N) \\ &= \sum_{i=1}^{N} \frac{P_i^2}{2m_i} + U(r_1, \cdots, r_N) \end{aligned}$$

Because a system described by conservative forces conserves the total energy, it follows that Hamilton's equations of motion conserve the total Hamiltonian. Hamilton's equations of motion conserve the Hamiltonian

$$H(p(t), r(t)) = H(p(0), r(0)) = E$$

Proof

$H = \text{const} \Rightarrow \frac{dH}{dt} = 0$

$$\frac{dH}{dt} = \sum_{i=1}^{N}\left(\frac{\partial H}{\partial r_i}\cdot\dot{r}_i + \frac{\partial H}{\partial p_i}\cdot\dot{p}_i\right)$$

$$= \sum_{i=1}^{N}\left(\frac{\partial H}{\partial r_i}\cdot\frac{\partial H}{\partial p_i} - \frac{\partial H}{\partial p_i}\cdot\frac{\partial H}{\partial r_i}\right) = 0$$

QED. This, then, provides another expression of the law of conservation of energy.

1.3: The Microscopic Laws of Motion

Consider a system of N classical particles. The particles a confined to a particular region of space by a "container" of volume V. The particles have a finite kinetic energy and are therefore in constant motion, driven by the forces they exert on each other (and any external forces which may be present). At a given instant in time t, the Cartesian positions of the particles are $r_1(t), \cdots, r_N(t))$) . The time evolution of the positions of the particles is then given by Newton's second law of motion:

$$m_i \ddot{r}_i = F_i(r_1, \cdots, r_N)$$

where $F_1, \cdots, F_N$ are the forces on each of the N particles due to all the other particles in the system. The notation $\ddot{r}_i = \frac{d^2 r_i}{dt^2}$.

N Newton's equations of motion constitute a set of $3N$ coupled second order differential equations. In order to solve these, it is necessary to specify a set of appropriate initial conditions on the coordinates and their first time derivatives, $\{r_1(0), \cdots, r_N(0), \dot{r}_1(0), \cdots, \dot{r}_N(0)\}$. Then, the solution of Newton's equations gives the complete set of coordinates and velocities for all time t.

1.4: Phase Space

We construct a Cartesian space in which each of the $6N$ coordinates and momenta is assigned to one of $6N$ mutually orthogonal axes. Phase space is, therefore, a $6N$ dimensional space. A point in this space is specified by giving a particular set of values for the $6N$ coordinates and momenta. Denote such a point by

$$x = (p_1, \cdots, p_N, r_1, \cdots, r_N)$$

x is a $6N$ dimensional vector. Thus, the time evolution or trajectory of a system as specified by Hamilton's equations of motion, can be expressed by giving the phase space vector, x as a function of time.

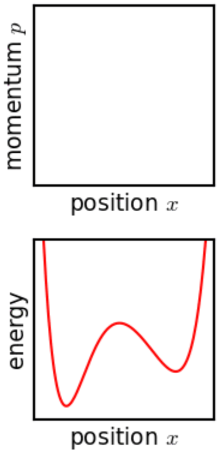

Figure 1.4.1: Evolution of an ensemble of classical systems in phase space (top). The systems are a massive particle in a one-dimensional potential well (red curve, lower figure). The initially compact ensemble becomes swirled up over time.

The law of conservation of energy, expressed as a condition on the phase space vector:

$$H(x(t)) = \text{const} = E$$

defines a $6N-1$ dimensional hypersurface in phase space on which the trajectory must remain.

1.5: Classical microscopic states or microstates and ensembles

A *microscopic state* or *microstate* of a classical system is a specification of the complete set of positions and momenta of the system at any given time. In the language of phase space vectors, it is a specification of the complete phase space vector of a system at any instant in time. For a conservative system, any valid microstate must lie on the constant energy hypersurface, $H(x) = E$. Hence, specifying a microstate of a classical system is equivalent to specifying a point on the constant energy hypersurface.

The concept of classical microstates now allows us to give a more formal definition of an ensemble. An ensemble is a collection of systems sharing one or more macroscopic characteristics but each being in a unique microstate. The complete ensemble is specified by giving *all* systems or microstates consistent with the common macroscopic characteristics of the ensemble.

The idea of ensemble averaging can also be expressed in terms of an average over all such microstates (which comprise the ensemble). A given macroscopic property, A, and its microscopic function $a = a(x)$, which is a function of the positions and momenta of a system, i.e. the phase space vector, are related by

$$A = \langle a \rangle_{ensemble} = \frac{1}{N} \sum_{\lambda=1}^{N} a(x_\lambda)$$

where x_λ is the microstate of the λ th member of the ensemble.

1.6: Phase space distribution functions and Liouville's theorem

Given an ensemble with many members, each member having a different phase space vector x corresponding to a different microstate, we need a way of describing how the phase space vectors of the members in the ensemble will be distributed in the phase space. That is, if we choose to observe one particular member in the ensemble, what is the probability that its phase space vector will be in a small volume dx around a point x in the phase space at time t. This probability will be denoted

$$f(x,t)dx$$

where $f(x,t)$ is known as the **phase space probability density** or **phase space distribution function**. It's properties are as follows:

$$f(x,t) \geq (0$$

$$\int dx\, f(x,t) = \text{Number of members in the ensemble}$$

Liouville's Theorem

> The total number of systems in the ensemble is a constant. What restrictions does this place on $f(x,t)$? For a given volume Ω in phase space, this condition requires that the rate of decrease of the number of systems from this region is equal to the flux of systems into the volume.

Let $\hat{n}$ be the unit normal vector to the surface of this region.

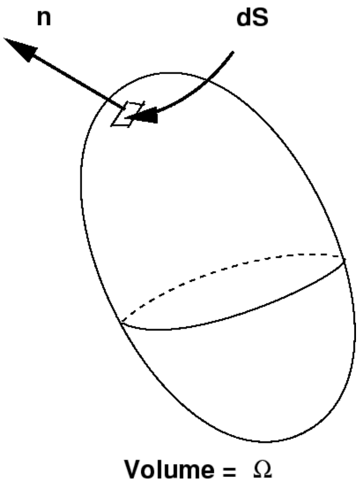

Figure 1.6.1: Divergence through a surface

The flux through the small surface area element, dS is just $\hat{n} \cdot \dot{x} f(x,t) dS$. Then the total flux out of volume is obtained by integrating this over the entire surface that encloses Ω:

$$\int dS \hat{n} \cdot (\dot{x} f(x,t)) = \int_{\Omega} \nabla_x \cdot (\dot{x} f(x,t))$$

which follows from the divergence theorem. ∇_x is the $6N$ dimensional gradient on the phase space

$$\begin{aligned} \nabla_x &= \left(\frac{\partial}{\partial p_1}, \cdots, \frac{\partial}{\partial p_N}, \frac{\partial}{\partial r_1}, \cdots, \frac{\partial}{\partial r_N} \right) \\ &= \left(\nabla_{p_1}, \cdots, \nabla_{p_N}, \nabla_{r_1}, \cdots, \nabla_{r_N} \right) \end{aligned}$$

On the other hand, the rate of decrease in the number of systems out of the volume is

$$-\frac{d}{dt} \int_{\Omega} dx\, f(x,t) = -\int_{\Omega} dx \frac{\partial}{\partial t} f(x,t)$$

Equating these two quantities gives

$$\int_{\Omega} dx \nabla_x \cdot (\dot{x} f(x,t)) = -\int_{\Omega} dx \frac{\partial}{\partial t} f(x,t)$$

But this result must hold for any arbitrary choice of the volume Ω, which we may also allow to shrink to 0 so that the result holds locally, and we obtain the local result:

$$\frac{\partial}{\partial t} f(x,t) + \nabla_x \cdot (\dot{x} f(x,t)) = 0$$

But

$$\nabla_x \cdot (\dot{x} f(x,t)) = \dot{x} \cdot \nabla_x f(x,t) + f(x,t) \nabla_x \cdot \dot{x}$$

This equation resembles an equation for a "hydrodynamic" flow in the phase space, with $f(x,t)$ playing the role of a density. The quantity $\nabla_x \cdot \dot{x}$, being the divergence of a velocity field, is known as the phase space compressibility, and it does not, for a general dynamical system, vanish. Let us see what the phase space compressibility for a Hamiltonian system is:

$$\nabla_x \cdot \dot{x} = \sum_{i=1}^{N} \left[\nabla_{p_i} \cdot \dot{p}_i + \nabla_{r_i} \cdot \dot{r}_i \right]$$

However, by Hamilton's equations:

$$\dot{p}_i = -\nabla_{r_i} H \qquad \qquad \dot{r}_i = \nabla_{p_i} H$$

Thus, the compressibility is given by

$$\nabla_x \cdot \dot{x} = \sum_{i=1}^{N} \left[-\nabla_{p_i} \cdot \nabla_{r_i} H + \nabla_{r_i} \cdot \nabla_{p_i} H \right] = 0$$

Thus, Hamiltonian systems are incompressible in the phase space, and the equation for $f(x,t)$ becomes

$$\frac{\partial}{\partial t} f(x,t) + \dot{x} \cdot \nabla_x f(x,t) = \frac{df}{dt} = 0$$

which is Liouville's equation, and it implies that $f(x,t)$ is a conserved quantity when x is identified as the phase space vector of a particular Hamiltonian system. That is, $f(x_t,t)$ will be conserved along a particular trajectory of a Hamiltonian system. However, if we view x is a *fixed* spatial label in the phase space, then the Liouville equation specifies how a phase space distribution function $f(x,t)$ evolves in time from an initial distribution $f(x,0)$.

CHAPTER OVERVIEW

2: Foundations of classical statistical mechanics

2.1: The Ensemble Concept (Heuristic Definition)

For a typical macroscopic system, the total number of particles $N \sim 10^{23}$. Since an essentially infinite amount of precision is needed in order to specify the initial conditions (due to exponentially rapid growth of errors in this specification), the amount of information required to specify a trajectory is essentially infinite. Even if we contented ourselves with quadrupole precision, however, the amount of memory needed to hold just one phase space point would be about 128 bytes = $2^7 \sim 10^2$ bytes for each number or $10^2 \times 6 \times 10^{23} \sim 10^{17}$ Gbytes. The largest computers we have today have perhaps 10^3 Gbytes of memory, so we are off by 14 orders of magnitude just to specify 1 point in phase space.

✓ **Example 2.1.1**

Do we need all this detail?

Yes

There are plenty of chemically interesting phenomena for which we really would like to know how individual atoms are moving as a process occurs. Experimental techniques such as ultrafast laser spectroscopy can resolve short time scale phenomena and, thus, obtain important insights into such motions. From a theoretical point of view, although we cannot follow 10^{23} particles, there is some hope that we could follow the motion of a system containing 10^4 or 10^5 particles, which might capture most of the features of true macroscopic matter. Thus, by solving Newton's equations of motion numerically on a computer, we have a kind of window into the microscopic world. This is the basis of what are known as *molecular dynamics calculations*.

No

Intuitively, we would expect that if we were to follow the evolution of a large number of systems all described by the same set of forces but having starting from different initial conditions, these systems would have essentially the same macroscopic characteristics, e.g. the same temperature, pressure, etc. even if the microscopic detailed evolution of each system in time would be very different. This idea suggests that the microscopic details are largely unimportant.

Since, from the point of view of macroscopic properties, precise microscopic details are largely unimportant, we might imagine employing a construct known as the *ensemble concept* in which a large number of systems with different microscopic characteristics but similar macroscopic characteristics is used to "wash out" the microscopic details via an averaging procedure. This is an idea developed by individuals such as Gibbs, Maxwell, and Boltzmann.

Ensemble

Consider a large number of systems each described by the same set of microscopic forces and sharing some common macroscopic property (e.g. the same total energy). Each system is assumed to evolve under the microscopic laws of motion from a different initial condition so that the time evolution of each system will be different from all the others. Such a collection of systems is called an **ensemble**. The ensemble concept then states that macroscopic observables can be calculated by performing averages over the systems in the ensemble. For many properties, such as temperature and pressure, which are time-independent, the fact that the systems are evolving in time will not affect their values, and we may perform averages at a particular instant in time. Thus, let A denote a macroscopic property and let a denote a microscopic function that is used to compute A. An example of A would be the temperature, and a would be the kinetic energy (a microscopic function of velocities). Then, A is obtained by calculating the value of a in each system of the ensemble and performing an average over all systems in the ensemble:

$$A = \frac{1}{N}\sum_{\lambda=1}^{N} a_\lambda$$

where N is the total number of members in the ensemble and a_λ is the value of a in the λ th system.

The questions that naturally arise are:

1. How do we construct an ensemble?
2. How do we perform averages over an ensemble?
3. How many systems will an ensemble contain?
4. How do we distinguish time-independent from time-dependent properties in the ensemble picture?

Answering these questions will be our main objective in Statistical Mechanics.

2.2: Liouville's Theorem for non-Hamiltonian systems

The equations of motion of a system can be cast in the generic form

$$\dot{x} = \xi(x)$$

where, for a Hamiltonian system, the vector function ξ would be

$$\xi(x) = \left(-\frac{\partial H}{\partial r_1}, \cdots, -\frac{\partial H}{\partial r_N}, \frac{\partial H}{\partial p_1}, \cdots, \frac{\partial H}{\partial p_N}\right)$$

and the incompressibility condition would be a condition on ξ:

$$\Delta_x \cdot \dot{x} = \Delta_x \cdot \xi = 0$$

A non-Hamiltonian system, described by a general vector funciton ξ, will not, in general, satisfy the incompressibility condition. That is:

$$\Delta_x \cdot \dot{x} = \Delta_x \cdot \xi \neq 0$$

Non-Hamiltonian dynamical systems are often used to describe open systems, i.e., systems in contact with heat reservoirs or mechanical pistons or particle reservoirs. They are also often used to describe driven systems or systems in contact with external fields.

The fact that the compressibility does not vanish has interesting consequences for the structure of the phase space. The Jacobian, which satisfies

$$\frac{dJ}{dt} = J\Delta_x \cdot \dot{x}$$

will no longer be 1 for all time. Defining $k = \Delta_x \cdot \dot{x}$, the general solution for the Jacobian can be written as

$$J(x_t; x_0) = J(x_0; x_0) exp\left(\int_0^t dRk(x_A)\right)$$

Note that $J(x_0; x_0) = 1$ as before. Also, note that $k = d\ln\frac{J}{dt}$. Thus, k can be expressed as the total time derivative of some function, which we will denote *W*, i.e., $k = \dot{W}$. Then, the Jacobian becomes

$$\begin{aligned} J(x_t; x_0) &= exp\left(\int_0^t dRW(x_A)\right) \\ &= exp(W(x_t) - W(x_0)) \end{aligned}$$

Thus, the volume element in phase space now transforms according to

$$dx_t = exp\left(W(x_t) - W(x_0)\right) dx_0$$

which can be arranged to read as a conservation law:

$$e^{-W(x_t)} dx_t = e^{-W(x_0)} dx_0$$

{

Thus, we have a conservation law for a modified volume element, involving a "metric factor" $exp(-W(x))$. Introducing the suggestive notation $\sqrt{g} = exp(-W(x))$, the conservation law reads $\sqrt{g(x_t} dx_t = \sqrt{g(x_0} dx_0$. This is a generalized version of Liouville's theorem. Furthermore, a generalized Liouville equation for non-Hamiltonian systems can be derived which incorporates this metric factor. The derivation is beyond the scope of this course, however, the result is

$$\partial(f\sqrt{g}) + \nabla_x \cdot (\dot{x} f\sqrt{g}) = 0$$

We have called this equation, the **generalized Liouville equation** Finally, noting that $\sqrt{g}$ satisfies the same equation as *J*, i.e.,

$$\frac{d\sqrt{g}}{dt} = k\sqrt{g}$$

the presence of $\sqrt{g}$ in the generalized Liouville equation can be eliminated, resulting in

$$\frac{\partial f}{\partial t} + \dot{x} \cdot \nabla_x f = \frac{df}{dt} = 0$$

which is the ordinary Liouville equation from before. Thus, we have derived a modified version of Liouville's theorem and have shown that it leads to a conservation law for f equivalent to the Hamiltonian case. This, then, supports the generality of the Liouville equation for both Hamiltonian and non-Hamiltonian based ensembles, an important fact considering that this equation is the foundation of statistical mechanics.

2.3: The Liouville Operator and the Poisson Bracket

From the last lecture, we saw that Liouville's equation could be cast in the form

$$\frac{\partial f}{\partial t} + \nabla_x \cdot \dot{x} f = 0$$

The **Liouville equation** is the foundation on which statistical mechanics rests. It will now be cast in a form that will be suggestive of a more general structure that has a definite quantum analog (to be revisited when we treat the quantum Liouville equation).

Define an operator

$$iL = \dot{x} \cdot \nabla_x$$

known as the **Liouville operator** ($i = \sqrt{-1}$ - the *i* is there as a matter of convention and has the effect of making L a Hermitian operator). Then Liouville's equation can be written

$$\frac{\partial f}{\partial t} + iLf = 0$$

The Liouville operator also be expressed as

$$iL = \sum_{i=1}^{N} \left[\frac{\partial H}{\partial p_i} \cdot \frac{\partial}{\partial r_i} - \frac{\partial H}{\partial r_i} \cdot \frac{\partial}{\partial p_i} \right] \equiv \{\cdots, H\}$$

where $\{A, B\}$ is known as the **Poisson bracket** between $A(x)$ and $B(x)$:

$$\{A, B\} = \sum_{i=1}^{N} \left[\frac{\partial A}{\partial r_i} \cdot \frac{\partial B}{\partial p_i} - \frac{\partial A}{\partial p_i} \cdot \frac{\partial B}{\partial r_i} \right]$$

Thus, the Liouville equation can be written as

$$\frac{\partial f}{\partial t} + \{f, H\} = 0$$

The Liouville equation is a partial differential equation for the phase space probability distribution function. Thus, it specifies a general class of functions $f(x, t)$ that satisfy it. In order to obtain a specific solution requires more input information, such as an initial condition on *f*, a boundary condition on *f*, and other control variables that characterize the ensemble.

2.4: Equilibrium ensembles

An equilibrium ensemble is one for which there is no explicit time-dependence in the phase space distribution function, $\frac{\partial f}{\partial t} = 0$. In this case, Liouville's equation reduces to

$$\{f, H\} = 0$$

which implies that $f(x)$ must be a pure function of the Hamiltonian

$$f(x) = F(H(x))$$

The specific form that $F(H(x))$ has depends on the specific details of the ensemble.

The integral over the phase space distribution function plays a special role in statistical mechanics:

$$F = \int dx F(H(x)) \tag{2.4.1}$$

It is known as the partition function and is equal to the number of members in the ensemble. That is, it is equal to the number of microstates that all give rise to a given set of macroscopic observables. Thus, it is the quantity from which all thermodynamic properties are derived.

If a measurement of a macroscopic observable $A(x)$ is made, then the value obtained will be the ensemble average:

$$\langle A \rangle = \frac{1}{F} \int dx A(x) F(H(x)) \tag{2.4.2}$$

Equations 2.4.1 and 2.4.2 are the central results of ensemble theory, since they determine all thermodynamic and other observable quantities.

CHAPTER OVERVIEW

3: The Microcanonical Ensemble

The microcanonical ensemble is built upon the so called postulate of equal *a priori* probabilities:

Postulate of equal a priori probabilities: For an isolated macroscopic system in equilibrium, all microscopic states corresponding to the same set of macroscopic observables are equally probable.

3.1: Basic Thermodynamics

In the microcanonical ensemble, the entropy S is a natural function of N,V and E, i.e., $S = S(N,V,E)$. This can be inverted to give the energy as a function of N, V, and S, i.e., $E = E(N,V,S)$. Consider using Legendre transformation to change from S to T using the fact that

$$T = \left(\frac{\partial E}{\partial S}\right)_{N,V}$$

The Legendre transform $\tilde{E}$ of $E(N,V,S)$ is

$$\begin{aligned}\tilde{E}(N,V,T) &= E(N,V,S(T)) - S\frac{\partial E}{\partial S} \\ &= E(N,V,S(T)) - TS\end{aligned}$$

The quantity $\tilde{E}(N,V,T)$ is called the **Hemlholtz free energy** and is given the symbol $A(N,V,T)$ and is the fundamental energy in the canonical ensemble. The differential of A is

$$dA = \left(\frac{\partial A}{\partial T}\right)_{N,V} dT + \left(\frac{\partial A}{\partial V}\right)_{N,T} dV + \left(\frac{\partial A}{\partial N}\right)_{T,V} dN$$

However, from $A = E - TS$, we have

$$dA = dE - TdS - SdT$$

From the first law, dE is given by

$$dE = TdS - PdV + \mu dN$$

Thus,

$$dA = -PdV - SdT + \mu dN$$

Comparing the two expressions, we see that the thermodynamic relations are

$$S = -\left(\frac{\partial A}{\partial T}\right)_{N,V}$$

$$P = -\left(\frac{\partial A}{\partial V}\right)_{N,T}$$

$$\mu = -\left(\frac{\partial A}{\partial N}\right)_{V,T}$$

3.2: The Partition Function

Consider two systems (1 and 2) in thermal contact such that

- $N_2 \gg N_1$
- $E_2 \gg E_1$
- $N = N_1 + N_2$
- $E = E_1 + E_2$
- $\dim(x_1) \gg \dim(x_2)$

and the total Hamiltonian is just

$$H(x) = H_1(x_1) + H_2(x_2)$$

Since system 2 is infinitely large compared to system 1, it acts as an infinite heat reservoir that keeps system 1 at a constant temperature T without gaining or losing an appreciable amount of heat, itself. Thus, system 1 is maintained at canonical conditions, N, V, T.

The full partition function $\Omega(N, V, E)$ for the combined system is the microcanonical partition function

$$\Omega(N, V, E) = \int dx \delta(H(x) - E) = \int dx_1 dx_2 \delta(H_1(x_1) + H_2(x_2) - E)$$

Now, we define the distribution function, $f(x_1)$ of the phase space variables of system 1 as

$$f(x_1) = \int dx_2 \delta(H_1(x_1) + H_2(x_2) - E)$$

Taking the natural log of both sides, we have

$$\ln f(x_1) = \ln \int dx_2 \delta(H_1(x_1) + H_2(x_2) - E)$$

Since $E_2 \gg E_1$, it follows that $H_2(x_2) \gg H_1(x_1)$, and we may expand the above expression about $H_1 = 0$. To linear order, the expression becomes

$$\begin{aligned} \ln f(x_1) &= \ln \int dx_2 \delta(H_2(x_2) - E) + H_1(x_1) \frac{\partial}{\partial H_1(x_1)} \ln \int dx_2 \delta(H_1(x_1) + H_2(x_2) - E)|_{H_1(x_1)=0} \\ &= \ln \int dx_2 \delta(H_2(x_2) - E) - H_1(x_1) \frac{\partial}{\partial E} \ln \int dx_2 \delta(H_2(x_2) - E) \end{aligned}$$

where, in the last line, the differentiation with respect to H_1 is replaced by differentiation with respect to E. Note that

$$\ln \int dx_2 \delta(H_2(_2) - E) = \frac{S_2(E)}{k}$$

$$\frac{\partial}{\partial E} \ln \int dx_2 \delta(H_2(x_2) - E = \frac{\partial}{\partial E} \frac{S_2(E)}{k} = \frac{1}{kT}$$

where T is the common temperature of the two systems. Using these two facts, we obtain

$$\ln f(x_1) = \frac{S_2(E)}{k} - \frac{H_1(x_1)}{kT}$$

$$f(x_1) = e^{\frac{S_2(E)}{k}} e^{\frac{-H_1(x_1)}{kT}}$$

Thus, the distribution function of the canonical ensemble is

$$f(x) \propto e^{\frac{-H(x)}{kT}}$$

The prefactor $exp(\frac{S_2(E)}{k})$ is an irrelevant constant that can be disregarded as it will not affect any physical properties.

The normalization of the distribution function is the integral:

$$\int dx e^{\frac{-H(x)}{kT}} \equiv Q(N,V,T)$$

where $Q(N,V,T)$ is the canonical partition function. It is convenient to define an inverse temperature $\beta = \frac{1}{kT}$. $Q(N,V,T)$ is the canonical partition function. As in the microcanonical case, we add in the *ad hoc* quantum corrections to the classical result to give

$$Q(N,V,T) = \frac{1}{N!h^{3N}} \int dx e^{-\beta H(x)}$$

The thermodynamic relations are thus,

3.3: The Classical Virial Theorem (Microcanonical Derivation)

Consider a system with Hamiltonian $H(x)$. Let x_i and x_j be specific components of the phase space vector.

Theorem 3.3.1: Classical Virial Theorem

The classical virial theorem states that

$$\langle x_i \frac{\partial H}{\partial x_j} \rangle = kT\delta_{ij}$$

where the average is taken with respect to a microcanonical ensemble.

To prove the theorem, start with the definition of the average:

$$\langle x_i \frac{\partial H}{\partial x_j} \rangle = \frac{C}{\Omega(E)} \int dx x_i \frac{\partial H}{\partial x_j} \delta(E-H(x))$$

where the fact that $\delta(x) = \delta(-x)$ has been used. Also, the N and V dependence of the partition function have been suppressed. Note that the above average can be written as

$$\begin{aligned} \langle x_i \frac{\partial H}{\partial x_j} \rangle &= \frac{C}{\Omega(E)} \frac{\partial}{\partial E} \int dx x_i \frac{\partial H}{\partial x_j} \theta(E-H(x)) \\ &= \frac{C}{\Omega(E)} \frac{\partial}{\partial E} \int_{H(x)<E} dx x_i \frac{\partial H}{\partial x_j} \\ &= \frac{C}{\Omega(E)} \frac{\partial}{\partial E} \int_{H(x)<E} dx x_i \frac{\partial (H-E)}{\partial x_j} \end{aligned}$$

However, writing

$$x_i \frac{\partial (H-E)}{\partial x_j} = \frac{\partial}{\partial x_j}[x_i(H-E)] - \delta_{ij}(H-E)$$

allows the average to be expressed as

$$\begin{aligned} \langle x_i \frac{\partial H}{\partial x_j} \rangle &= \frac{C}{\Omega(E)} \frac{\partial}{\partial E} \int_{H(x)<E} dx \left\{ \frac{\partial}{\partial x_j}[x_i(H-E)] + \delta_{ij}(E-H(x)) \right\} \\ &= \frac{C}{\Omega(E)} \frac{\partial}{\partial E} \left[\oint_{H=E} x_i(H-E) dS_j + \delta_{ij} \int_{H<E} dx (E-H(x)) \right] \end{aligned}$$

The first integral in the brackets is obtained by integrating the total derivative with respect to x_j over the phase space variable x_j. This leaves an integral that must be performed over all other variables at the boundary of phase space where $H = E$, as indicated by the surface element dS_j. But the integrand involves the factor $H - E$, so this integral will vanish. This leaves:

$$\begin{aligned} \langle x_i \frac{\partial H}{\partial x_j} \rangle &= \frac{C\delta_{ij}}{\Omega(E)} \frac{\partial}{\partial E} \int_{H(x)<E} dx (E-H(x)) \\ &= \frac{C\delta_{ij}}{\Omega(E)} \int_{H(x)<E} dx \\ &= \frac{\delta_{ij}}{\Omega(E)} \Sigma(E) \end{aligned}$$

where $\Sigma(E)$ is the partition function of the uniform ensemble. Recalling that $\Omega(E) = \frac{\partial}{\partial E}\Sigma(E)$ we have

$$
\begin{aligned}
\langle x_i \frac{\partial H}{\partial x_j} \rangle &= \delta_{ij} \frac{\Sigma(E)}{\frac{\partial \Sigma(E)}{\partial E}} \\
&= \delta_{ij} \frac{1}{\frac{\partial \ln \Sigma(E)}{\partial E}} \\
&= k \delta_{ij} \frac{1}{\frac{\partial \tilde{S}}{\partial E}} \\
&= kT \delta_{ij}
\end{aligned}
$$

which proves the theorem.

Example 3.3.1

$x_i = p_i$: and $i = j$ The virial theorem says that

$$\langle p_i \frac{\partial H}{\partial p_j} \rangle = kT$$

$$\langle \frac{p_i^2}{m_i} \rangle = kT$$

$$\langle \frac{p_i^2}{2m_i} \rangle = \frac{1}{2} kT$$

Thus, at equilibrium, the kinetic energy of each particle must be $\frac{kT}{2}$. By summing both sides over all the particles, we obtain a well know result

$$\sum_{i=1}^{3N} \langle \frac{p_i^2}{2m_i} \rangle = \sum_{i=1}^{3N} \langle \frac{1}{2} m_i v_i^2 \rangle = \frac{3}{2} NkT$$

CHAPTER OVERVIEW

4: The Canonical Ensemble

4.1: Classical Virial Theorem (Canonical Ensemble Derivation)

Again, let x_i and x_j be specific components of the phase space vector $x = (p_1, \cdots, p_{3N}, q_1, \cdots, q_{3N})$. Consider the canonical average

$$\langle x_i \frac{\partial H}{\partial x_j} \rangle$$

given by

$$\begin{aligned} \langle x_i \frac{\partial H}{\partial x_j} \rangle &= \frac{1}{Q} C_N \int dx x_i \frac{\partial H}{\partial x_j} e^{-\beta H(x)} \\ &= \frac{1}{Q} C_N \int dx x_i \left(-\frac{1}{\beta} \frac{\partial}{\partial x_j} \right) e^{-\beta H(x)} \end{aligned}$$

But

$$\begin{aligned} x_i \frac{\partial}{\partial x_j} e^{-\beta H(x)} &= \frac{\partial}{\partial x_j} \left(x_i e^{-\beta H(x)} \right) - e^{-\beta H(x)} \frac{\partial x_i}{\partial x_j} \\ &= \frac{\partial}{\partial x_j} \left(x_i e^{-\beta H(x)} \right) - \delta_{ij} e^{-\beta H(x)} \end{aligned}$$

Thus,

$$\begin{aligned} \langle x_i \frac{\partial H}{\partial x_j} \rangle &= -\frac{1}{\beta Q} C_N \int dx \frac{\partial}{\partial x_j} \left(x_i e^{-\beta H(x)} \right) + \frac{1}{\beta Q} \delta_{ij} C_N \int dx e^{-\beta H(x)} \\ &= -\frac{1}{\beta Q} C_N \int dx' \int dx_j \frac{\partial}{\partial x_j} \left(x_i e^{-\beta H(x)} \right) + kT \delta_{ij} \\ &= \int dx' x_i e^{-\beta H(x)} \Big|_{x_j=-\infty}^{\infty} + kT \delta_{ij} \end{aligned}$$

Several cases exist for the surface term $x_i exp(-\beta H(x))$:

1. $x_i = p_i$ a momentum variable. Then, since $H \sim p_i^2, exp(-\beta H)$ evaluated at $p_i = \pm\infty$ clearly vanishes.
2. $x_i = q_i$ and $U \rightarrow \infty$ as $q_i \rightarrow \pm\infty$, thus representing a bound system. Then, $exp(-\beta H)$ also vanishes at $q_i = \pm\infty$.
3. $x_i = q_i$ and $U \rightarrow 0$ as $q_i \rightarrow \pm\infty$, representing an unbound system. Then the exponential tends to 1 both at $q_i = \pm\infty$, hence the surface term vanishes.
4. $x_i = q_i$ and the system is periodic, as in a solid. Then, the system will be represented by some supercell to which periodic boundary conditions can be applied, and the coordinates will take on the same value at the boundaries. Thus, H and $exp(-\beta H)$ will take on the same value at the boundaries and the surface term will vanish.
5. $x_i = q_i$ and the particles experience elastic collisions with the walls of the container. Then there is an infinite potential at the walls so that $U \rightarrow \infty$ at the boundary and $exp(-\beta H) \rightarrow 0$ at the boundary.

Thus, we have the result

$$\langle x_i \frac{\partial H}{\partial x_j} \rangle = kT \delta_{ij}$$

The above cases cover many but not all situations, in particular, the case of a system confined within a volume V with reflecting boundaries. Then, surface contributions actually give rise to an observable pressure (to be discussed in more detail in the next lecture).

4.2: Legendre Transforms

The microcanonical ensemble involved the thermodynamic variables N, V and E as its variables. However, it is often convenient and desirable to work with other thermodynamic variables as the control variables. Legendre transforms provide a means by which one can determine how the energy functions for different sets of thermodynamic variables are related. The general theory is given below for functions of a single variable.

Consider a function $f(x)$ and its derivative

$$y = f'(x) = \frac{df}{dx} \equiv g(x)$$

The equation $y = g(x)$ defines a *variable transformation* from x to y. Is there a unique description of the function $f(x)$ in terms of the variable y? That is, does there exist a function $\phi(y)$ that is equivalent to $f(x)$?

Given a point x_0, can one determine the value of the function $f(x_0)$ given only $f'(x_0)$? No, for the reason that the function $f(x_0)+c$ for any constant c will have the same value of $f'(x_0)$ as shown in Figure $4.2.1$.

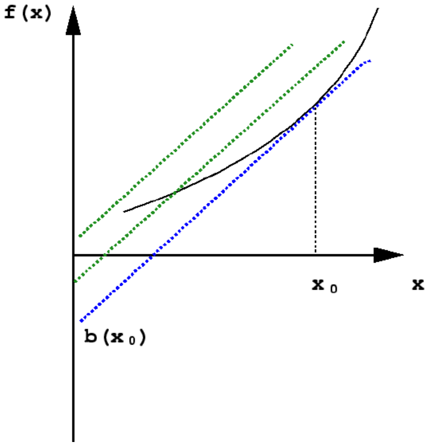

Figure $4.2.1$: The Legendre transfer in action (Mark Tuckerman)

However, the value $f(x_0)$ can be determined uniquely if we specify the slope of the line tangent to f at x_0, i.e., $f'(x_0)$ and the y-intercept, $b(x_0)$ of this line. Then, using the equation for the line, we have

$$f(x_0) = x_0 f'(x_0) + b(x_0)$$

This relation must hold for any general x:

$$f(x) = x f'(x) + b(x)$$

Note that $f'(x)$ is the variable y, and $x = g^{-1}(y)$, where g_{-1} is the functional inverse of g, i.e., $g(g^{-1}(x)) = x$. Solving for $b(x) = b(g^{-1}(y))$ gives

$$b(g^{-1}(y)) = f(g^{-1}(y)) - y g^{-1}(y) \equiv \phi(y)$$

where $\phi(y)$ is known as the **Legendre transform** of $f(x)$. In shorthand notation, one writes

$$\phi(y) = f(x) - xy$$

however, it must be kept in mind that x is a function of y.

4.3: Relation between Canonical and Microcanonical Ensembles

We saw that the $E(N, V, S)$ and $A(N, V, T)$ could be related by a Legendre transformation. The partition functions $\Omega(N, V, E)$ and $Q(N, V, T)$ can be related by a Laplace transform. Recall that the Laplace transform $\tilde{f}(\lambda)$ of a function $f(x)$ is given by

$$\tilde{f}(\lambda) = \int_0^\infty dx e^{-\lambda x} f(x)$$

Let us compute the Laplace transform of $\Omega(N, V, E)$ with respect to E:

$$\tilde{\Omega}(N, V, \lambda) = C_N \int_0^\infty dE e^{-\lambda E} \int dx \delta(H(x) - E)$$

Using the δ-function to do the integral over E:

$$\tilde{\Omega}(N, V, \lambda) = C_N \int dx e^{-\lambda H(x)}$$

By identifying $\lambda = \beta$, we see that the Laplace transform of the microcanonical partition function gives the canonical partition function $Q(N, V, T)$.

4.4: Preservation of Phase Space Volume and Liouville's Theorem

Consider a phase space volume element dx_0 at *t*=0, containing a small collection of initial conditions on a set of trajectories. The trajectories evolve in time according to Hamilton's equations of motion, and at a time *t* later will be located in a new volume element dx_t as shown in the figure below:

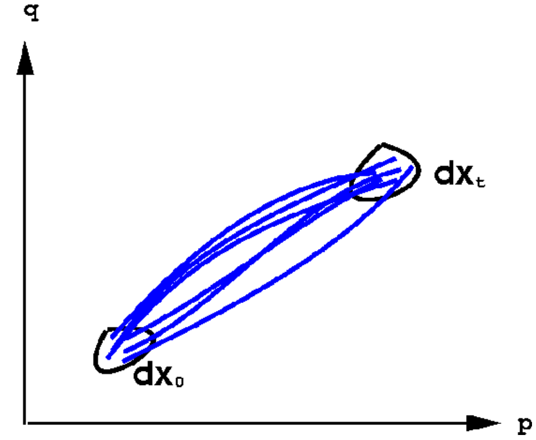

Figure 4.4.1

How is dx_0 related to dx_tdxdd ? To answer this, consider a trajectory starting from a phase space vector x_0 in dx_0 and having a phase space vector x_t at time t in dx_t. Since the solution of Hamilton's equations depends on the choice of initial conditions, x_t depends on x_0 :

$$\begin{aligned} x_0 &= (p_1(0), \cdots, p_N(0), r_1(0), \cdots, r_N(0)) \\ x_0 &= (p_1(t), \cdots, p_N(t), r_1(t), \cdots, r_N(t)) \\ x_t^i &= x_t^i\left(x_0^1, \cdots, x_0^{6N}\right) \end{aligned}$$

Thus, the phase space vector components can be viewed as a coordinate transformation on the phase space from $t = 0$ to time t. The phase space volume element then transforms according to

$$dx_t = J(x_t; x_0) dx_0$$

where $J(x_t; x_0)$ is the Jacobian of the transformation:

$$J(x_t; x_0) = \frac{\partial(x_t^1 \cdots x_t^n)}{\partial(x_0^1 \cdots x_0^n)}$$

where $n = 6N$. The precise form of the Jacobian can be determined as will be demonstrated below.

The Jacobian is the determinant of a matrix M,

$$J(x_t; x_0) = \det(M) = e^{TrlnM}$$

whose matrix elements are

$$M_{ij} = \frac{\partial x_t^i}{\partial x_0^j}$$

Taking the time derivative of the Jacobian, we therefore have

$$\begin{aligned} \frac{dJ}{dt} &= Tr\left(M^{-1}\frac{dM}{dt}\right) e^{TrlnM} \\ &= J \sum_{i=1}^{n} \sum_{j=1}^{n} M_{ij}^{-1} \frac{dM_{ij}}{dt} \end{aligned}$$

The matrices M_{-1} and $\frac{dM}{dt}$ can be seen to be given by

$$M_{ij}^{-1} = \frac{\partial x_0^i}{\partial x_t^j}$$

$$\frac{dM_{ji}}{dt} = \frac{\partial \dot{x}_t^i}{\partial x_0^i}$$

Substituting into the expression for dJ/dt gives

$$\begin{aligned} \frac{dJ}{dt} &= J \sum_{i,j=1}^{n} \frac{\partial x_0^i}{\partial x_t^j} \frac{\partial \dot{x}_t^i}{\partial x_0^i} \\ &= J \sum_{i,j,k=1}^{n} \frac{\partial x_0^i}{\partial x_t^j} \frac{\partial \dot{x}_t^i}{\partial x_t^k} \frac{\partial x_t^k}{\partial x_0^i} \end{aligned}$$

where the chain rule has been introduced for the derivative $\frac{\partial x_t^j}{\partial x_0^i}$. The sum over *i* can now be performed:

$$\sum_{i=1}^{n} \frac{\partial x_0^i}{\partial x_t^j} \frac{\partial x_t^k}{\partial x_0^i} = \sum_{i=1}^{n} M_{ij}^{-1} M_{ki} = \sum_{i=1}^{n} M_{ki} M_{ij}^{-1} = \delta_{kj}$$

Thus,

$$\frac{dJ}{dt} = J \sum_{j,k=1}^{n} \delta_{jk} \frac{\partial \dot{x}_t^j}{\partial x_0^k}$$

$$J \sum_{j=1}^{n} \frac{\partial \dot{x}_t^j}{\partial x_t^j} = J \nabla_x \cdot \dot{x}$$

or

$$\frac{dJ}{dt} = J \nabla_x \cdot \dot{x}$$

The initial condition on this differential equation is $J(0) \equiv J(x_0; x_0) = 1$. Moreover, for a Hamiltonian system $\nabla_x \cdot \dot{x} = 0$. This says that $dJ/dt = 0$ and $J(0) = 1$. Thus, $J(x_t; x_0) = 1$. If this is true, then the phase space volume element transforms according to

$$dx_o = dx_t$$

which is another conservation law. This conservation law states that the phase space volume occupied by a collection of systems evolving according to Hamilton's equations of motion will be preserved in time. This is one statement of Liouville's theorem.

Combining this with the fact that $df/dt = 0$, we have a conservation law for the phase space probability:

$$f(x_o, o) dx_o = f(x_t, t) dx_t$$

which is an equivalent statement of Liouville's theorem.

4.5: Energy Fluctuations in the Canonical Ensemble

In the canonical ensemble, the total energy is not conserved. ($H(x) \neq \text{const}$). What are the fluctuations in the energy? The energy fluctuations are given by the root mean square deviation of the Hamiltonian from its average $\langle H \rangle$:

$$\Delta E = \sqrt{\langle (H - \langle H \rangle)^2 \rangle} = \sqrt{\langle H^2 \rangle - \langle H \rangle^2}$$

$\langle H \rangle = -\frac{\partial}{\partial \beta} \ln Q(N,V,T)$

$\langle H^2 \rangle = \frac{1}{Q} C_N \int dx H^2(x) e^{-\beta H(x)}$ }}

$= \frac{1}{Q} C_N \int dx \frac{\partial^2}{\partial \beta^2} e^{-\beta H(x)}$

$= \frac{1}{Q} \frac{\partial^2}{\partial \beta^2} Q$

$= \frac{\partial^2}{\partial \beta^2} \ln Q + \frac{1}{Q^2} \left(\frac{\partial Q}{\partial \beta}\right)^2$

$= \frac{\partial^2}{\partial \beta^2} \ln Q + \left[\frac{1}{Q}\frac{\partial Q}{\partial \beta}\right]^2$

$= \frac{\partial^2}{\partial \beta^2} \ln Q + \left[\frac{\partial}{\partial \beta} \ln Q\right]^2$

Therefore

$$\langle H^2 \rangle - \langle H \rangle^2 = \frac{\partial^2}{\partial \beta^2} \ln Q$$

But

$$\frac{\partial^2}{\partial \beta^2} \ln Q = kT^2 C_V$$

Thus,

$$\Delta E = \sqrt{kT^2 C_V}$$

Therefore, the relative energy fluctuation $\frac{\Delta E}{E}$ is given by

$$\frac{\Delta E}{E} = \frac{\sqrt{kT^2 C_V}}{E}$$

Now consider what happens when the system is taken to be very large. In fact, we will define a formal limit called the **thermodynamic limit**, in which $N \longrightarrow \infty$ and $V \longrightarrow \infty$ such that $\frac{N}{V}$ remains constant.

Since C_V and E are both extensive variables, $C_V \sim N$ and $E \sim N$,

$$\frac{\Delta E}{E} \sim \frac{1}{\sqrt{N}} \longrightarrow 0 \quad as \quad N \rightarrow \infty$$

But $\frac{\Delta E}{E}$ would be exactly 0 in the microcanonical ensemble. Thus, in the thermodynamic limit, the canonical and microcanonical ensembles are equivalent, since the energy fluctuations become vanishingly small.

CHAPTER OVERVIEW

5: The Isothermal-Isobaric Ensemble

5.1: Basic Thermodynamics

The Helmholtz free energy $A(N,V,T)$ is a natural function of N,V and T. The isothermal-isobaric ensemble is generated by transforming the volume V in favor of the pressure P so that the natural variables are N, P, and T (which are conditions under which many experiments are performed, e.g., `standard temperature and pressure'. Performing a Legendre transformation of the Helmholtz free energy

$$\tilde{A}(N,P,T) = A(N,V(P),T) - V(P)\frac{\partial A}{\partial V}$$

But

$$\frac{\partial A}{\partial V} = -P$$

Thus,

$$\tilde{A}(N,P,T) = A(N,V(P),T) + PV \equiv G(N,P,T)$$

where $G(N,P,T)$ is the Gibbs free energy. The differential of G is

$$dG = \left(\frac{\partial G}{\partial P}\right)_{N,T} dP + \left(\frac{\partial G}{\partial T}\right)_{N,P} dT + \left(\frac{\partial G}{\partial N}\right)_{P,T} dN$$

But from $G = A + PV$, we have

$$dG = dA + PdV + VdP$$

but $dA = -SdT - PdV + \mu dN$, thus

$$dG = -SdT + VdP + \mu dN$$

Equating the two expressions for dG, we see that

$$V = \left(\frac{\partial G}{\partial P}\right)_{N,T}$$

$$S = -\left(\frac{\partial G}{\partial T}\right)_{N,P}$$

$$\mu = \left(\frac{\partial G}{\partial N}\right)_{P,T}$$

5.2: Pressure and Work Virial Theorems

As noted earlier, the quantity $-\partial H/\partial V$ is a measure of the instantaneous value of the internal pressure P_{int}. Let us look at the ensemble average of this quantity

$$\begin{aligned}\langle P_{\text{int}}\rangle &= -\frac{1}{\Delta}C_N\int_0^\infty dV e^{-\beta PV}\int d\text{x}\frac{\partial H}{\partial V}e^{-\beta H(\text{x})} \\ &= \frac{1}{\Delta}C_N\int_0^\infty dV e^{-\beta PV}\int d\text{x}kT\frac{\partial}{\partial V}e^{-\beta H(\text{x})} \\ &= \frac{1}{\Delta}\int_0^\infty dV e^{-\beta PV}kT\frac{\partial}{\partial V}Q(N,V,T)\end{aligned}$$

Doing the volume integration by parts gives

$$\begin{aligned}\langle P_{\text{int}}\rangle &= \frac{1}{\Delta}\left[e^{-\beta PV}kTQ(N,V,T)\right]\Big|_0^\infty - \frac{1}{\Delta}\int_0^\infty dVkT\left(\frac{\partial}{\partial V}e^{-\beta PV}\right)Q(N,V,T) \\ &= P\frac{1}{\Delta}\int_0^\infty dVe^{-\beta PV}Q(N,V,T) \\ &= P\end{aligned}$$

Thus,

$$\langle P_{\text{int}}\rangle = P$$

This result is known as the pressure virial theorem. It illustrates that the average of the quantity $-\partial H/\partial V$ gives the fixed pressure P that defines the ensemble. Another important result comes from considering the ensemble average $-\partial H/\partial V$

$$\langle P_{\text{int}}V\rangle = \frac{1}{\Delta}\int_0^\infty dVe^{-\beta PV}kTV\frac{\partial}{\partial V}Q(N,V,T)$$

Once again, integrating by parts with respect to the volume yields

$$\begin{aligned}\langle P_{\text{int}}V\rangle &= \frac{1}{\Delta}\left[e^{-\beta PV}kTVQ(N,V,T)\right]\Big|_0^\infty - \frac{1}{\Delta}\int_0^\infty dVkT\left(\frac{\partial}{\partial V}Ve^{-\beta PV}\right)Q(N,V,T) \\ &= \frac{1}{\Delta}\left[-kT\int_0^\infty dVe^{-\beta PV}Q(V)+P\int_0^\infty dVe^{-\beta PV}VQ(V)\right] \\ &= -kT+P\langle V\rangle\end{aligned}$$

or

$$\langle P_{\text{int}}V\rangle + kT = P\langle V\rangle$$

This result is known as the **work virial theorem**. It expresses the fact that equipartitioning of energy also applies to the volume degrees of freedom, since the volume is now a fluctuating quantity.

5.3: The partition function and relation to thermodynamics

In principle, we should derive the isothermal-isobaric partition function by coupling our system to an infinite thermal reservoir as was done for the canonical ensemble and also subject the system to the action of a movable piston under the influence of an external pressure P. In this case, both the temperature of the system and its pressure will be controlled, and the energy and volume will fluctuate accordingly.

However, we saw that the transformation from E to T between the microcanonical and canonical ensembles turned into a Laplace transform relation between the partition functions. The same result holds for the transformation from V to T. The relevant "energy" quantity to transform is the work done by the system against the external pressure P in changing its volume from $V=0$ to V, which will be PV. Thus, the isothermal-isobaric partition function can be expressed in terms of the canonical partition function by the Laplace transform:

$$\Delta(N,P,T)=\frac{1}{V_0}\int_0^\infty dVe^{-\beta PV}Q(N,V,T)$$

where V_0 is a constant that has units of volume. Thus,

$$\Delta(N,P,T)=\frac{1}{V_0N!h^{3N}}\int_0^\infty dV\int d\mathrm{x}e^{-\beta(H(\mathrm{x})+PV)}$$

The Gibbs free energy is related to the partition function by

$$G(N,P,T)=-\frac{1}{\beta}\ln\Delta(N,P,T)$$

This can be shown in a manner similar to that used to prove the $A=-(1/\beta)\ln Q$. The differential equation to start with is

$$G=A+PV=A+P\frac{\partial G}{\partial P}$$

Other thermodynamic relations follow:

Volume:

$$V=-kT\left(\frac{\partial\ln\Delta(N,P,T)}{\partial P}\right)_{N,T}$$

Enthalpy:

$$\bar{H}=\langle H(\mathrm{x})+PV\rangle=-\frac{\partial}{\partial\beta}\ln\Delta(N,P,T)$$

Heat capacity at constant pressure

$$C_P=\left(\frac{\partial\bar{H}}{\partial T}\right)_{N,P}=k\beta^2\frac{\partial^2}{\partial\beta^2}\ln\Delta(N,P,T)$$

Entropy:

S	$=$	$-\left(\frac{\partial G}{\partial T}\right)_{N,P}$	
	$=$	$k\ln\Delta(N,P,T)+\frac{\bar{H}}{T}$	

The fluctuations in the enthalpy $\Delta\bar{H}$ are given, in analogy with the canonical ensemble, by

$$\Delta\bar{H}=\sqrt{kT^2C_P}$$

so that

$$\frac{\Delta\bar{H}}{\bar{H}} = \frac{\sqrt{kT^2C_P}}{\bar{H}}$$

so that, since C_P and $\bar{H}$ are both extensive, $\Delta\bar{H}/\bar{H} \sim 1/\sqrt{N}$ which vanish in the thermodynamic limit.

5.4: Temperature and pressure estimators

From the classical virial theorem

$$\langle x_i \frac{\partial H}{\partial x_j} \rangle = kT\delta_{ij}$$

we arrived at the equipartition theorem:

$$\left\langle \sum_{i=1}^{N} \frac{p_i^2}{2m_i} \right\rangle = \frac{3}{2}NkT$$

where $\mathbf{p}_1, \cdots, \mathbf{p}_N$ are the N Cartesian momenta of the N particles in a system. This says that the microscopic function of the N momenta that corresponds to the temperature, a macroscopic observable of the system, is given by

$$K(\mathbf{p}_1, \cdots, \mathbf{p}_N) = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i}$$

The ensemble average of K can be related directly to the temperature

$$T = \frac{2}{3Nk}\langle K(\mathbf{p}_1, \cdots, \mathbf{p}_N)\rangle = \frac{2}{3nR}\langle K(\mathbf{p}_1, \cdots, \mathbf{p}_3)\rangle$$

$K(\mathbf{p}_1, \cdots, \mathbf{p}_N)$ \\) is known as an *estimator* (a term taken over from the Monte Carlo literature) for the temperature. An estimator is some function of the phase space coordinates, i.e., a function of microscopic states, whose ensemble average gives rise to a physical observable.

An estimator for the pressure can be derived as well, starting from the basic thermodynamic relation:

$$P = -\left(\frac{\partial A}{\partial V}\right)_{N,T} = kT\left(\frac{\partial \ln Q(N,V,T)}{\partial V}\right)_{N,T}$$

with

$$Q(N,V,T) = C_N \int dx\ e^{-\beta H(x)} = C_N \int d^N\mathbf{p} \int_V d^N\mathbf{r}\ e^{-\beta H(\mathbf{p},\mathbf{r})}$$

The volume dependence of the partition function is contained in the limits of integration, since the range of integration for the coordinates is determined by the size of the physical container. For example, if the system is confined within a cubic box of volume $V = L^3$, with L the length of a side, then the range of each q integration will be from 0 to L. If a change of variables is made to $s_i = \frac{q_i}{L}$, then the range of each s integration will be from 0 to 1. The coordinates s_i s_i are known as scaled coordinates. For containers of a more general shape, a more general transformation is

$$\mathbf{s}_i = V^{-1/3}\mathbf{r}_i$$

To preserve the phase space volume element, however, we need to ensure that the transformation is a canonical one. Thus, the corresponding momentum transformation is

$$\pi_i = V^{1/3}\mathbf{p}_i$$

With this coordinate/momentum transformation, the phase space volume element transforms as

$$d^N\mathbf{p}\ d^N\mathbf{r} = d^N\pi d^N\mathbf{s}$$

Thus, the volume element remains the same as required. With this transformation, the Hamiltonian becomes

$$H = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i} + U(\mathbf{r}_1, \cdots, \mathbf{r}_N) = \sum_{i=1}^{N} \frac{V^{-2/3}\pi_i^2}{2m_i} U(V_1^{\mathbf{s}}, \ldots, V^{1/3}\mathbf{s}_N)$$

and the canonical partition function becomes

$$Q(N,V,T) = C_N \int d^N\pi \int d^N\mathbf{s}\ \exp\left\{ -\beta \left[\sum_{i=1}^{N} \frac{V^{-2/3}\pi_i^2}{2m_i} + U(V^{1/3}\mathbf{s}_1, \cdots, V^{1/3}\mathbf{s}_N) \right] \right\}$$

Thus, the pressure can now be calculated by explicit differentiation with respect to the volume, V:

$$\begin{aligned} P &= kT \tfrac{1}{Q} \tfrac{\partial Q}{\partial V} \\ &= \tfrac{kT}{Q} C_N \int d^N\pi \int d^N\mathbf{s}\ \left[\tfrac{2}{3}\beta V^{-5/3} \textstyle\sum_{i=1}^N \tfrac{\pi_i^2}{2m_i} - \tfrac{\beta}{3} V^{-2/3} \textstyle\sum_{i=1}^N \mathbf{s}_i \cdot \tfrac{\partial U}{\partial (V^{1/3}\mathbf{s}_i)} \right] e^{-\beta H} \\ &= \tfrac{kT}{Q} C_N \int d^N\mathbf{p} \int d^N\mathbf{r} \left[\tfrac{\beta}{3V} \textstyle\sum_{i=1}^N \tfrac{\mathbf{P}_i^2}{m_i} - \tfrac{\beta}{3V} \textstyle\sum_{i=1}^N \mathbf{r}_i \cdot \tfrac{\partial U}{\partial \mathbf{r}_i} \right] e^{-\beta H(\mathbf{p},\mathbf{r})} \\ &= \tfrac{1}{3V} \left\langle \textstyle\sum_{i=1}^N \left(\tfrac{\mathbf{p}_i^2}{m_i} + \mathbf{r}_i \cdot \mathbf{F}_i \right) \right\rangle \\ &= \langle -\tfrac{\partial H}{\partial V} \rangle \end{aligned}$$

Thus, the pressure estimator is

$$\Pi(\mathbf{p}_1, \ldots, \mathbf{p}_N, \mathbf{r}_1, \ldots, \mathbf{r}_N) = \Pi(x) = \frac{1}{3V} \sum_{i=1}^{N} \left[\frac{\mathbf{p}_i^2}{2m_i} + \mathbf{r}_i \cdot \mathbf{F}_i(\mathbf{r}) \right]$$

and the pressure is given by

$$P = \langle \Pi(x) \rangle$$

For periodic systems, such as solids and currently used models of liquids, an absolute Cartesian coordinate q_i is ill-defined. Thus, the virial part of the pressure estimator $\sum_i q_i F_i$ must be rewritten in a form appropriate for periodic systems. This can be done by recognizing that the force F_i is obtained as a sum of contributions F_{ij}, which is the force on particle i due to particle j. Then, the classical virial becomes

$$\begin{aligned} \textstyle\sum_{i=1}^N \mathbf{r}_i \cdot \mathbf{F}_i &= \textstyle\sum_{i=1}^N \mathbf{r}_i \cdot \sum_{j \neq i} \mathbf{F}_{ij} \\ &= \tfrac{1}{2} \left[\textstyle\sum_i \mathbf{r}_i \sum_{j \neq i} \cdot F_{ij} + \sum_j \mathbf{r}_j \cdot \sum_{i \neq j} \mathbf{F}_{ji} \right] \\ &= \tfrac{1}{2} \left[\textstyle\sum_i \mathbf{r}_i \cdot \sum_{j \neq i} \mathbf{F}_{ij} - \sum_j \mathbf{r}_j \cdot \sum_{i \neq j} \mathbf{F}_{ij} \right] \\ &= \tfrac{1}{2} \textstyle\sum_{i,j,i \neq j} (\mathbf{r}_i - \mathbf{r}_j) \cdot \mathbf{F}_{ij} = \tfrac{1}{2} \sum_{i,j,i \neq j} \mathbf{r}_{ij} \cdot \mathbf{F}_{ij} \end{aligned}$$

where $\mathbf{r}_{ij}$ is now a relative coordinate. $\mathbf{r}_{ij}$ must be computed consistent with periodic boundary conditions, i.e., the relative coordinate is defined with respect to the closest periodic image of particle j with respect to particle i. This gives rise to surface contributions, which lead to a nonzero pressure, as expected.

CHAPTER OVERVIEW

6: The Grand Canonical Ensemble

In the grand canonical ensemble, the control variables are the chemical potential μ, the volume V and the temperature T. The total particle number N is therefore allowed to fluctuate. It is therefore related to the canonical ensemble by a Legendre transformation with respect to the particle number N. Its utility lies in the fact that it closely represents the conditions under which experiments are often performed and, as we shall see, it gives direct access to the equation of state.

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6.1: Thermodynamics

In the canonical ensemble, the Helmholtz free energy $A(N,V,T)$ is a natural function of N,V and T. As usual, we perform a Legendre transformation to eliminate N in favor of $\mu = \frac{\partial A}{\partial N}$:

$$\tilde{A}(\mu,V,T) = A(N(\mu),V,T) - N\left(\frac{\partial A}{\partial N}\right)_{V,T} \tag{6.1.1}$$

$$= A(N(\mu),V,T) - \mu N \tag{6.1.2}$$

It turns out that the free energy $\tilde{A}(\mu,V,T)$ is the quantity $-PV$. We shall derive this result below in the context of the partition function. Thus,

$$-PV = A(N(\mu),V,T) - \mu N$$

To motivate the fact that PV is the proper free energy of the grand canonical ensemble from thermodynamic considerations, we need to introduce a mathematical theorem, known as Euler's theorem:

Euler's Theorem

Let $f(x_1,\ldots,x_N)$ be a function such that

$$f(\lambda x_1,\ldots,\lambda x_N) = \lambda^n f(x_1,\ldots,x_N)$$

Then f is said to be a *homogeneous function of degree* n. For example, the function $f(x) = 3x^2$ is a homogeneous function of degree 2, $f(x,y,z) = xy^2 + z^3$ is a homogeneous function of degree 3, however, $f(x,y) = e^{xy} - xy$ is not a homogeneous function. *Euler's Theorem* states that, for a homogeneous function f,

$$nf(x_1,\ldots,x_N) = \sum_{i=1}^{N} x_i \frac{\partial f}{\partial x_i}$$

Proof

To prove Euler's theorem, simply differentiate the the homogeneity condition with respect to lambda:

$$\begin{aligned} \frac{d}{d\lambda} f(\lambda x_1,\ldots,\lambda x_N) &= \frac{d}{d\lambda}\lambda^n f(x_1,\ldots,x_N) \\ \sum_{i=1}^{N} x_i \frac{\partial f}{\partial(\lambda x_i)} &= n\lambda^{n-1} f(x_1,\ldots,x_N) \end{aligned}$$

Then, setting $\lambda = 1$, we have

$$\sum_{i=1}^{N} x_i \frac{\partial f}{\partial x_i} = nf(x_1,\ldots,x_N)$$

which is exactly Euler's theorem.

Now, in thermodynamics, extensive thermodynamic functions are homogeneous functions of degree 1. Thus, to see how Euler's theorem applies in thermodynamics, consider the familiar example of the Gibbs free energy:

$$G = G(N,P,T)$$

The extensive dependence of G is on N, so, being a homogeneous function of degree 1, it should satisfy

$$G(\lambda N,P,T) = \lambda G(N,P,T)$$

Applying Euler's theorem, we thus have

$$G(N,P,T) = N\frac{\partial G}{\partial N} = \mu N$$

or, for a multicomponent system,

$$G = \sum_j \mu_j N_j$$

But, since

$$G = E - TS + PV$$

it can be seen that $G = \mu N$ is consistent with the first law of thermodynamics.

Now, for the Legendre transformed free energy in the grand canonical ensemble, the thermodynamics are

$$\begin{aligned} d\tilde{A} &= dA - \mu dN - Nd\mu \\ &= -PdV - SdT - Nd\mu \end{aligned}$$

But, since

$$\begin{aligned} \tilde{A} &= \tilde{A}(\mu, V, T) \\ d\tilde{A} &= \left(\frac{\partial \tilde{A}}{\partial \mu}\right)_{V,T} d\mu + \left(\frac{\partial \tilde{A}}{\partial V}\right)_{\mu,T} dV + \left(\frac{\partial \tilde{A}}{\partial T}\right)_{\mu,V} dT \end{aligned}$$

the thermodynamics will be given by

$$\begin{aligned} N &= -\left(\frac{\partial \tilde{A}}{\partial \mu}\right)_{V,T} \\ P &= -\left(\frac{\partial \tilde{A}}{\partial V}\right)_{\mu,T} \\ S &= -\left(\frac{\partial \tilde{A}}{\partial T}\right)_{V,\mu} \end{aligned}$$

Since, $\tilde{A}$ is a homogeneous function of degree 1, and its extensive argument is V, it should satisfy

$$\tilde{A}(\mu, \lambda V, T) = \lambda \tilde{A}(\mu, V, T)$$

Thus, applying Euler's theorem,

$$\tilde{A}(\mu, V, T) = V\frac{\partial \tilde{A}}{\partial V} = -PV$$

and since

$$\tilde{A} = A - \mu N = E - TS - \mu N$$

the assignment $\tilde{A} = -PV$ is consistent with the first law of thermodynamics. It is customary to work with PV, rather than $-PV$, so PV is the natural free energy in the grand canonical ensemble, and, unlike the other ensembles, it is not given a special name or symbol!

6.2: Partition Functions

Consider two canonical systems, 1 and 2, with particle numbers N_1 and N_2, volumes V_1 and V_2 and at temperature T. The systems are in chemical contact, meaning that they can exchange particles. Furthermore, we assume that $N_2 \gg N_1$ and $V_2 \gg V_1$ so that system 2 is a particle reservoir. The total particle number and volume are

$$V = V_1 + V_2$$

$$N = N_1 + N_2$$

The total Hamiltonian $H(x, N)$ is

$$H(x, N) = H_1(x_1, N_1) + H_2(x_2, N_2)$$

If the systems *could not* exchange particles, then the canonical partition function for the whole system would be

$$\begin{aligned} Q(N, V, T) &= \frac{1}{N! h^{3N}} \int dx\, e^{-\beta(H_1(x_1,N_1)+H_2(x_2,N_2))} \\ &= \frac{N_1! N_2!}{N!} Q_1(N_1, V_1, T) Q_2(N_2, V_2, T) \end{aligned}$$

where

$$\begin{aligned} Q_1(N_1, V_1, T) &= \frac{1}{N_1! h^{3N_1}} \int dx\, e^{-\beta H_1(x_1,N_1)} \\ Q_2(N_2, V_2, T) &= \frac{1}{N_2! h^{3N_2}} \int dx\, e^{-\beta H_2(x_2,N_2)} \end{aligned}$$

However, N_1 and N_2 are *not* fixed, therefore, in order to sum over all microstates, we need to sum over all values that N_1 can take on subject to the constraint $N = N_1 + N_2$. Thus, we can write the canonical partition function for the whole system as

$$Q(N, V, T) = \sum_{N_1=0}^{N} f(N_1, N) \frac{N_1! N_2!}{N!} Q_1(N_1, V_1, T) Q_2(N_2, V_2, T)$$

where $f(N_1, N_2)$ is a function that weights each value of N_1 for a given N.

Thus,

- $f(0, N)$ is the number of configurations with 0 particles in V_1 and N particles in V_2.
- $f(1, N)$ is the number of configurations with 1 particles in V_1 and $N-1$ particles in V_2.
- etc.

Determining the values of $f(N_1, N)$ amounts to a problem of counting the number of ways we can put N identical objects into 2 baskets. Thus,

$$\begin{aligned} f(0, N) &= 1 \\ f(1, N) &= N \\ &= \frac{N!}{1!(N-1)!} \\ f(2, N) &= \frac{N(N-1)}{2} \\ &= \frac{N!}{2!(N-2)!} \end{aligned}$$

etc. or generally,

$$f(N_1, N) = \frac{N!}{N_1!(N-N_1)!} = \frac{N!}{N_1! N_2!}$$

which is clearly a classical degeneracy factor. If we were doing a purely classical treatment of the grand canonical ensemble, then this factor would appear in the sum for $Q(N,V,T)$, however, we always include the *ad hoc* quantum correction $\frac{1}{N!}$ in the expression for the canonical partition function, and we see that these quantum factors will exactly cancel the classical degeneracy factor, leading to the following expression:

$$Q(N,V,T) = \sum_{N_1=0}^{N} Q_1(N_1,V_1,T)Q_2(N_2,V_2,T)$$

which expresses the fact that, in reality, the various configurations are not distinguishable from each other, and so each one should count with equal weighting. Now, the distribution function $\rho(x)$ is given by

$$\rho(x,N) = \frac{\frac{1}{N!h^{3N}}e^{-\beta H(x,N)}}{Q(N,V,T)}$$

which is chosen so that

$$\int dx\rho(x,N) = 1$$

However, recognizing that $N_2 \approx N$, we can obtain the distribution for $\rho_1(x_1,N_1)$ immediately, by integrating over the phase space of system 2:

$$\rho_1(x_1,N_1) = \frac{1}{Q(N,V,T)}\frac{1}{N_1!h^{3N_1}}e^{-\beta H_1(x_1,N_1)}\frac{1}{N_2!h^{3N_2}}\int dx_2 e^{-\beta H_2(x_2,N_2)}$$

where the $\frac{1}{N_1!h^{3N_1}}$ prefactor has been introduced so that

$$\sum_{N_1=0}^{N}\int dx_1\rho(x_1,N_1) = 1$$

and amounts to the usual *ad hoc* quantum correction factor that must be multiplied by the distribution function for each ensemble to account for the identical nature of the particles. Thus, we see that the distribution function becomes

$$\rho_1(x_1,N_1) = \frac{Q_2(N_2,V_2,T)}{Q(N,V,T)}\frac{1}{N_1!h^{3N_1}}e^{-\beta H_1(x_1,N_1)}$$

Recall that the Hemlholtz free energy is given by

$$A = -\frac{1}{\beta}\ln Q$$

Thus,

$Q(N,V,T) = e^{-\beta A(N,V,T)}$

$Q_2(N_2,V_2,T) = e^{-\beta A(N_2,V_2,T)} = e^{-\beta A(N-N_1,V-V_1,T)}$

or

$$\frac{Q_2(N_2,V_2,T)}{Q(N,V,T)} = e^{-\beta(A(N-N_1,V-V_1,T)-A(N,V,T))}$$

But since $N \gg N_1$ and $V \gg V_1$, we may expand:

$$\begin{aligned} A(N-N_1,V-V_1,T) &= A(N,V,T) - \frac{\partial A}{\partial N}N_1 - \frac{\partial A}{\partial V}V_1 + \cdots \\ &= A(N,V,T) - \mu N_1 + PV_1 + \cdots \end{aligned}$$

Therefore the distribution function becomes

$$\rho_1(x_1,N_1) = \frac{1}{N_1!h^{3N_1}}e^{\beta\mu N_1}e^{-\beta PV_1}e^{-\beta H_1(x_1,N_1)} = \frac{1}{N_1!h^{3N_1}}\frac{1}{e^{\beta PV_1}}e^{\beta\mu N_1}e^{-\beta H_1(x_1,N_1)} \tag{6.2.1}$$

Dropping the "1" subscript, we have

$$\rho(x,N) = \frac{1}{e^{\beta PV}}\left[\frac{1}{N!h^{3N}}e^{\beta\mu N}e^{-\beta H(x,N)}\right]$$

We require that $\rho(x,N)$ be normalized:

$\sum_{N=0}^{\infty}\int dx\,\rho(x,N) = 1$

$\frac{1}{e^{\beta PV}}\left[\sum_{N=0}^{\infty}\frac{1}{N!h^{3N}}e^{\beta\mu N}\int dx\,e^{-\beta H(x,N)}\right] = 1$

Now, we define the grand canonical partition function

$$\mathcal{Z}(\mu,V,T) = \sum_{N=0}^{\infty}\frac{1}{N!h^{3N}}e^{\beta\mu N}\int dx\,e^{-\beta H(x,N)}$$

Then, the normalization condition clearly requires that

$$\mathcal{Z}(\mu,V,T) = e^{\beta PV}$$

$$\ln\mathcal{Z}(\mu,V,T) = \frac{PV}{kT}$$

Therefore PV is the free energy of the grand canonical ensemble, and the entropy $S(\mu,V,T)$ is given by

$$S(\mu,V,T) = \left(\frac{\partial(PV)}{\partial T}\right)_{\mu,V} = k\ln\mathcal{Z}(\mu,V,T) - k\beta\left(\frac{\partial}{\partial\beta}\ln\mathcal{Z}(\mu,V,T)\right)_{\mu,V}$$

We now introduce the **fugacity** ζ defined to be

$$\zeta = e^{\beta\mu}$$

Then, the grand canonical partition function can be written as

$$\begin{aligned}\mathcal{Z}(\zeta,V,T) &= \sum_{N=0}^{\infty}\frac{1}{N!h^{3N}}\zeta^N\int dx\,e^{-\beta H(x,N)}\\ &= \sum_{N=0}^{\infty}\zeta^N Q(N,V,T)\end{aligned}$$

which allows us to view the grand canonical partition function as a function of the thermodynamic variables ζ, V and T.

Other thermodynamic quantities follow straightforwardly:

$$\frac{\partial}{\partial\mu} = \frac{\partial\zeta}{\partial\zeta} = \beta\zeta\frac{\partial}{\partial\zeta}$$

Thus,

$$\langle N\rangle = \zeta\frac{\partial}{\partial\zeta}\ln\mathcal{Z}(\zeta,V,T)$$

6.3: Ideal Gas

Recall the canonical partition function expression for the ideal gas:

$$Q(N,V,T) = \frac{1}{N!}\left[\frac{V}{h^3}\left(\frac{2\pi m}{\beta}\right)^{3/2}\right]^N$$

Define the thermal wavelength $\lambda(\beta)$ as

$$\lambda(\beta) = \left(\frac{\beta h^2}{2\pi m}\right)^{1/2}$$

which has a quantum mechanical meaning as the width of the free particle distribution function. Here it serves as a useful parameter, since the canonical partition can be expressed as

$$Q(N,V,T) = \frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N$$

The grand canonical partition function follows directly from $Q(N,V,T)$:

$$\mathcal{Z}(\zeta,V,T) = \sum_{N=0}^{\infty}\frac{1}{N!}\left(\frac{V\zeta}{\lambda^3}\right)^N = e^{V\zeta/\lambda^3}$$

Thus, the free energy is

$$\frac{PV}{kT} = \ln\mathcal{Z} = \frac{V\zeta}{\lambda^3}$$

In order to obtain the equation of state, we first compute the average particle number $\langle N\rangle$

$$\langle N\rangle = \zeta\frac{\partial}{\partial\zeta}\ln\mathcal{Z} = \frac{V\zeta}{\lambda^3}$$

Thus, eliminating ζ in favor of $\langle N\rangle$ in the equation of state gives

$$PV = \langle N\rangle kT$$

as expected. Similarly, the average energy is given by

$$E = -\left(\frac{\partial\ln\mathcal{Z}}{\partial\beta}\right)_{\zeta V} = \frac{3V\zeta}{\lambda^4}\frac{\partial\lambda}{\partial\beta} = \frac{3}{2}\langle N\rangle kT$$

where the fugacity has been eliminated in favor of the average particle number. Finally, the entropy

$$S(\mu,V,T) = k\ln\mathcal{Z}(\mu,V,T) - k\beta\left(\frac{\partial\ln\mathcal{Z}(\mu,V,T)}{\partial\beta}\right)_{\mu,V} = \frac{5}{2}\langle N\rangle k + \langle N\rangle k\ln\left[\frac{V\lambda^3}{\langle N\rangle}\right]$$

which is the Sackur-Tetrode equation derived in the context of the canonical and microcanonical ensembles.

6.4: Particle Number Fluctuations

In the grand canonical ensemble, the particle number N is not constant. It is, therefore, instructive to calculate the fluctuation in this quantity. As usual, this is defined to be

$$\Delta N = \sqrt{\langle N^2\rangle - \langle N\rangle^2}$$

Note that

$$\begin{aligned}\zeta\frac{\partial}{\partial\zeta}\zeta\frac{\partial}{\partial\zeta}\ln \mathcal{Z}(\zeta,V,T) &= \frac{1}{\mathcal{Z}}\sum_{N=0}^{\infty} N^2\zeta^N Q(N,V,T) - \frac{1}{\mathcal{Z}^2}\left[\sum_{N=0}^{\infty} N\zeta^N Q(N,V,T)\right]^2 \\ &= \langle N^2\rangle - \langle N\rangle^2\end{aligned}$$

Thus,

$$\begin{aligned}(\Delta N)^2 &= \zeta\frac{\partial}{\partial\zeta}\zeta\frac{\partial}{\partial\zeta}\ln \mathcal{Z}(\zeta,V,T) \\ &= (KT^2)\frac{\partial^2}{\partial\mu^2}\ln \mathcal{Z}(\mu,V,T) \\ &= kTV\frac{\partial^2 P}{\partial\mu^2}\end{aligned}$$

In order to calculate this derivative, it is useful to introduce the Helmholtz free energy per particle defined as follows:

$$a(v,T) = \frac{1}{N}A(N,V,T)$$

where $v = \frac{V}{N} = \frac{1}{\rho}$ is the volume per particle. The chemical potential is defined by

$$\begin{aligned}\mu &= \frac{\partial A}{\partial N} \\ &= a(v,T) + N\frac{\partial a}{\partial v}\frac{\partial v}{\partial N} \\ &= a(v,T) - v\frac{\partial a}{\partial v}\end{aligned}$$

Similarly, the pressure is given by

$$P = -\frac{\partial A}{\partial V} = -N\frac{\partial a}{\partial v}\frac{\partial v}{\partial V} = -\frac{\partial a}{\partial v}$$

Also,

$$\frac{\partial\mu}{\partial v} = -v\frac{\partial^2 a}{\partial v^2}$$

Therefore,

$$\begin{aligned}\frac{\partial P}{\partial\mu} &= \frac{\partial P}{\partial v}\frac{\partial v}{\partial\mu} \\ &= \frac{\partial^2 a}{\partial v^2}\left[v\frac{\partial^2 a}{\partial v^2}\right]^{-1} \\ &= \frac{1}{v}\end{aligned}$$

and

$$\begin{aligned}\frac{\partial^2 P}{\partial \mu^2} &= \frac{\partial}{\partial v}\frac{\partial P}{\partial \mu}\frac{\partial v}{\partial \mu}\\ &= \frac{1}{v^2}\left[v\frac{\partial^2 a}{\partial v^2}\right]^{-1}\\ &= -\frac{1}{v^3 \partial P/\partial v}\end{aligned}$$

But recall the definition of the **isothermal compressibility**:

$$\kappa_T = -\frac{1}{V}\frac{\partial V}{\partial P} = -\frac{1}{v\partial p/\partial v}$$

Thus,

$$\frac{\partial^2 P}{\partial \mu^2} = \frac{1}{v^2}\kappa_T$$

and

$$\Delta N = \sqrt{\frac{\langle N\rangle kT\kappa_T}{v}}$$

and the relative fluctuation is given by

$$\frac{\Delta N}{N} = \frac{1}{\langle N\rangle}\sqrt{\frac{\langle N\rangle kT\kappa_T}{v}} \sim \frac{1}{\sqrt{\langle N\rangle}} \rightarrow 0 \;\; as\langle N\rangle \rightarrow \infty$$

Therefore, in the thermodynamic limit, the particle number fluctuations vanish, and the grand canonical ensemble is equivalent to the canonical ensemble.

CHAPTER OVERVIEW

7: Distribution Functions and Liquid Structure

7.1: General Formulation of Distribution Functions

Recall the expression for the configurational partition function:

$$Z_N = \int d\mathbf{r}_1 \cdots d\mathbf{r}_N e^{-\beta U(r_1,\ldots,r_N)}$$

Suppose that the potential U can be written as a sum of two contributions

$$U(\mathbf{r}_1,\ldots,\mathbf{r}_N) = U_0(\mathbf{r}_1,\ldots,\mathbf{r}_N) + U_1(\mathbf{r}_1,\ldots,\mathbf{r}_N)$$

where U_1 is, in some sense, small compared to U_0. An extra bonus can be had if the partition function for U_0 can be evaluated analytically.

Let

$$Z_N{}^{(0)} = \int d\mathbf{r}_1 \cdots d\mathbf{r}_N e^{-\beta U_0(r_1,\ldots,r_N)}$$

Then, we may express Z_N as

$$\begin{aligned} Z_N &= \frac{Z_N{}^{(0)}}{Z_N{}^{(0)}} \int d\mathbf{r}_1 \cdots d\mathbf{r}_N e^{-\beta U_0(r_1,\ldots,r_N)} e^{-\beta U_1(r_1,\ldots,r_N)} \\ &= Z_N{}^{(0)} \langle e^{-\beta U_1(r_1,\ldots,r_N)} \rangle_0 \end{aligned}$$

where $\langle \cdots \rangle_0$ means average with respect to U_0 only. If U_1 is small, then the average can be expanded in powers of U_1:

$$\begin{aligned} \langle e^{-\beta U_1} \rangle_0 &= 1 - \beta \langle U_1 \rangle_0 + \frac{\beta^2}{2!} \langle U_1^2 \rangle_0 - \frac{\beta^3}{3!} \langle U_1^3 \rangle_0 + \cdots \\ &= \sum_{k=0}^{\infty} \frac{(-\beta)^k}{k!} \langle U_1^k \rangle_0 \end{aligned}$$

The free energy is given by

$$A(N,V,T) = -\frac{1}{\beta} \ln\left(\frac{Z_N}{N!\lambda^{3N}}\right) = -\frac{1}{\beta} \ln\left(\frac{Z_N^{(0)}}{N!\lambda^{3N}}\right) - -\frac{1}{\beta} \ln\langle e^{-\beta U_1} \rangle_0$$

Separating A into two contributions, we have

$$A(N,V,T) = A^{(0)}(N,V,T) + A^{(1)}(N,V,T)$$

where $A^{(0)}$ is independent of U_1 and is given by

$$A^{(0)}(N,V,T) = -\frac{1}{\beta} \ln\left(\frac{Z_N{}^{(0)}}{N!\lambda^{3N}}\right)$$

and

$$\begin{aligned} A^{(1)}(N,V,T) &= -\frac{1}{\beta} \ln\langle e^{-\beta U_1} \rangle_0 \\ &= -\frac{1}{\beta} \ln\langle \sum_{k=0}^{\infty} \frac{(-\beta)^k}{k!} \langle U_1^k \rangle_0 \end{aligned}$$

We wish to develop an expansion for $A^{(1)}$ of the general form

$$A^{(1)} = \sum_{k=1}^{\infty} \frac{(-\beta)^{k-1}}{k!} \omega_k$$

where ω_k are a set of expansion coefficients that are determined by the condition that such an expansion be consistent with $\ln\langle \sum_{k=0}^{\infty} (-\beta)^k \langle U_1^k \rangle_0 / k!$.

Using the fact that

$$\ln(1+x) = \sum_{k=1}^{\infty}(-1)^{k-1}\frac{x^k}{k}$$

we have that

$$\begin{aligned} -\frac{1}{\beta}\ln\left(\sum_{k=0}^{\infty}\frac{(-\beta)^k}{k!}\langle U_1^k\rangle_0\right) &= -\frac{1}{\beta}\ln\left(1+\sum_{k=0}^{\infty}\frac{(-\beta)^k}{k!}\langle U_1^k\rangle_0\right) \\ &= -\frac{1}{\beta}\sum_{k=1}^{\infty}(-1)^{k-1}\frac{1}{k}\left(\sum_{l=1}^{\infty}\frac{(-\beta)^l}{l!}\langle U_1^l\rangle_0\right)^k \end{aligned}$$

Equating this expansion to the proposed expansion for $A^{(1)}$, we obtain

$$\sum_{k=1}^{\infty}(-1)^{k-1}\frac{1}{k}\left(\sum_{l=1}^{\infty}\frac{(-\beta)^l}{l!}\langle U_1^l\rangle_0\right)^k = \sum_{k=1}^{\infty}(-\beta)^k\frac{\omega_k}{k!}$$

This must be solved for each of the undetermined parameters ω_k, which can be done by equating like powers of β on both sides of the equation. Thus, from the β^1 term, we find, from the right side:

$$\text{Right Side}: \quad -\frac{\beta\omega_1}{1!}$$

and from the left side, the $j=1$ and $k=1$ term contributes:

$$\text{Left Side}: \quad -\frac{\beta\langle U_1\rangle_0}{1!}$$

from which it can be easily seen that

$$\omega_1 = \langle U_1\rangle_0$$

Likewise, from the β^2 term,

$$\text{Right Side}: \quad \frac{\beta^2}{2!}\omega_2$$

and from the left side, we see that the $l=1, k=2$ and $l=2, k=1$ terms contribute:

$$\text{Left Side}: \quad \frac{\beta^2}{2}\left(\langle U_1^2\rangle_0 - \langle U_1\rangle_0^2\right)$$

Thus,

$$\omega_2 = \langle U_1^2\rangle_0 - \langle U_1\rangle_0^2$$

For β^3, the right sides gives:

$$\text{Right Side}: \quad -\frac{\beta^3}{3!}\omega_3$$

the left side contributes the $l=1, k=3, k=2, l=2$ and $l=3, k=1$ terms:

$$\text{Left Side}: -\frac{\beta^3}{6}\langle U_1^3\rangle + (-1)^2\frac{1}{3}(-\beta\langle U_1\rangle_0)^3 - \frac{1}{2}\left(-\beta\langle U_1\rangle_0 + \frac{1}{2}\beta^2\langle U_1^2\rangle\right)^2$$

Thus,

$$\omega_3 = \langle U_1^3\rangle_0 + 2\langle U_1\rangle_0^3 - 3\langle U_1\rangle_0\langle U_1^2\rangle_0$$

Now, the free energy, up to the third order term is given by

$$\begin{aligned} A &= A^{(0)} + \omega_1 - \frac{\beta}{2}\omega_2 + \frac{\beta^2}{6}\omega_3 \cdots \\ &= -\frac{1}{\beta}\ln\left(\frac{Z_N{}^{(0)}}{N!\lambda^{3N}}\right) + \langle U_1\rangle_0 - \frac{\beta}{2}\left(\langle U_1^2\rangle_0 - \langle U_1\rangle_0^2\right) + \frac{\beta^2}{6}\left(\langle U_1^3\rangle - 3\langle U_1\rangle_0\langle U_1^2\rangle_0 + 2\langle U_1\rangle_0^3\right) + \cdots \end{aligned}$$

In order to evaluate $\langle U_1\rangle_0$, suppose that U_1 is given by a pair potential

$$U_1(\mathbf{r}_1,\ldots,\mathbf{r}_N) = \frac{1}{2}\sum_{i\neq j} u_1(|\mathbf{r}_i - \mathbf{r}_j|)$$

Then,

$$\begin{aligned} \langle U_1\rangle_0 &= \frac{1}{Z_N{}^{(0)}}\int d\mathbf{r}_1\cdots d\mathbf{r}_N \frac{1}{2}\sum_{i\neq j} u_1(|\mathbf{r}_i - \mathbf{r}_j|)e^{-\beta U_0(r_1,\ldots,r_N)} \\ &= \frac{N(N-1)}{2Z_N{}^{(0)}}\int d\mathbf{r}_1 d\mathbf{r}_2 u_1(|r_1 - r_2|)\int d\mathbf{r}_3\cdots d\mathbf{r}_N e^{-\beta U_0(\mathbf{r}_1,\ldots,\mathbf{r}_N)} \\ &= \frac{N^2}{2V^2}\int d\mathbf{r}_1 d\mathbf{r}_2 u_1(|\mathbf{r}_1 - \mathbf{r}_2|)g_0^{(2)}(\mathbf{r}_1,\mathbf{r}_2) \\ &= \frac{\rho^2 V}{2}\int_0^\infty 4\pi r^2 u_1(r)g_0(r)dr \end{aligned}$$

The free energy is therefore given by

$$A(N,V,T) = -\frac{1}{\beta}\ln\left(\frac{Z_N^{(0)}}{N!\lambda^{3N}}\right) + \frac{1}{2}\rho^2 V\int_0^\infty 4\pi r^2 u_1(r)g_0(r)dr - \frac{\beta}{2}\left(\langle U_1^2\rangle_0 - \langle U_1\rangle_0^2\right)\cdots$$

7.2: General Distribution Functions and Correlation Functions

We begin by considering a general N-particle system with Hamiltonian

$$H = \sum_{i=1}^{3N} \frac{p_i^2}{2m} + U(r_1, \cdots, r_N)$$

For simplicity, we consider the case that all the particles are of the same type. Having established the equivalence of the ensembles in the thermodynamic limit, we are free to choose the ensemble that is the most convenient on in which to work. Thus, we choose to work in the canonical ensemble, for which the partition function is

$$Q(N,V,T) = \frac{1}{N!h^{3N}} \int d^{3N}pd^{3N}re^{-\beta\sum_{i=1}^{3N}\frac{P_i^2}{2m}}e^{-\beta U(r_1,\cdots,r_N)}$$

The 3N integrations over momentum variables can be done straightforwardly, giving

$$\begin{aligned} Q(N,V,T) &= \frac{1}{N!\lambda^{3N}} \int dr_1 \cdots dr_N e^{-\beta U(r_1,\cdots,r_N)} \\ &= \frac{Z_N}{N!\lambda^{3N}} \end{aligned}$$

where $\lambda = \sqrt{\frac{\beta h^2}{2\pi m}}$ is the thermal wavelength and the quantity Z_N is known as the **configurational partition function**

$$Z_N = \int dr_1 \cdots dr_N e^{-\beta U(r_1,\cdots,r_N)}$$

The quantity

$$\frac{e^{-\beta U(r_1,\cdots,r_N)}}{Z_N} dr_1 \cdots dr_N \equiv P^{(N)}(r_1, \cdots, r_N) dr_1 \cdots dr_N$$

represents the probability that particle 1 will be found in a volume element dr_1 at the point r_1, particle 2 will be found in a volume element dr_2 at the point r_2,..., particle N will be found in a volume element dr_N at the point r_N. To obtain the probability associated with some number *n*;*SPMlt*;*N* of the particles, irrespective of the locations of the remaining *n*+1,...,*N* particles, we simply integrate this expression over the particles with indices *n*+1,...,*N*:

$$P^{(n)}(r_1, \cdots, r_n) dr_1 \cdots dr_n = \frac{1}{Z_N} \left[\int dr_{n+1} \cdots dr_N e^{-\beta U(r_1,\cdots,r_N)} \right] dr_1 \cdots dr_n$$

The probability that *any* particle will be found in the volume element dr_1 at the point r_1 and *any* particle will be found in the volume element dr_2 at the point r_2,...,*any* particle will be found in the volume element dr_n at the point r_n is defined to be

$$P^{(n)}(r_1, \cdots, r_n) dr_1 \cdots dr_n = \frac{N!}{(N-n)!} P^{(n)}(r_1, \cdots, r_n) dr_1 \cdots dr_n$$

which comes about since the first particle can be chosen in N ways, the second chosen in N-1 ways, etc.

Consider the special case of $n = 1$. Then, by the above formula,

$$\begin{aligned} P^{(1)}(r_1) &= \frac{1}{Z_N} \frac{N!}{(N-1)!} \int dr_2 \cdots dr_N e^{-\beta U(r_1,\cdots,r_N)} \\ &= \frac{N}{Z_N} \int dr_2 \cdots dr_N e^{-\beta U(r_1,\cdots,r_N)} \end{aligned}$$

Thus, if we integrate over all r_1, we find that

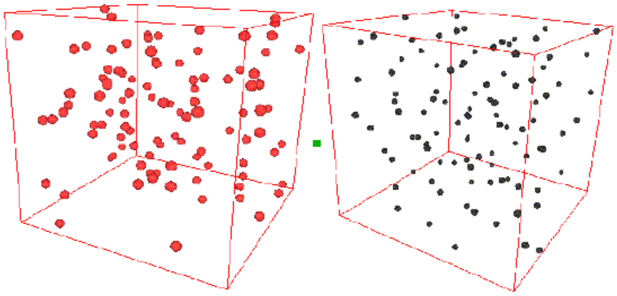
$$\frac{1}{V} \int dr_1 p^{(1)}(r_1) = \frac{N}{V} = p$$

Thus, $P^{(1)}$ actually counts the number of particles likely to be found, on average, in the volume element dr_1 at the point r_1. Thus, integrating over the available volume, one finds, not surprisingly, all the particles in the system.

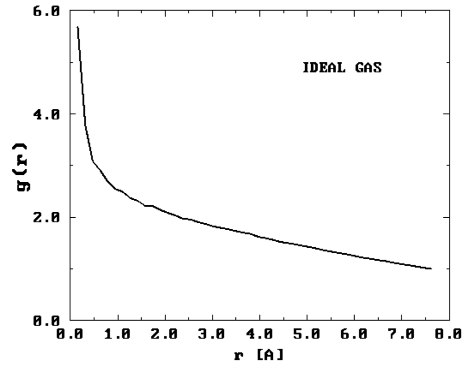
7.3: Structure and distribution functions in classical liquids and gases

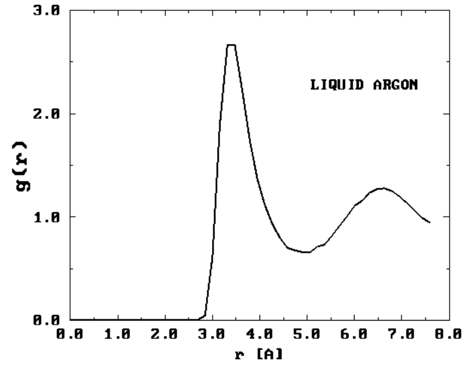
So far, we have developed the classical theory of ensembles and applied it to the ideal gas, for which there was no potential of interaction between the particles: $U = 0$. We were able to derive all the thermodynamics for this system using the various ensembles available to us, and, in particular, we could compute the equation of state. Now, we wish to consider the general case that the potential is not zero. Of course, all of the interesting physics and chemistry of real systems results from the specific interactions between the particles. Real systems can exhibit spatial structure, undergo phase transitions, undergo chemical changes, exhibit interesting dynamics, basically, a wide variety of rich behavior.

Consider the two snapshots below.



On the left is shown a configuration of an ideal gas, and on the right is shown a configuration of liquid argon. Can you see any inherent structure in the snapshot of liquid argon? While it may not be readily apparent, there is considerable structure in the liquid argon system that is clearly not present in the ideal gas. One way of quantifying spatial structure is through the use of the radial distribution function g(r), which will be discussed in great detail later. For now, it is sufficient to know that g(r) is a measure of the probability that a particle will be located a distance r from a another particle in the system. The figure below shows the function g(r) for the ideal gas and for the liquid argon systems.

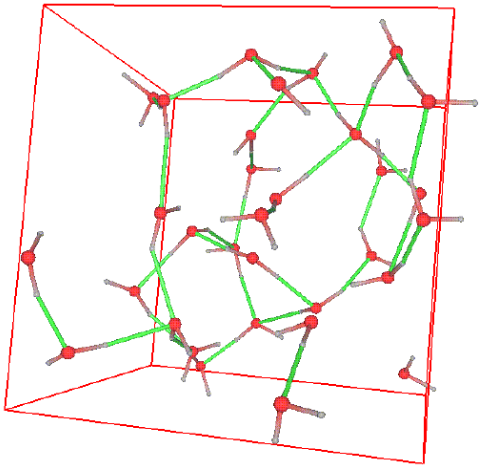




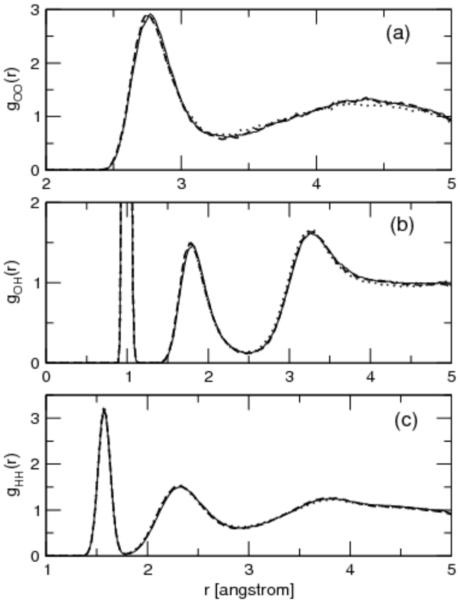
It can be seen that the radial distribution function for the ideal gas is completely featureless signifying that it is equally likely to find a particle at any distance r from a given particle. (Since the probability is uniform, $g(r) \sim \frac{1}{r^2}$ for small r. This is the particularly normalization condition on $g(r)$ that gives rise to uniform probability. Hence its rapidly rising behavior for small r.)

For the liquid argon system, $g(r)$ exhibits several peaks, indicating that at certain radial values, it is more likely to find particles than at others. This is a result of the attractive nature of the interaction at such distances. The plot of $g(r)$ also shows that there is essentially zero probability of finding particles at distances less than about 2.5 Å from each other. This is due to the presence of very strong repulsive forces at short distances.

Sometimes, the structure can be readily seen in snapshots of configurations. Consider the following snapshot of a system of water molecules:



The red spheres are oxygen atoms, the grey spheres are hydrogen atoms, the green lines are hydrogen bonds, and the reddish-grey lines are covalent bonds. A good deal of structure can be seen in the form of a complex network of hydrogen bonds. This high degree of structure is characteristic of water and gives rise to the ease which with water can form stable, organized structures around other molecules. In water, one can ask several questions related to structure. For example, what is the probability that an oxygen atom will be found at a distance r away from another oxygen atoms? What is the probability that a hydrogen atom will be located at a distance r from an oxygen atom, etc. The plot below shows the radial distribution functions corresponding to these two scenarios.



The peak in the O-O radial distribution function occurs at roughly 2.8Å which is the well known average hydrogen bond length in water. Of course, one could also ask about structure from the point of view of a hydrogen atom and obtain two other representations of structure in water.

7.4: General Correlation Functions

A general correlation function can be defined in terms of the probability distribution function $p^{(n)}(r_1,\cdots,r_n)$ according to

$$\begin{aligned} g^{(n)}(r_1,\cdots,r_n) &= \frac{1}{p^n} p^{(n)}(r_1,\cdots,r_n) \\ &= \frac{V^n N!}{Z_N N^n (N-n)!}\int dr_{n+1}\cdots dr_N e^{-\beta U(r_1,\cdots,r_N)} \end{aligned}$$

Another useful way to write the correlation function is

$$\begin{aligned} g^{(n)}(r_1,\cdots,r_n) &= \frac{V^n N!}{Z_N N^n (N-n)!}\int dr_1'\cdots dr_N' e^{-\beta U(r_1,\cdots,r_N)} \delta(r_1-r_1')\cdots\delta(r_n-r_n') \\ &= \frac{V^n N!}{Z_N N^n (N-n)!}\left\langle \Pi_{i=1}^n \delta(r_i-r_i')\right\rangle_{r_1',\cdots,r_N'} \end{aligned}$$

i.e., the general n-particle correlation function can be expressed as an ensemble average of the product of δ -functions, with the integration being taken over the variables $r_1',\cdots,r_N'$.

7.5: Thermodynamic quantities in terms of g(r)

In the canonical ensemble, the average energy is given by

$$E = -\frac{\partial}{\partial \beta} \ln Q(N, V, \beta)$$

$$\ln Q(N, V, \beta) = \ln Z_N - 3N \ln \lambda(\beta) - \ln N!$$

Therefore,

$$E = \frac{3N}{\lambda}\frac{\partial \lambda}{\partial \beta} - \frac{1}{Z_N}\frac{\partial Z_N}{\partial \beta}$$

Since

$$\lambda = \left[\frac{\beta h^2}{2\pi m}\right]^{1/2}$$

$$\frac{\partial \lambda}{\partial \beta} = \frac{1}{2\beta}\lambda$$

Thus,

$$\begin{aligned} E &= \frac{3}{2}NkT + \frac{1}{Z_N}\int dr_1 \cdots dr_N U(r_1, \cdots, r_N) e^{\beta U(r_1,\cdots,r_N)} \\ &= \frac{3}{2}NkT + \langle U \rangle \end{aligned}$$

In order to compute the average energy, therefore, one needs to be able to compute the average of the potential $\langle U \rangle$. In general, this is a nontrivial task, however, let us work out the average for the case of a *pairwise-additive* potential of the form

$$U(r_1, \cdots, r_N) = \frac{1}{2}\sum_{i,j,i \neq j} u(|r_i - r_j|) \equiv U_{pair}(r_1, \cdots, r_N)$$

i.e., U is a sum of terms that depend only the distance between two particles at a time. This form turns out to be an excellent approximation in many cases. U therefore contains $N(N\text{-}1)$ total terms, and $\langle U \rangle$ becomes

$$\begin{aligned} \langle U \rangle &= \frac{1}{2Z_N}\sum_{i,j,i \neq j}\int dr_1 \cdots dr_N u(|r_i - r_j|) e^{-\beta U_{pair}(r_1,\cdots,r_N)} \\ &= \frac{N(N-1)}{2Z_N}\int dr_1 \cdots dr_N u(|r_1 - r_2|) e^{-\beta U_{pair}(r_1,\cdots,r_N)} \end{aligned}$$

The second line follows from the fact that all terms in the first line are the exact same integral, just with the labels changed. Thus,

$$\begin{aligned} \langle U \rangle &= \frac{1}{2}\int dr_1 dr_2 u(|r_1 - r_2|)\left[\frac{N(N-1)}{Z_N}\int dr_3 \cdots dr_N e^{-\beta U_{pair}(r_1,\cdots,r_N)}\right] \\ &= \frac{1}{2}\int dr_1 dr_2 u(|r_1 - r_2|)\rho^{(2)}(r_1, r_2) \\ &= \frac{N^2}{2V^2}\int\int dr_1 dr_2 u(|r_1 - r_2|) p^{(2)}(r_1, r_2) \end{aligned}$$

Once again, we change variables to $r = r_1 - r_2$ and $R = \frac{(r_1 + r_2)}{2}$. Thus, we find that

$$\begin{aligned} \langle U \rangle &= \frac{N^2}{2V^2}\int dr dR u(r) \tilde{g}^{(2)}(r, R) \\ &= \frac{N^2}{2V^2}\int dr u(r)\int dR \tilde{g}^{(2)}(r, R) \end{aligned}$$

$$= \frac{N^2}{2V^2}\int dr u(r)\tilde{g}(r)$$

$$= \frac{N^2}{2V^2}\int_0^\infty dr 4\pi r^2 u(r) g(r)$$

Therefore, the average energy becomes

$$E = \frac{3}{2}NkT + \frac{N}{2}4\pi\rho\int_0^\infty dr r^2 u(r) g(r)$$

Thus, we have an expression for E in terms of a simple integral over the pair potential form and the radial distribution function. It also makes explicit the deviation from "ideal gas" behavior, where E=3NkT/2.

By a similar procedure, we can develop an equation for the pressure P in terms of $g(r)$. Recall that the pressure is given by

$$P = \frac{1}{\beta}\frac{\partial \ln Q}{\partial V}$$

$$= \frac{1}{\beta Z_N}\frac{\partial Z_N}{\partial \beta}$$

The volume dependence can be made explicit by changing variables of integration in Z_N to

$$s_i = V^{-1/3} r_i$$

Using these variables, Z_N becomes

$$Z_N = V^N \int ds_1 \cdots ds_N e^{-\beta U(V_1^{1/R}, \cdots, V_N^{1/R})}$$

Carrying out the volume derivative gives

$$\frac{\partial Z_N}{\partial V} = \frac{N}{V}Z_N - \beta V^N \int ds_1 \cdots ds_N \frac{1}{3V}\sum_{i=1}^N r_i \cdot \frac{\partial U}{\partial r_i} e^{-\beta U(V_1^{1/R}, \cdots, V_N^{1/R})}$$

$$= \frac{N}{V}Z_N + \beta \int dr_1 \cdots dr_N \frac{1}{3V}\sum_{i=1} r_i \cdot F_i e^{-\beta U(r_1, \cdots, r_N)}$$

$$= ds_1 \cdots ds_N \frac{1}{3V}\sum_{i=1}^N r_i \cdot ds_1 \cdots ds_N \frac{1}{3V}\sum_{i=1}^N r_i \cdot ds_1 \cdots ds_N \frac{1}{3V}\sum_{i=1}^N r_i \backslash \mathrm{cdo}$$

Thus,

$$\frac{1}{Z_N}\frac{\partial Z_N}{\partial V} = \frac{N}{V} + \frac{\beta}{3V}\left\langle \sum_{i=1}^N r_i \cdot F_i \right\rangle$$

Let us consider, once again, a pair potential. We showed in an earlier lecture that

$$\sum_{i=1}^N r_i \cdot F_i = \sum_{i=1} \sum_{j=1, j\neq i}^N r_i \cdot F_{ij}$$

where F_{ij} is the force on particle *i* due to particle *j*. By interchaning the *i* and *j* summations in the above expression, we obtain

$$\sum_{i=1}^N r_i \cdot F_i = \frac{1}{2}\left[\sum_{i,j,i\neq j} r_i \cdot F_{ij} + \sum_{i,j,i\neq j} r_j \cdot F_{ij}\right]$$

However, by Newton's third law, the force on particle *i* due to particle *j* is equal and opposite to the force on particle *j* due to particle *i*:

$$F_{ij} = -F_{ji}$$

Thus,

$$\sum_{i=1}^{N} r_i \cdot F_i = \frac{1}{2}\left[\sum_{i,j,i\neq j} r_i \cdot F_{ij} - \sum_{i,j,i\neq j} r_j \cdot F_{ij}\right] = \frac{1}{2}\sum_{i,j,i\neq j}(r_i - r_j)\cdot F_{ij} \equiv \frac{1}{2}\sum_{i,j,i\neq j} r_{ij}\cdot F_{ij}$$

The ensemble average of this quantity is

$$\frac{\beta}{3V}\left\langle\sum_{i=1}^{N} r_i \cdot F_i\right\rangle = \frac{\beta}{6V}\left\langle\sum_{i,j,i\neq j} r_{ij}\cdot F_{ij}\right\rangle = \frac{\beta}{6VZ_N}\int dr_1\cdots dr_N \sum_{i,j,i\neq j} r_{ij}\cdot F_{ij}e^{-\beta U_{pair}(r_1,\cdots,r_N)}$$

As before, all integrals are exactly the same, so that

$$\frac{\beta}{3V}\left\langle\sum_{i=1}^{N} r_i \cdot F_i\right\rangle = \frac{\beta N(N-1)}{6VZ_N}\int d_1\cdot r_N r_{12}\cdot F_{12}e^{-\beta U_{pair}(r_1,\cdots,r_N)}$$

$$= \frac{\beta}{6V}\int dr_1 dr_2 r_{12}\cdot F_{12}\left[\frac{N(N-1)}{Z_N}\int dr_3\cdots dr_N e^{-\beta U_{pair}(r_1,\cdots,r_N)}\right]$$

$$= \frac{\beta}{6V}\int dr_1 dr_2 r_{12}\cdot F_{12}\rho^{(2)}(r_1,r_2)$$

$$= \frac{\beta N^2}{6V^3}\int dr_1 dr_2 r_{12}\cdot F_{12}g^{(2)}(r_1,r_2)$$

Then, for a pair potential, we have

$$F_{12} = -\frac{\partial U_{pair}}{\partial r_{12}} = -u'(|r_1 - r_2|)\frac{(r_1-r_2)}{|r_1-r_2|} = -u'(r_{12})\frac{r_{12}}{r_{12}}$$

where $u'(r) = du/dr$, and $r_{12} = |r_{12}|$. Substituting this into the ensemble average gives

$$\frac{\beta}{3V}\left\langle\sum_{i=1}^{N} r_i \cdot F_i\right\rangle = -\frac{\beta N^2}{6V^3}\int dr_1 dr_2 u'(r_{12})r_{12}g^{(2)}(r_1,r_2)$$

As in the case of the average energy, we change variables at this point to $r = r_1 - r_2$ and $R = \frac{(r_1+r_2)}{2}$. This gives

$$\frac{\beta}{3V}\left\langle\sum_{i=1}^{N} r_i \cdot F_i\right\rangle = -\frac{\beta N^2}{6V^3}\int drdRu^t(r)r\tilde{g}^{(2)}(r,R)$$

$$= -\frac{\beta N^2}{6V^2}\int dru^t(r)r\tilde{g}(r)$$

$$= -\frac{\beta N^2}{6V^2}\int_0^\infty dr4\pi r^3 u^t(r)g(r)$$

Therefore, the pressure becomes

$$\frac{P}{kT} = \rho - \frac{\rho^2}{6kT}\int_0^\infty dr4\pi r^3 u^t(r)g(r)$$

which again gives a simple expression for the pressure in terms only of the derivative of the pair potential form and the radial distribution function. It also shows explicitly how the equation of state differs from the that of the ideal gas $\frac{P}{kT} = \rho$.

From the definition of $g(r)$ it can be seen that it depends on the density ρ and temperature T: $g(r) = g(r;\rho,T)$. Note, however, that the equation of state, derived above, has the general form

$$\frac{P}{kT} = \rho + B\rho^2$$

which looks like the first few terms in an expansion about ideal gas behavior. This suggests that it may be possible to develop a general expansion in all powers of the density ρ about ideal gas behavior. Consider representing $g(r;\rho,T)$ as such a power series:

$$g(r;\rho,T) = \sum_{j=0}^{\infty} \rho^j g_j(r;T)$$

Substituting this into the equation of state derived above, we obtain

$$\frac{P}{kT} = \rho + \sum_{j=0}^{\infty} B_{j+2}(T)\rho^{j+2}$$

This is known as the **virial equation of state**, and the coefficients $B_{j+2}(T)$ are given by

$$B_{j+2}(T) = -\frac{1}{6kT}\int_0^\infty dr 4\pi r^3 u^t(r) g_j(r;T)$$

are known as the *virial coefficients*. The coefficient $B_2(T)$ is of particular interest, as it gives the leading order deviation from ideal gas behavior. It is known as the second virial coefficient. In the low density limit, $g(r;\rho,T) \approx g_0(r;T)$ and $B_2(T)$ is directly related to the radial distribution function.

7.6: The Pair Correlation Function

Of particular importance is the case *n*=2, or the correlation function $g^{(2)}(r_1, r_2)$ known as the *pair correlation function*. The explicit expression for $g^{(2)}(r_1, r_2)$ is

$$\begin{aligned} g^{(2)}(r_1, r_2) &= \frac{V^2 N!}{N^2 (N-2)!} \langle \delta(r_1 - r'_1) \delta(r_2 - r'_2) \rangle \\ &= \frac{V^2 (N-1)}{N Z_N} \int dr_3 \cdots dr_N e^{-\beta U(r_1, \cdots, r_N)} \\ &= \frac{N(N-1)}{p^2} \langle \delta(r_1 - r'_1) \delta(r_2 - r'_2) \rangle_{r'_1 \cdots r'_N} \end{aligned}$$

In general, for homogeneous systems in equilibrium, there are no special points in space, so that $g^{(2)}$ should depend only on the relative position of the particles or the difference $r_1 - r_2$. In this case, it proves useful to introduce the change of variables

$$r = r_1 - r_2 R = \frac{1}{2}(r_1 + r_2)$$

$$r_1 = R + \frac{1}{2} r, r_2 = R - \frac{1}{2} r$$

Then, we obtain a new function $\tilde{g}^{(2)}$, a function of r and R:

$$\begin{aligned} \tilde{g}^{(2)}(r, R) &= \frac{V^2 (N-1)}{N Z_N} \int dr_3 \cdots dr_N e^{-\beta U(R + \frac{1}{2} r, R - \frac{1}{2} r, r_R, \cdots, r_N)} \\ &= \frac{N(N-1)}{p^2} \left\langle \delta \left(R + \frac{1}{2} r - r'_1 \right) \delta \left(R - \frac{1}{2} r - r'_2 \right) \right\rangle_{r'_1, \cdots r'_N} \end{aligned}$$

In general, we are only interested in the dependence on r. Thus, we integrate this expression over R and obtain a new correlation function $\tilde{g}(r)$ defined by

$$\tilde{g}(r) = \frac{1}{V} \int dR \tilde{g}^{(2)}(r, R)$$

$$= \frac{V(N-1)}{N Z_N} \int dR dr_3 \cdots dr_N e^{-\beta U(R + \frac{1}{2} r, R - \frac{1}{2} r, rR, \cdots, rN)}$$

$$= \frac{(N-1)}{p Z_N} \int dR dr_3 \cdots dr_N e^{-\beta U(R + \frac{1}{2} r, R - \frac{1}{2} r, rR, \cdots, rN)}$$

For an isotropic system such as a liquid or gas, where there is no preferred direction in space, only the maginitude or r, $|r| \equiv r$ is of relevance. Thus, we seek a choice of coordinates that involves r explicitly. The spherical-polar coordinates of the vector r is the most natural choice. If $r = (x, y, z)$ then the spherical polar coordinates are

$$x = r \sin\theta \cos\phi$$

$$y = r \sin\theta \sin\phi$$

$$x = r \cos\theta$$

$$dr = r^2 \sin\theta \, dr \, d\theta \, d\phi$$

where θ and ϕ are the polar and azimuthal angles, respectively. Also, note that

$$r = rn$$

where

$$n = (\sin\theta \cos\phi, \sin\theta \sin\phi, \cos\theta)$$

Thus, the function $g(r)$ that depends only on the distance r between two particles is defined to be

$$\begin{aligned} g(r) &= \frac{1}{4\pi}\int \sin\theta d\theta d\phi \tilde{g}(r) \\ &= \frac{(N-1)}{4\pi p Z_N}\int \sin\theta\, d\theta\, d\phi\, dR dr_3 \cdots dr_N e^{-\beta U(R+\frac{1}{2}r, R-\frac{1}{2}r, rR, \cdots, rN)} \\ &= \frac{(N-1)}{4\pi p}\left\langle \frac{\delta(r-r')}{rr'} \right\rangle_{r^t, \theta^t, \phi^t, R^t, r^t_R, \cdots, r^t_N} \end{aligned}$$

Integrating $g(r)$ over the radial dependence, one finds that

$$4\pi p\int_0^\infty drr^2 g(r) = N-1 \approx N$$

The $g(r)$ function is important for many reasons. It tells us about the structure of complex, isotropic systems, as we will see below, it determines the thermodynamic quantities at the level of the pair potential approximation, and it can be measured in neutron and X-ray diffraction experiments. In such experiments, one observes the scattering of neutrons or X-rays from a particular sample. If a detector is placed at an angle θ from the wave-vector direction of an incident beam of particles, then the intensity $I(\theta)$ that one observes is proportional to the structure factor

$$\begin{aligned} I(\theta) \sim \frac{1}{N}\left\langle \left| \sum_m e^{ik\cdot r_m} \right|^2 \right\rangle &= \frac{1}{N}\left\langle \sum_m e^{ik\cdot(r_m - r_n)} \right\rangle \\ &\equiv S(k) \end{aligned}$$

where k is the vector difference in the wave vector between the incident and scattered neutrons or X-rays (since neutrons and X-rays are quantum mechanical particles, they must be represented by plane waves of the form $exp(ik\cdot r)$). By computing the ensemble average (see problem 4 of problem set #5), one finds that $S(k) = S(k)$ and S(k) is given by

$$S(k) = 1 + \frac{4\pi p}{k}\int_0^\infty dr r \sin(kr) g(r)$$

Thus, if one can measure $S(k)$, $g(r)$ can be determined by Fourier transformation.

7.7: Derivation of the Van der Waals equation

As a specific example of the application of perturbation theory, we consider the Van der Waals equation of state. Let U_0 be given by a pair potential:

$$U_0(\mathbf{r}_1,\ldots,\mathbf{r}_N) = \frac{1}{2}\sum_{i\neq j} u_0(|\mathbf{r}_i - \mathbf{r}_j|)$$

with

$$u_0(r) = \begin{cases} 0 & r > \sigma \\ \infty & r \le \sigma \end{cases}$$

This potential is known as the *hard sphere* potential. In the low-density limit, the radial distribution function can be shown to be given correctly by $g_0(r) \sim \exp(-\beta u_0(r))$ or

$$\begin{aligned} g_0(r) &= \theta(r-\sigma) \\ &= u_1(r) \end{aligned}$$

$u(r) = u_0(r) + u_1(r)$ is taken to be some arbitrary attractive potential, whose specific form is not particularly important. Then, the full potential might look like:

$$A^{(1)} \approx u(r) = u_0(r) + u_1(r) \tag{7.7.1}$$

Now, the first term in $A^{(1)}$ is

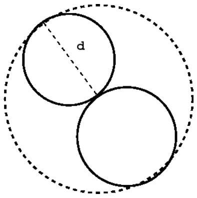
$$\begin{aligned} \frac{1}{2}\rho^2 V \int_0^\infty 4\pi r^2 u_1(r) g_0(r) &= \frac{1}{2}\rho^2 V \int_0^\infty 4\pi r^2 u_1(r)\theta(r-\sigma) \\ &= 2\pi\rho^2 V \int_\sigma^\infty r^2 u_1(r) dr \equiv -aN\rho \\ &= a = -2\pi \int_\sigma^\infty dr r^2 u_1(r) > 0 \end{aligned}$$

where σ is a number that depends on $u_0(r)$ and the specific form of $u(r) = u_0(r) + u_1(r)$.

Since the potential $Z_N(0)$ is a hard sphere potential, u_0 can be determined analytically. If $u_0(r)$ were 0, then $Z_N^{(0)} = V^N$ would describe an ideal gas and

$$Z_N{}^{(0)} = V^N$$

However, because two particles may not approach each other closer than a distance $u_0(r)$ between their centers, there is some excluded volume:



If we consider two hard spheres at closest contact and draw the smallest imaginary sphere that contains both particles, then we find this latter sphere has a radius $u_0(r)$:

$$\frac{4}{3}\pi\sigma^3 \tag{7.7.2}$$

Hence the excluded volume for these two particles is

$$\frac{2}{3}\pi\sigma^3 \equiv b$$

and hence the excluded volume per particle is just half of this:

$$Nb$$

Therefore $Z_N{}^{(0)} = (V - Nb)^N$ is the total excluded volume, and we find that, in the low density limit, the partition function is given approximately by

$$A(N,V,T) \approx -\frac{1}{\beta}\ln\left[\frac{(V-Nb)^N}{N!\lambda^{3N}}\right] - \frac{aN^2}{V}$$

Thus, the free energy is

$$P = -\left(\frac{\partial A}{\partial V}\right)_{N,T}$$

If we now use this free energy to compute the pressure from

$$\frac{P}{kT}$$

we find that

$$\begin{aligned} \frac{N}{V-Nb} - \frac{aN^2}{kTV^2} &= \frac{\rho}{1-\rho b} - \frac{a\rho^2}{kT} \\ &= \rho b \gg 1 \end{aligned}$$

This is the well know Van der Waals equation of state. In the very low density limit, we may assume that

$$\frac{1}{1-\rho b} \approx 1 + \rho b,$$

hence

$$\frac{P}{kT} \approx \rho + \rho^2\left(b - \frac{a}{kT}\right)$$

Thus,

$$B_2(T) \approx b - \frac{a}{kT} = \frac{2}{3}\pi\sigma^3 + \frac{2\pi}{kT}\int_\sigma^\infty drr^2 u_1(r)$$

from which we can approximate the second virial coefficient:

$$B_2(T) \approx b - \frac{a}{kT} = \frac{2}{3}\pi\sigma^3 + \frac{2\pi}{kT}\int_\sigma^\infty drr^2 u_1(r) \tag{7.7.3}$$

A plot of the isotherms of the Van der Waals equation of state is shown below:

$$\frac{\partial P}{\partial V} = 0 \tag{7.7.4}$$

$$\frac{\partial^2 P}{\partial V} = 0 \tag{7.7.5}$$

The red and blue isotherms appear similar to those of an ideal gas, i.e., there is a monotonic decrease of pressure with increasing volume. The black isotherm exhibits an unusual feature not present in any of the ideal-gas isotherms - a small region where the curve is essentially horizontal (flat) with no curvature. At this point, there is no change in pressure as the volume changes. Below this isotherm, the Van der Waals starts to exhibit unphysical behavior. The green isotherm has a region where the pressure decreases with decreasing volume, behavior that is not expected on physical grounds. What is observed experimentally, in fact, is that at a certain pressure, there is a dramatic, discontinuous change in the volume. This dramatic jump in volume signifies that a phase transition has occurred, in this case, a change from a gaseous to a liquid state. The dotted line shows this jump in the volume. Thus, the small flat neighborhood along the black isotherm becomes larger on isotherms below this one. The black isotherm just represents a boundary between those isotherms along which no such phase transition occurs and those that exhibit phase transitions in the form of discontinuous changes in the volume. For this reason, the black isotherm is called the critical isotherm, and the point at which the isotherm is flat and has zero curvature is called a **critical point**.

A critical point is a point at which

$$V_c$$

Using these two conditions, we can solve for the critical volume (V_c) and critical temperature ((T_c):

$$V_c = 3Nb$$

$$kT_c = \frac{8a}{27b}$$

$$P_c = \frac{a}{27b^2}$$

and the critical pressure is therefore

$$\kappa_{\mathrm{T}} = \frac{1}{V}\frac{\partial V}{\partial P}$$

Using these values for the critical pressure, temperature and volume, we can show that the isothermal compressibility, given by

$$\left.\frac{\partial P}{\partial V}\right|_{V=V_c} = -\frac{NkT}{2N^2b^2} + \frac{2aN^2}{27N^3b^3} = -\frac{kT}{4Nb^2} + \frac{2a}{27Nb^3} = \frac{1}{4Nb^2}\left(\frac{8a}{27b} - kT\right) \sim (T - T_c)$$

diverges as the critical point is approached. To see this, note that

$$\kappa_T \sim (T - T_c)^{-1}$$

Thus,

$$\kappa_T$$

It is observed that at a critical point, $|T - T_c|^{-\gamma}$ diverges, generally, as $Q(N,V,T) = e^{-\beta A(N,V,T)} = \frac{(V-Nb)^N}{N!\lambda^{3N}} e^{\beta aN^2/V}$. To determine the heat capacity, note that

$$E$$

so that

$$-\frac{\partial}{\partial\beta}\ln Q(N,V,T) = -\frac{\partial}{\partial\beta}\left[N\ln(V-Nb) - \ln N! - 3N\ln\lambda + \frac{\beta aN^2}{V}\right]$$
$$= \frac{3N}{\lambda}\frac{\partial\lambda}{\partial\beta} + \frac{aN^2}{V}$$
$$= \frac{3N}{\lambda}\frac{\lambda}{\partial\beta} + \frac{aN^2}{V}$$
$$= \frac{3NkT}{2} + \frac{aN^2}{V}$$
$$= C_V = \left(\frac{\partial E}{\partial T}\right)_V$$

Then, since

$$C_V = \frac{3}{2}Nk \sim |T - T_c|^0$$

it follows that

$$|T - T_c|^{-\alpha}$$

The heat capacity is observed to diverge as α. Exponents such as γ and δ are known as **critial exponents**.

Finally, one other exponent we can easily determine is related to how the pressure depends on density near the critical point. The exponent is called $\frac{P}{kT} \sim \mathrm{const} + C(\rho - \rho_c)^\delta$, and it is observed that

$$\frac{P_c}{kT_c} + \frac{1}{kT_c}\frac{\partial P}{\partial\rho}|_{\rho=\rho_c}(\rho - \rho_c) + \frac{1}{2kT_c}\frac{\partial^2 P}{\partial\rho^2}|_{\rho=rho_c}(\rho - \rho_c)^2 + \frac{1}{6kT_c}\frac{\partial^3 P}{\partial\rho^3}|_{\rho=\rho_c}(\rho - \rho_c)^3 + \cdots$$

What does our theory predict for

$\frac{P}{kT} \sim const + C(\rho - \rho_c)^\delta$? To determine $\frac{P}{kT} \sim const + C(\rho - \rho_c)^\delta$ we expand the equation of state about the critical density and temperature:

\begin{algin*} {N \over V - Nb} - {aN^2 \over kTV^2} &= {P_c \over kT_c} + {1 \over kT_c}\left.{\partial P \over \partial V}{\partial V \over \partial \rho}_{\rho= \rho_c} (\rho - rho_c) + {1 \over 2kT_c} \left [{\partial^

The second and third terms vanish by the conditions of the critical point. The third derivative term can be worked out straightforwardly and does not vanish. Rather

$$\delta = 03$$

Thus, we see that, by the above expansion, $\alpha = 0\gamma = 1\delta = 3$.

The behavior of these quantities near the critical temperature determine three critical exponents. To summarize the results, the Van der Waals theory predicts that

$$\alpha = 0.1, \gamma = 1.45$$

The determination of critical exponents such as these is an active area in statistical mechanical research. The reason for this is that such exponents can be grouped into *universality classes* - groups of systems with exactly the same sets of critical exponents. The existence of universality classes means that very different kinds of systems exhibit essentially the same behavior at a critical point, a fact that makes the characterization of phase transitions via critical exponents quite general. The values obtained above for γ, δ and $\frac{P}{kT} \sim const + C(\rho - rho_c)^{\delta}$ are known as the **mean-field exponents** and shows that the Van der Waals theory is really a mean field theory.

These exponents do not agree terribly well with experimental values ($\delta = 4.2$, $\frac{\partial P}{\partial V} > 0$). However, the simplicity of mean-field theory and its ability to give, at least, qualitative results, makes it, nevertheless, useful. To illustrate universality classes, it can be shown that, within mean field theory, the Van der Waals gas/liquid and a magnetic system composed of spins at particular lattice sites, which composes the so called **Ising model**, have exactly the same mean field theory exponents, despite the completely different nature of these two systems.

Another problem with the Van der Waals theory that is readily apparent is the fact that it predicts ρ for certain values of the density $g_0(r)$. Such behavior is unstable. Possible ways of improving the approximations used are the following:

1. Improve the approximation to $U_0(r_1, \cdots, r_N)$.
2. Choose a better zeroth order potential .
3. Go to a higher order in perturbation theory.

Barker and Henderson have shown that going to second order in perturbation theory (see discussion in McQuarrie's book, chapter 14), yields well converged results for a square well fluid, compared to "exact" results from a molecular dynamics simulation.

CHAPTER OVERVIEW

8: Rare-event sampling and free energy calculations

Our treatment of the classical ensembles makes clear that the free energy is a quantity of particular importance in statistical mechanics. Being related to the logarithm of the partition function, the free energy is the generator through which other thermodynamic quantities are obtained, via differentiation. In many cases, the free energy difference between two thermodynamic states is sought. Such differences tell, for example, whether or not a chemical reaction can occur spontaneously or requires input of work and is directly related to the equilibrium constant for the reaction. Thus, for example, from free energy differences, one can compute solvation free energies, acid ionization constants K_a and associated pK_a values, or drug inhibition constants K_i, that quantify the ability of a compound to bind to the active site of an enzyme. Another type of free energy often sought is the free energy as a function of one or more generalized coordinates in a system. An example might be the free energy surface as a function of a pair of Ramachandran angles ϕ and ψ in an oligopeptide. Such a surface would provide a map of the stable conformations of the molecule, the relative stability of such conformations and the heights of barriers that need to be crossed in a conformational change.

8.2: Free-energy Perturbation Theory

We begin our treatment of free energy differences by examining the problem of transforming a system from one thermodynamic state to another. Let these states be denoted generically as $\mathcal{A}$ and $\mathcal{B}$. At the microscopic level, these two states are characterized by potential energy functions $U_{\mathcal{A}}(\mathbf{r}_1,\dots,\mathbf{r}_N)$ and $U_{\mathcal{B}}(\mathbf{r}_1,\dots,\mathbf{r}_N)$. For example, in a drug-binding study, the state $\mathcal{A}$ might correspond to the unbound ligand and enzyme, while $\mathcal{B}$ would correspond to the bound complex. In this case, the potential $U_{\mathcal{A}}$ would exclude all interactions between the enzyme and the ligand and the enzyme, whereas they would be included in the potential $U_{\mathcal{B}}$.

The Helmholtz free energy difference between the states $\mathcal{A}$ and $\mathcal{B}$ is simply $A_{\mathcal{AB}} = A_{\mathcal{B}} - A_{\mathcal{A}}$. The two free energies $A_{\mathcal{A}}$ and $A_{\mathcal{B}}$ are given in terms of their respective canonical partition functions $Q_{\mathcal{A}}$ and $Q_{\mathcal{B}}$, respectively by $A_{\mathcal{A}} = -kT\ln Q_{\mathcal{A}}$ and $A_{\mathcal{B}} = -kT\ln Q_{\mathcal{B}}$, where

$$Q_{\mathcal{A}}(N,V,T) = C_N \int d^N\mathbf{p}\, d^N\mathbf{r}\; exp\left\{-\beta\left[\sum_{i=1}^{N}\frac{\mathbf{p}_i^2}{2m_i} + U_{\mathcal{A}}(\mathbf{r}_1,\dots,\mathbf{r}_N)\right]\right\} \tag{8.2.1}$$

$$\frac{= Z_{\mathcal{A}}(N,V,T)}{N!\lambda^{3N}} \tag{8.2.2}$$

$$Q_{\mathcal{B}}(N,V,T) = C_N \int d^N\mathbf{p}\, d^N\mathbf{r}\; exp\left\{-\beta\left[\sum_{i=1}^{N}\frac{\mathbf{p}_i^2}{2m_i} + U_{\mathcal{B}}(\mathbf{r}_1,\dots,\mathbf{r}_N)\right]\right\} \tag{8.2.3}$$

$$= \frac{Z_{\mathcal{B}}(N,V,T)}{N!\lambda^{3N}} \tag{8.2.4}$$

The free energy difference is, therefore,

$$A_{\mathcal{AB}} = A_{\mathcal{B}} - A_{\mathcal{A}} = -kT\ln\left(\frac{Q_{\mathcal{A}}}{Q_{\mathcal{A}}}\right) = -kT\ln\left(\frac{Z_{\mathcal{B}}}{Z_{\mathcal{A}}}\right) \tag{8.2.5}$$

where $Z_{\mathcal{A}}$ and $Z_{\mathcal{B}}$ are the configurational partition functions for states $\mathcal{A}$ and $\mathcal{B}$, respectively,

$$Z_{\mathcal{A}} = \int d^N\mathbf{r}\; e^{-\beta U_{\mathcal{A}}(\mathbf{r}_1,\dots,\mathbf{r}_N)} \tag{8.2.6}$$

$$Z_{\mathcal{B}} = \int d^N\mathbf{r}\; e^{-\beta U_{\mathcal{B}}(\mathbf{r}_1,\dots,\mathbf{r}_N)} \tag{8.2.7}$$

The ratio of full partition functions $Q_{\mathcal{B}}/Q_{\mathcal{A}}$ reduces to the ratio of configurational partition functions $Z_{\mathcal{B}}/Z_{\mathcal{A}}$ because the momentum integrations in the former cancel out of the ratio.

Equation 8.2.5 is difficult to implement in practice because in any numerical calculation via either molecular dynamics or Monte Carlo, we do not have direct access to the partition function only averages of phase-space functions corresponding to physical observables. However, if we are willing to extend the class of phase-space functions whose averages we seek to functions that do not necessarily correspond to direct observables, then the ratio of configurational partition functions can be manipulated to be in the form of such an average. Consider inserting unity into the expression for $Z_{\mathcal{B}}$ as follows:

$$Z_{\mathcal{B}} = \int d^N\mathbf{r}\; e^{-\beta U_{\mathcal{B}}(\mathbf{r}_1,\dots,\mathbf{r}_N)} \tag{8.2.8}$$

$$= \int d^N\mathbf{r}\; e^{-\beta U_{\mathcal{B}}(\mathbf{r}_1,\dots,\mathbf{r}_N)} e^{-\beta U_{\mathcal{A}}(\mathbf{r}_1,\dots,\mathbf{r}_N)} e^{\beta U_{\mathcal{A}}(\mathbf{r}_1,\dots,\mathbf{r}_N)} \tag{8.2.9}$$

$$= \int d^N\mathbf{r}\; e^{-\beta U_{\mathcal{A}}(\mathbf{r}_1,\dots,\mathbf{r}_N)} e^{-\beta(U_{\mathcal{B}}(\mathbf{r}_1,\dots,\mathbf{r}_N) - U_{\mathcal{A}}(\mathbf{r}_1,\dots,\mathbf{r}_N))} \tag{8.2.10}$$

If we now take the ratio $\frac{Z_{\mathcal{B}}}{Z_{\mathcal{A}}}$, we find

$$\frac{Z_\mathcal{B}}{Z_\mathcal{A}} = \frac{1}{Z_\mathcal{A}}\int d^N\mathbf{r}\; e^{-\beta U_\mathcal{A}(\mathbf{r}_1,\dots,\mathbf{r}_N)} e^{-\beta(U_\mathcal{B}(\mathbf{r}_1,\dots,\mathbf{r}_N)-U_\mathcal{A}(\mathbf{r}_1,\dots,\mathbf{r}_N))} \tag{8.2.11}$$

$$= \left\langle e^{-\beta(U_\mathcal{B}(\mathbf{r}_1,\dots,\mathbf{r}_N)-U_\mathcal{A}(\mathbf{r}_1,\dots,\mathbf{r}_N))}\right\rangle_\mathcal{A} \tag{8.2.12}$$

where the notation $\langle\cdots\rangle_\mathcal{A}$ indicates an average taken with respect to the canonical configurational distribution of the state $\mathcal{A}$. Substituting Equation 8.2.12 into Equation 8.2.5, we find

$$A_{\mathcal{AB}} = -kT\ln\left\langle e^{-\beta(U_\mathcal{B}-U_\mathcal{A})}\right\rangle_\mathcal{A} \tag{8.2.13}$$

Equation 8.2.13 is known as the **free-energy perturbation formula**; it should be reminiscent of the thermodynamic perturbation formula used to derive the van der Waals equation. Equation 8.2.13 can be interpreted as follows: We start with microstates $\{\mathbf{r}_1,\dots,\mathbf{r}_N\}$ selected from the canonical ensemble of state $\mathcal{A}$ and use these to compute $Z_\mathcal{B}$ by placing them in the state $\mathcal{B}$ by simply changing the potential energy from $U_\mathcal{A}$ to $U_\mathcal{B}$. In so doing, we need to "unbias" our choice to sample the configurations from the canonical distribution of state $\mathcal{A}$ $\mathcal{A}$ by removing the weight factor $exp(-\beta U_\mathcal{A})$ from which the microstates are sample and reweighting the states by the factor $exp(-\beta U_\mathcal{B})$ corresponding to state $\mathcal{B}$. This leads to Equation 8.2.12. The difficulty with this approach is that the microstates corresponding to the canonical distribution of state $\mathcal{A}$ may not be states of high probability in the canonical distribution of state $\mathcal{B}$. If this is the case, then the potential enegy difference $U_\mathcal{B}-U_\mathcal{A}$ will be large, he exponential factor $exp\left[-\beta(U_\mathcal{B}-U_\mathcal{A})\right]$ will be negligibly small, and the free energy difference will be very slow to converge in an actual simulation. For this reason, it is clear that the free-energy perturbation formula is only useful for cases in which the two states $\mathcal{A}$ and $\mathcal{B}$ are not that different from each other.

If $U_\mathcal{B}$ is not a small perturbation to $U_\mathcal{A}$, then the free-energy perturbation formula can still be salvaged by introducing a set of $M-2$ intermediate states with potentials $U_\alpha(r_1,\cdots,r_N)$, where $\alpha=1,\cdots,M$, $\alpha=1$ corresponds to the state $\mathcal{A}$ and $\alpha=M$ corresponds to the state $\mathcal{B}$. Let $\Delta U_{\alpha,\alpha+1}=U_{\alpha+1}-U_\alpha$. We can now imagine transforming the system from state $\mathcal{A}$ to state $\mathcal{B}$ by passing through these intermediate states and computing the average of $\Delta U_{\alpha,\alpha+1}$ in the state α. Applying the free-energy perturbation formula to this protocol yields the free-energy difference as

$$A_{\mathcal{AB}} = -kT\sum_{\alpha=1}^{M-1}\ln\left\langle e^{-\beta\Delta U_{\alpha,\alpha+1}}\right\rangle_\alpha \tag{8.2.14}$$

where $\langle\cdots\rangle_\alpha$ means an average taken over the distribution $exp(-\beta U_a)$. The key to applying Equation 8.2.14 is choosing the intermediate states so as to achieve sufficient overlap between the intermediate states without requiring a large number of them, i.e. choosing the thermodynamic path between states $\mathcal{A}$ and $\mathcal{B}$ effectively.

8.3: Adiabatic Switching and Thermodynamic Integration

The free-energy perturbation approach evokes a physical picture in which configurations sampled from the canonical distribution of state $\mathcal{A}$ are immediately "switched" to the state $\mathcal{B}$ by simply changing the potential from $U_{\mathcal{A}}$ to $U_{\mathcal{B}}$. Such "instantaneous" switching clearly represents an unphysical path from one state to the other, but we need not concern ourselves with this because the free energy is a state function and, therefore, independent of the path connecting the states. Nevertheless, we showed that the free-energy perturbation theory formula, Equation (6), is only useful if the states $\mathcal{A}$ and $\mathcal{B}$ do not differ vastly from one another, thus naturally raising the question of what can be done if the states are very different.

The use of a series of intermediate states, by which Equation (7) is derived, exploits the fact that any path between the states can be employed to obtain the free energy difference. In this section, we will discuss an alternative approach in which the system is switched slowly or *adiabatically* from one state to the other, allowing the system to fully relax at each point along a chosen path from state $\mathcal{A}$ to state $\mathcal{B}$, rather than instantaneously switching the system between intermediate states, as occurs in Equation (7). In order to effect the switching from one state to the other, we will employ a common trick in the form of an "external" switching parameter, λ. This parameter is introduced by defining a new potential energy function

$$U(\mathbf{r}_1,\ldots,\mathbf{r}_N,\lambda) \equiv f(\lambda)U_{\mathcal{A}}(\mathrm{r}_1,\ldots,\mathbf{r}_N)+g(\lambda)U_{\mathcal{B}}(\mathbf{r}_1,\ldots,\mathbf{r}_N) \tag{8.3.1}$$

The functions $f(\lambda)$ and $g(\lambda)$ are referred to as **switching functions,** and they required to satisfy the conditions $f(0)=1, f(1)=0$, corresponding to the state $\mathcal{A}$, and $g(0)=0, g(1)=1$, corresponding to the state $\mathcal{B}$. Apart from these conditions, $f(\lambda)$ and $g(\lambda)$ are completely arbitrary. The mechanism embodied in Equation 8.3.1 is one in which some imaginary external controlling influence ("hand of God"), represented by the λ parameter, starts the system off in state $\mathcal{A}(\lambda=0)$ and slowly switches off the potential $U_{\mathcal{A}}$ while simultaneously switching on the potential $U_{\mathcal{B}}$. The process is complete when $\lambda=1$, when the system is in state $\mathcal{B}$. A simple choice for the functions $f(\lambda)$ and $g(\lambda)$ is, for example, $f(\lambda)=1-\lambda$ and $g(\lambda)=\lambda$.

In order to see how Equation 8.3.1 can be used to compute the free energy difference $A_{\mathcal{AB}}$, consider the canonical partition function of a system described by the potential of Equation 8.3.1 for a particular choice of λ:

$$Q(N,V,T,\lambda)=C_N\int d^N\mathbf{p}\; d^N\mathbf{r}\; exp\left\{-\beta\left[\sum_{i=1}^{N}\frac{\mathbf{P}_i^2}{2m_i}+U(\mathbf{r}_1,\ldots,\mathbf{r}_N,\lambda)\right]\right\} \tag{8.3.2}$$

This partition function leads to a free energy $A(N,V,T,\lambda)$ via

$$A(N,V,T,\lambda)=-kT\ln Q(N,V,T,\lambda) \tag{8.3.3}$$

Recall, however, that the derivatives of the free energy with repsect to N, and V and T lead to the chemical potential, pressure and entropy, respectively. What does the derivative of the free energy $A(N,V,T,\lambda)$ with respect to λ represent? According to Equation 8.3.3

$$\frac{\partial A}{\partial\lambda}=-\frac{kT}{Q}\frac{\partial Q}{\partial\lambda}=-\frac{kT}{Z}\frac{\partial Z}{\partial\lambda} \tag{8.3.4}$$

The reader should check that the expressions involving Q and Z are equivalent. Computing the derivative of Z with respect to λ, we find

$$\frac{kT}{Z}\frac{\partial Z}{\partial\lambda}=\frac{kT}{Z}\frac{\partial}{\partial\lambda}\int d^N\mathbf{r}\; e^{-\beta U(\mathbf{r}_1,\ldots,\mathbf{r}_N,\lambda)} \tag{8.3.5}$$

$$=\frac{kT}{Z}\int d^N\mathbf{r}\;\left(-\beta\frac{\partial U}{\partial\lambda}\right)e^{-\beta U(\mathbf{r}_1,\ldots,\mathbf{r}_N,\lambda)} \tag{8.3.6}$$

$$=-\left\langle\frac{\partial U}{\partial\lambda}\right\rangle \tag{8.3.7}$$

Now, the free energy difference $A_{\mathcal{AB}}$ can be obtained trivially from the relation

$$A_{\mathcal{AB}}=\int_0^1\frac{\partial A}{\partial\lambda}d\lambda \tag{8.3.8}$$

Substituting eqns. 8.3.4 and 8.3.7 into Equation 8.3.8, we obtain the free energy difference as

$$A_{\mathcal{AB}} = \int_0^1 \left\langle \frac{\partial U}{\partial \lambda} \right\rangle_\lambda d\lambda \tag{8.3.9}$$

where $\langle \cdots \rangle_\lambda$ denotes an average over the canonical ensemble described by the distribution $\exp[-\beta U(\mathbf{r}_1, \dots, \mathbf{r}_N, \lambda)]$ with λ fixed at a particular value. The special choice of $f(\lambda) = 1 - \lambda$ and $g(\lambda) = \lambda$ has a simple interpretation. For this choice, Equation 8.3.9 becomes

$$A_{\mathcal{AB}} = \int_0^1 \langle U_{\mathcal{B}} - U_{\mathcal{A}} \rangle_\lambda d\lambda \tag{8.3.10}$$

The content of Equation (15) can be understood by recalling the relationship between work and free energy from the second law of thermodynamics. If, in transforming the system from state $\mathcal{A}$ to state $\mathcal{B}$, an amount of work W is performed on the system, then

$$W \geq A_{\mathcal{AB}} \tag{8.3.11}$$

where equality holds *only* if the transformation is carried out along a *reversible path*. Since reversible work is related to a change in potential energy, Equation 8.3.10 is actually a statistical version of Equation 8.3.11 for the special case of equality. Equation (15) tells us that the free energy difference is the ensemble average of the microscopic reversible work needed to change the potential energy of each configuration from $U_{\mathcal{A}}$ to $U_{\mathcal{B}}$ along the chosen λ-path. Note, however, that Equation (14), which is known as the *thermodynamic integration* formula, is true independent of the choice of $f(\lambda)$ and $g(\lambda)$, which means that Equation (14) always yields the reversible work via the free energy difference. The flexibility in the choice of the λ-path, however, can be exploited to design adiabatic switching algorithms of greater efficiency that can be achieved with the simple choice $f(\lambda) = 1 - \lambda, g(\lambda) = \lambda$.

In practice, the thermodynamic integration formula is implemented as follows: A set of M values of λ is chosen from the interval $[0, 1]$, and at each chosen value λ_k, a full molecular dynamics or Monte Carlo calculation is carried out in order to generate the average $\left\langle \frac{\partial U}{\partial \lambda_k} \right\rangle_{\lambda_k}$. The resulting values of $\left\langle \frac{\partial U}{\partial \lambda_k} \right\rangle_{\lambda_k}$, $k = 1, \cdots, M$ are then substituted into Equation (14), and the resulted is integrated numerically to produce the free energy difference $A_{\mathcal{AB}}$. Thus, we see that the selected values $\{\lambda_k\}$ can be evenly spaced, for example, or they could be a set of Gaussian quadrature nodes, depending on how $A(N, V, T, \lambda)$ is expected to vary with λ for the chosen $f(\lambda)$ and $g(\lambda)$.

As with free-energy perturbation theory, the thermodynamic integration approach can be implemented very easily. An immediately obvious disadvantage of the method, however, is the same one that applies to Equation (7): In order to perform the numerical integration, it is necessary to perform many simulations of a system at physically uninteresting intermediate values of λ where the potential $U(\mathbf{r}_1, \dots, \mathbf{r}_N, \lambda)$ is, itself, unphysical. Only $\lambda = 0, 1$ correspond to actual physical states and ultimately, we can only attach physical meaning to the free energy difference $A_{\mathcal{AB}} = A(N, V, T, 1) - A(N, V, T, 0)$. Nevertheless, the intermediate averages must be accurately calculated in order for the integration to yield a correct result. The approach to be presented in the next section attempts to reduce the time spent in such unphysical intermediate states and focuses the sampling in the important regions $\lambda = 0, 1$.

8.4: Reaction Coordinates

It is frequently the case that the progress of some chemical, mechanical, or thermodynamics process can be followed by following the evolution of a small subset of generalized coordinates in a system. When generalized coordinates are used in this manner, they are typically referred to as *reaction coordinates*, *collective variables*, or *order parameters*, often depending on the context and type of system. Whenever referring to these coordinates, we will refer to them as *reaction coordinates*, although the reader should be aware that the other two designations are also used in the literature.

As an example of a useful reaction coordinate, consider a simple gas-phase diatomic dissociation process

$$\mathrm{AB} \longrightarrow \mathrm{A} + \mathrm{B}.$$

If $\mathbf{r}_A$ and $\mathbf{r}_B$ denote the Cartesian coordinates of atom A and B, then a useful generalized coordinate for following the progress of the dissociation is simply the distance $r = |\mathbf{r}_B - \mathbf{r}_A|$. A complete set of generalized coordinates that contains$r$ as one of the coordinates is the set that contains the center of mass

$$\mathbf{R} = \frac{m_A \mathbf{r}_A + m_B \mathbf{r}_B}{m_A + m_B},$$

the magnitude of the relative coordinate

$r = |\mathbf{r}_B - \mathbf{r}_A|$

and the two angles $\phi = \tan^{-1}(y/x)$ and $\theta = \tan^{-1}(\sqrt{x^2 + y^2}/z)$, where x, y and z are the components of the relative coordinate

$$\mathbf{r} = \mathbf{r}_B - \mathbf{r}_A.$$

Of course, in the gas-phase, where the potential between A and B likely only depends on the distance between A and B, r is really the *only* interesting coordinate. However, if the reaction were to take place in solution, then other coordinate such as θ and ϕ become more relevant as specific orientations might change the mechanism or thermodynamic picture of the process, depending on the complexity of the solvent, and averaging over these degrees of freedom to produce a free energy profile $A(r)$ in r alone will wash out some of this information.

As another example, consider a gas-phase proton transfer reaction

$$\mathrm{A{-}H} \cdots \mathrm{B} \longrightarrow \mathrm{A} \cdots \mathrm{H{-}B}.$$

Here, although the distance $|\mathbf{r}_H - \mathbf{r}_A|$ can be used to monitor the progress of the proton away from A and the distance $|\mathbf{r}_H - \mathbf{r}_B|$ can be used to monitor the progress of the proton toward B, neither distance alone is sufficient for following the progress of the reaction. However, the difference

$$\delta = |\mathbf{r}_H - \mathbf{r}_B| - |\mathbf{r}_H - \mathbf{r}_A|$$

can be used to follow the progress of the proton transfer from A to B and, therefore, is a potentially useful reaction coordinate. A complete set of generalized coordinates involving δ can be constructed as follows. If $\mathbf{r}_A$, $\mathbf{r}_B$ and $\mathbf{r}_H$ denote the Cartesian coordinates of the three atoms, then first introduce the center-of-mass

$$\mathbf{R} = \frac{m_A \mathbf{r}_A + m_B \mathbf{r}_B + m_H \mathbf{r}_H}{m_A + m_B + m_H}$$

the relative coordinate between A and B, $\mathbf{r} = \mathbf{r}_\mathrm{B} - \mathbf{r}_\mathrm{A}$, and a third relative coordinate s between H and the center-of-mass of A and B,

$$\mathbf{s} = \mathbf{r} - \frac{m_\mathrm{A} \mathbf{r}_\mathrm{A} + m_\mathrm{B} \mathbf{r}_\mathrm{B}}{m_\mathrm{A} + m_\mathrm{B}}.$$

Finally, $\mathbf{r}$ is transformed into spherical polar coordinates, (r, θ, ϕ), and from $\mathbf{r}$ and s, three more coordinates are formed:

$$\sigma = \left|\mathbf{s} + \frac{m_\mathrm{B}}{m_\mathrm{A} + m_\mathrm{B}}\mathbf{r}\right| + \left|\mathbf{s} - \frac{m_\mathrm{A}}{m_\mathrm{A} + m_\mathrm{B}}\mathbf{r}\right| \delta = \left|\mathbf{s} + \frac{m_\mathrm{B}}{m_\mathrm{A} + m_\mathrm{B}}\mathbf{r}\right| - \left|\mathbf{s} - \frac{m_\mathrm{A}}{m_\mathrm{A} + m_\mathrm{B}}\mathbf{r}\right|$$

and the angle α, which measures the "tilt" of the plane containing the three atoms from the vertical. The coordinates (σ, δ, α) are known as **confocal elliptic coordinates**. These coordinates could also be used if the reaction takes place in solution. As expected, the generalized coordinates are functions of the original Cartesian coordinates. The alanine-dipeptide example above also employs the Ramachandran angles ϕ and ψ as reaction coordinates, and these can also be expressed as part of a set of generalized coordinates that are functions of the original Cartesian coordinates of a system.

While reaction coordinates or collective variables are potentially very useful constructs, they must be used with care, particularly when enhanced sampling methods are applied to them. Enhanced sampling of a poorly chosen reaction coordinate can bias the system in unnatural ways, leading to erroneous predictions of free energy barriers and associated mechanisms. A dramatic example of this is the autodissociation of liquid water following the classic reaction

$$2\,\mathrm{H_2O(l)} \longrightarrow \mathrm{H_3O^+(aq)} + \mathrm{OH^-(aq)}$$

the ostensibly only requires transferring a proton from one water molecule to another. If this notion of the reaction is pursued, then a seemingly sensible reaction coordinate would simply be the distance between the oxygen and the transferring proton or the number of hydrogens covalently bonded to the oxygen. These reaction coordinates, as it turns out, are inadequate for describing the true nature of the reaction and, therefore, fail to yield reasonable free energies (and hence, values of the autoionization constant K_w). Chandler and coworkers showed that the dissociation reaction can only be considered to have occurred when the $\mathrm{H_3O^+}$ and $\mathrm{OH^-}$ ions are sufficiently far apart that no contiguous or direct path of hydrogen-bonding in the liquid can allow the proton to transfer back to the water or its origin. In order to describe such a process correctly, a very different type of reaction coordinate would clearly be needed.

Keeping in mind such caveats about the use of reaction coordinates, we now proceed to describe a number of popular methods designed to enhance sampling along pre-selected reaction coordinates. All of these methods are designed to generate, either directly or indirectly, the probability distribution function $P(q_1, \cdots, q_n)$ of a subset of n reaction coordinates of interest in a system. If these reaction coordinates are obtained from a transformation of the Cartesian coordinates $q_\alpha = f_\alpha(\mathbf{r}_1, \ldots, \mathbf{r}_N)$, $\alpha = 1, \cdots, n$, then the probability density that these n coordinates will have values $q_\alpha = s_\alpha$ in the canonical ensemble is

$$P(s_1, \ldots, s_n) = \frac{C_N}{Q(N,V,T)} \int d^N\mathbf{p}\; d^N\mathbf{r} e^{-\beta H(p,r)} \Phi^n_{\alpha=1} \delta(f_\alpha(\mathbf{r}_1, \ldots, \mathbf{r}_N) - s_\alpha)$$

where the δ-functions are introduced to fix the reaction coordinates at values $q_1, \cdots, q_n$ at $s_1, \cdots, s_n$. Once $P(s_1, \cdots, s_n)$ is known, the **free energy hypersurface** in these coordinates is given by

$$A(s_1, \ldots, s_n) = -kT \ln P(s_1, \ldots, s_n)$$

8.5: Jarzynski's Equality and Nonequilibrium Methods

In this section, the relationship between work and free energy will be explored in greater detail. We have already introduced the inequality in Equation ???, which states that if an amount of work $W_{\mathcal{AB}}$ is performed on a system, taking from state $\mathcal{A}$ to state $\mathcal{B}$, then $W_{\mathcal{AB}} \geq A_{\mathcal{AB}}$. Here, equality holds only if the work is performed reversibly. The work referred to here is thermodynamic quantity and, as such, must be regarded as an ensemble average. In statistical mechanics, we can also introduce the mechanical or microscopic work $\mathcal{W}_{\mathcal{AB}}(\mathrm{x})$ performed on one member of the ensemble to drive it from state $\mathcal{A}$ to state $\mathcal{B}$. Then, $W_{\mathcal{AB}}$ is simply an ensemble average of $\mathcal{W}_{\mathcal{AB}}$. However, we need to be somewhat careful about how we define this ensemble average because the work is defined along a particular path or trajectory which takes the system from state $\mathcal{A}$ to state $\mathcal{B}$, and equilibrium averages do not refer not to paths but to microstates. This distinction is emphasized by the fact that the work could be carried out irreversibly, such that the system is driven out of equilibrium. Thus, the proper definition of the ensemble average follows along the lines already discussed in the context of the free-energy perturbation approach, namely, averaging over the canonical distribution for the state $\mathcal{A}$. In this case, since we will be discussing actual paths $\mathrm{x_t}$, we let the initial condition x_0 be the phase space vector for the system in the (initial) state $\mathcal{A}$. Recall that $x_t = x_t(x_0)$ is a unique function of the initial conditions. Then

$$W_{\mathcal{AB}} = \langle \mathcal{W}_{\mathcal{AB}}(\mathrm{x}_0)\rangle_{\mathcal{A}} \tag{8.5.1}$$

$$= \frac{C_N}{Q_{\mathcal{A}}(N,V,T)} \int d\mathrm{x}_0 \mathrm{e}^{-\beta \mathrm{H}_{\mathcal{A}}(\mathrm{x}_0)} \mathcal{W}_{\mathcal{AB}}(\mathrm{x}_0) \tag{8.5.2}$$

and the Clausius inequality can be stated as $\langle \mathcal{W}_{\mathcal{AB}}(\mathrm{x}_0)\rangle_{\mathcal{A}} \geq A_{\mathcal{AB}}$.

From such an inequality, it would seem that using the work as a method for calculating the free energy is of limited utility, since the work necessarily must be performed reversibly, otherwise one obtains only upper bound on the free energy. It turns out, however, that irreversible work can be used to calculate free energy differences by virtue of a connection between the two quantities first discovered in 1997 by C. Jarzynski that as come to be known as the **Jarzynski equality**. This equality states that if, instead of averaging $\mathcal{W}_{\mathcal{AB}}(\mathrm{x}_0)$ over the initial canonical distribution (that of state $\mathcal{A}$), an average of $\exp[-\beta \mathcal{W}_{\mathcal{AB}}(\mathrm{x}_0)]$ is performed over the same distribution, the result is $\exp[-\beta A_{\mathcal{AB}}]$, i.e.

$$e^{-\beta A_{\mathcal{AB}}} = \langle e^{-\beta \mathcal{W}_{\mathcal{AB}}(\mathrm{x}_0)}\rangle_{\mathcal{A}} \tag{8.5.3}$$

$$= \frac{C_N}{Q_{\mathcal{A}}(N,V,T)} \int d\mathrm{x}_0 \mathrm{e}^{-\beta \mathrm{H}_{\mathcal{A}}(\mathrm{x}_0)} \mathrm{e}^{-\beta \mathcal{W}_{\mathcal{AB}}(\mathrm{x}_0)} \tag{8.5.4}$$

This remarkable result not only provides a foundation for the development of nonequilibrium free-energy methods but also has profound implications for thermodynamics, in general.

The Jarzynski equality be proved using different strategies. Here, however, we will present a proof that is most relevant for the finite-sized systems and techniques employed in molecular dynamics calculations. Consider a time-dependent Hamiltonian of the form

$$H(\mathbf{p},\mathbf{r},t) = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i} + U(\mathbf{r}_1,\ldots,\mathbf{r}_N,t) \tag{8.5.5}$$

For time-dependent Hamiltonian's, the usual conservation law $dH/dt = 0$ no longer holds, which can be seen by computing

$$\frac{dH}{dt} = \nabla_{\mathrm{x}_t} H \dot{\mathrm{x}}_t + \frac{\partial H}{\partial t} \tag{8.5.6}$$

where the phase space vector $\mathrm{x} = (\mathbf{p}_1,\ldots,\mathbf{p}_N,\mathbf{r}_1,\ldots,\mathbf{r}_N) \equiv (\mathbf{p},\mathbf{r})$ has been introduced. Integrating both sides over time from $t=0$ to a final time $t=\tau$, we find

$$\int_0^\tau dt\ \frac{dH}{dt} = \int_0^\tau dt\ \nabla_{\mathrm{x}_t} H \mathrm{x}_t + \int_0^\tau dt\ \frac{\partial H}{\partial t} \tag{8.5.7}$$

Equation 8.5.7 can be regarded as a microscopic version of the first law of thermodynamics, in which the first and second terms represent the heat absorbed by the system and the work done on the system over the trajectory, respectively. Note that the work is actually a function of the initial phase-space vector x_0, which can be seen by writing this term explicitly as

$$W_\tau(\mathrm{x}_0) = \int_0^\tau \; dt \; \frac{\partial}{\partial t} H(\mathrm{x}_t(\mathrm{x}_0), t) \tag{8.5.8}$$

where the fact that the work depends explicitly on τ in Equation 8.5.8 is indicated by the subscript. In the present discussion, we will consider that each initial condition, selected from a canonical distribution in x_0, evolves according to Hamilton's equations in isolation. In this case, the heat term $\nabla_{\mathrm{x}_t} H \cdot \mathrm{x}_t = 0$, and we have the usual addition to Hamilton's equations $dH/dt = \partial H/\partial t$.

With the above condition, we can write the microscopic work as

$$\mathcal{W}_{\mathcal{AB}} = \int_0^\tau \frac{d}{dt} H(\mathrm{x}_t(\mathrm{x}_0), \mathrm{t})\mathrm{dt} = \mathrm{H}(\mathrm{x}_\tau(\mathrm{x}_0), \tau) - \mathrm{H}(\mathrm{x}_0, 0) \tag{8.5.9}$$

The last term $H(\mathrm{x}_0, 0)$ is also $H_{\mathcal{A}}(\mathrm{x}_0)$. Thus, the ensemble average of the exponential of the work becomes

$$\langle e^{-\beta \mathcal{W}_{\mathcal{AB}}} \rangle_{\mathcal{A}} = \frac{C_N}{Q_{\mathcal{A}}(N,V,T)} \int d\mathrm{x}_0 \; e^{-\beta H_{\mathcal{A}}(\mathrm{x}_0)} e^{-\beta[H(\mathrm{x}_\tau(\mathrm{x}_0),\tau) - H_{\mathcal{A}}(\mathrm{x}_0)]} \tag{8.5.10}$$

$$\frac{C_N}{Q_{\mathcal{A}}(N,V,T)} \int d\mathrm{x}_0 \; e^{-\beta H(\mathrm{x}_\tau(\mathrm{x}_0),\tau)} \tag{8.5.11}$$

The numerator in this expression becomes much more interesting if we perform a change of variables from x_0 to x_τ. Since the solution of Hamilton's equations for the time-dependent Hamiltonian uniquely map the initial condition x_0 onto x_t, when $t = \tau$, we have a new set of phase-space variables, and by Liouville's theorem, the phase-space volume element is preserved

$$d\mathrm{x}_\tau = d\mathrm{x}_0 \tag{8.5.12}$$

When the Hamiltonian is transformed, we find $H(\mathrm{x}_\tau, \tau) = H_{\mathcal{B}}(\mathrm{x}_\tau)$. Consequently,

$$\langle e^{-\beta \mathcal{W}_{\mathcal{AB}}} \rangle_{\mathcal{A}} = \frac{C_N}{Q(N,V,T)} \int d\mathrm{x}_\tau \; e^{-\beta H_{\mathcal{B}}(\mathrm{x}_\tau)} \tag{8.5.13}$$

$$= \frac{Q_{\mathcal{B}}(N,V,T)}{Q_{\mathcal{A}}(N,V,T)} \tag{8.5.14}$$

$$= e^{-\beta A_{\mathcal{AB}}} \tag{8.5.15}$$

thus proving the equality. The implication of the Jarzynski equality is that the work can be carried out along a reversible or irreversible path, and the correct free energy will still be obtained.

Note that due to Jensen's inequality:

$$\langle e^{-\beta \mathcal{W}_{\mathcal{AB}}} \rangle_{\mathcal{A}} \geq e^{-\beta \langle \mathcal{W}_{\mathcal{AB}} \rangle_{\mathcal{A}}} \tag{8.5.16}$$

Using Jarzynski's equality, this becomes

$$e^{-\beta A_{\mathcal{AB}}} \geq e^{-\beta \langle \mathcal{W}_{\mathcal{AB}} \rangle_{\mathcal{A}}} \tag{8.5.17}$$

which implies, as expected, that

$$A_{\mathcal{AB}} \leq \langle \mathcal{W}_{\mathcal{AB}} \rangle_{\mathcal{A}} \tag{8.5.18}$$

8.6: The "blue moon" Ensemble Approach

The term "blue moon" in the present context describes rare events, *i.e.* events that happen once in a blue moon. The blue moon ensemble approach was introduced by Ciccotti and coworkers as a technique for computing the free energy profile along a reaction coordinate direction characterized by one or more barriers high enough that they would not likely be crossed in a normal thermostatted molecular dynamics calculation.

Suppose a process of interest can be monitored by a single reaction coordinate $q_1 = f_1(\mathbf{r}_1, \dots, \mathbf{r}_N)$ so that eqns. (29) and (30) reduce to

$$P(s) = \frac{C_N}{Q(N,V,T)} \int d^N\mathbf{p}\; d^N\mathbf{r} e^{-\beta H(\mathbf{p},\mathbf{r})}\, \delta(f_1(\mathbf{r}_1, \dots, \mathbf{r}_N) - s) \tag{8.6.1}$$

$$= \frac{1}{N!\lambda^{3N} Q(N,V,T)} \int d^N\mathbf{r} e^{-\beta U(\mathbf{r})}\, \delta(f_1(\mathbf{r}_1, \dots, \mathbf{r}_N) - s) \tag{8.6.2}$$

$$A(s) = -kT \ln P(s) \tag{8.6.3}$$

The "1" subscript on the value s of q_1 is superfluous and will be dropped throughout this discussion. In the second line, the integration over the momenta has been performed giving the thermal prefactor factor λ^{3N}. In the blue moon ensemble approach, a holonomic constraint $\sigma(\mathbf{r}_1, \dots, \mathbf{r}_N) = f_1(\mathbf{r}_1, \dots, \mathbf{r}_N) - s$ is introduced in a molecular dynamics calculation as a means of "driving" the reaction coordinate from an initial value s_i to a final value s_f via a set of intermediate points $s_1, \dots, s_n$ between s_i and s_f. Unfortunately, the introduction of a holonomic, constraint does not yield the single δ-function condition $\delta(\sigma(\mathbf{r}) = \delta(f_1(\mathbf{r}) - s)$, where $\mathbf{r} \equiv \mathbf{r}_1, \dots, \mathbf{r}_N$ required by Equation 8.6.3 but rather the product of δ-functions $\delta(\sigma(\mathbf{r}))\delta(\dot{\sigma}(\mathbf{r}, \mathbf{p}))$, since both the constraint and its first time derivative are imposed in a constrained dynamics calculation. We will return to this point a bit later in this section. In addition to this, the blue moon ensemble approach does not yield $A(s)$ directly but rather the derivative

$$\frac{dA}{ds} = -\frac{kT}{P(s)} \frac{dP}{ds} \tag{8.6.4}$$

from which the free energy profile $A(q)$ along the reaction coordinate and the free energy difference $\Delta A = A(s_f) - A(s_i)$ are given by the integrals

$$A(q) = A(s_i) + \int_{s_i}^{q} ds \frac{dA}{ds} \qquad \Delta A = \int_{s_i}^{s_f} ds \frac{dA}{ds} \tag{8.6.5}$$

In the free-energy profile expression $A(s_i)$ is just an additive constant that can be left off. The values $s_1, \dots, s_n$ at which the reaction coordinate is constrained can be chosen at equally-spaced intervals between s_i and s_f, in which a standard numerical quadrature can $q = f_1(\mathbf{r})$ be applied for evaluating the integrals in Equation 8.6.5, or they can be chosen according to a more sophisticated quadrature scheme.

We next turn to the evaluation of the derivative in Equation 8.6.4. Noting that $P(s) = \langle \delta(f_1(\mathbf{r}) - s) \rangle$, the derivative can be written as

$$\frac{1}{P(s)} \frac{dP}{ds} = \frac{C_N}{Q(N,V,T)} \frac{\int d^N\mathbf{p} d^N\mathbf{r} e^{-\beta H_{(p,r)}} \frac{\partial}{\partial s} \delta(f_1(\mathbf{r}) - s)}{\langle \delta(f_1(\mathbf{r}) - s) \rangle} \tag{8.6.6}$$

In order to avoid evaluating the derivative of the δ-function, an integration by parts can be used. First, we introduce a complete set of $3N$ generalized coordinates:

$$q_\alpha = f_\alpha(\mathbf{r}_1, \dots, \mathbf{r}_N) \tag{8.6.7}$$

and their conjugate momenta p_α. Such a transformation has a unit Jacobian so that $d^N\mathbf{p}\; d^N\mathbf{r} = d^{3N}p\; d^{3N}q$. Denoting the transformed Hamiltonian as $\tilde{H}(p,q)$, Equation 8.6.6 becomes

$$\frac{1}{P(s)} \frac{dP}{ds} = \frac{C_N}{Q(N,V,T)} \frac{\int d^{3N}P d^{3N}q e^{-\beta \tilde{H}(p,q)} \frac{\partial}{\partial s} \delta(q_1 - s)}{\langle \delta(q_1 - s) \rangle} \tag{8.6.8}$$

Changing the derivative in front of the δ-function from $\partial/\partial s$ to $\partial/\partial q_1$, which introduces an overall minus sign, and then integrating by parts yields

$$\frac{1}{P(s)}\frac{dP}{ds} = \frac{C_N}{Q(N,V,T)}\frac{\int d^{3N}p\, d^{3N}q \left[\frac{\partial}{\partial q_1}e^{-\beta\tilde{H}(p,q)}\right]\delta(q_1-s)}{\langle\delta(q_1-s)\rangle} \tag{8.6.9}$$

$$= -\frac{\beta C_N}{Q(N,V,T)}\frac{\int d^{3N}p\, d^{3N}q\, \frac{\partial\tilde{H}}{\partial q_1}e^{-\beta\tilde{H}(p,q)}\delta(q_1-s)}{\langle\delta(q_1-s)\rangle} \tag{8.6.10}$$

$$= -\beta\frac{\left\langle\left(\frac{\partial\tilde{H}}{\partial q_1}\right)\delta(q_1-s)\right\rangle}{\langle\delta(q_1-s)\rangle} \tag{8.6.11}$$

The last line defines a new ensemble average, specifically an average subject to the condition (not constraint) that the coordinate q_1 have the particular value s. This average will be denoted $\langle\cdots\rangle_s^{\text{cond}}$. Thus, the derivative becomes

$$\frac{1}{P(s)}\frac{dP}{ds} = -\beta\left\langle\frac{\partial\tilde{H}}{\partial q_1}\right\rangle_s^{\text{cond}} \tag{8.6.12}$$

Substituting Equation 8.6.12 yields a free energy profile of the form

$$A(q) = A(s_i) + \int_{s_i}^{q} ds \left\langle\frac{\partial\tilde{H}}{\partial q_1}\right\rangle_s^{\text{cond}} \tag{8.6.13}$$

from which ΔA can be computed by letting $q = s_f$. Given that - $\langle\partial\tilde{H}/\partial q_1\rangle_s^{\text{cond}}$ is the expression for the average of the generalized force on q_1 when $q_1 = s$, the integral represents the work done *on* the system, i.e. the negative of the work done by the system, in moving from s_i to an arbitrary final point q. Since the conditional average implies a full simulation at each fixed value of q_1, the thermodynamic transformation is certainly carried out reversibly, so that Equation 8.6.13 is consistent with the Clausius inequality.

Although Equation 8.6.13 provides a very useful insight into the underlying statistical mechanical expression for the free energy, technically, the need for a full canonical transformation of both coordinates and momenta is inconvenient since, from the chain rule

$$\frac{\partial\tilde{H}}{\partial q_1} = \sum_{i=1}^{N}\left[\frac{\partial H}{\partial\mathbf{p}_i}\cdot\frac{\partial\mathbf{p}_i}{\partial q_1} + \frac{\partial H}{\partial\mathbf{r}_i}\cdot\frac{\partial\mathbf{r}_i}{\partial q_1}\right] \tag{8.6.14}$$

A more useful expression results if the momenta integrations are performed before introducing the transformation to generalized coordinates. Starting again with Equation 8.6.6, we carry out the momentum integrations, yielding

$$\frac{1}{P(s)}\frac{dP}{ds} = \frac{1}{N!\lambda^{3N}Q(N,V,T)}\frac{\int d^N\mathbf{r}e^{-\beta U(r)}\frac{\partial}{\partial s}\delta(f_1(\mathbf{r})-s)}{\langle\delta(f_1(\mathbf{r})-s)\rangle} \tag{8.6.15}$$

Now, we introduce *only* the transformation of the coordinates to generalized coordinates $q_\alpha = f_\alpha(\mathbf{r}_1,\dots,\mathbf{r}_N)$. However, because there is no corresponding momentum transformation, the Jacobian of the transformation is not unity. Let $J(q) \equiv J(q_1,\dots,q_{3N}) = \partial(\mathbf{r}_1,\dots,\mathbf{r}_N)/\partial(q_1,\dots,q_{3N})$ denote the Jacobian of the transformation. Then, Equation 8.6.15 becomes

$$\frac{1}{P(s)}\frac{dP}{ds} = \frac{1}{N!\lambda^{3N}Q(N,V,T)}\frac{\int d^{3N}q\, J(q)e^{-\beta\tilde{U}(q)}\frac{\partial}{\partial s}\delta(q_1-s)}{\langle\delta(q_1-s)\rangle} \tag{8.6.16}$$

$$= \frac{1}{N!\lambda^{3N}Q(N,V,T)}\frac{\int d^{3N}q\, e^{-\beta(U(q)-kTJ(q))}\frac{\partial}{\partial s}\delta(q_1-s)}{\langle\delta(q_1-s)\rangle} \tag{8.6.17}$$

where, in the last line, the Jacobian has been exponentiated. Changing the derivative $\partial/\partial s$ to $\partial/\partial q_1$ and performing the integration by parts as was done in Equation 8.6.11, we obtain

$$\frac{1}{P(s)}\frac{dP}{ds} = \frac{1}{N!\lambda^{3N}Q(N,V,T)}\frac{\int d^{3N}q\,\frac{\partial}{\partial q_1}e^{-\beta\left(\tilde{U}(q)-kT\ln J(q)\right)}\delta(q_1-s)}{\langle\delta(q_1-s)\rangle} \tag{8.6.18}$$

$$= -\frac{\beta}{N!\lambda^{3N}Q(N,V,T)}\frac{\int d^{3N}q\,\left[\frac{\partial\tilde{U}}{partial q_1} - KT\frac{\partial}{\partial q_1}\ln J(q)\right]e^{-\beta\left(\tilde{U}(q)-kT\ln J(q)\right)}\delta(q_1-s)}{\langle\delta(q_1-s)\rangle} \tag{8.6.19}$$

$$= -\beta\left\langle\left[\frac{\partial\tilde{U}}{\partial q_1} - kT\frac{\partial}{\partial q_1}\ln J(q)\right]\right\rangle_s^{\text{cond}} \tag{8.6.20}$$

Therefore, the free energy profile becomes

$$A(q) = A(s_i) + \int_{s_i}^{q} ds\,\left\langle\left[\frac{\partial\tilde{U}}{\partial q_1} - KT\frac{\partial}{\partial q_1}\ln J(q)\right]\right\rangle_s^{\text{cond}} \tag{8.6.21}$$

Again, the derivative of $\tilde{U}$, the transformed potential, can be computed form the untransformed potential via the chain rule

$$\frac{\partial\tilde{U}}{\partial q_1} = \sum_{i=1}^{N}\frac{\partial U}{\partial \mathbf{r}_i}\cdot\frac{\partial \mathbf{r}_i}{\partial q_1} \tag{8.6.22}$$

Equation 8.6.21 is useful for simple reaction coordinates in which the full transformation to generalized coordinates is known. We will see shortly how the expression for $A(q)$ can be further simplified in a way that does not require knowledge of the transformation at all. First, however, we must tackle the problem alluded to earlier of computing the conditional ensemble averages from the constrained dynamics employed by the blue moon ensemble method.

CHAPTER OVERVIEW

9: Review of the basic postulates of quantum mechanics

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9.1: Measurement

The result of a measurement of the observable A must yield one of the eigenvalues of $\hat{A}$. Thus, we see why A is required to be a hermitian operator: Hermitian operators have *real* eigenvalues. If we denote the set of eigenvalues of $\hat{A}$ by $\{a_i\}$, then each of the eigenvalues a_i satisfies an eigenvalue equation

$$\hat{A}|a_i\rangle = a_i|a_i\rangle$$

where $|a_i\rangle$ is the corresponding eigenvector. Since the operator $\hat{A}$ is hermitian and a_i is therefore real, we have also the left eigenvalue equation

$$\langle a_i|\hat{A} = \langle a_i|a_i$$

The probability amplitude that a measurement of A will yield the eigenvalue a_i is obtained by taking the inner product of the corresponding eigenvector $|a_i\rangle$ with the state vector $|\Psi(t)\rangle$, $\langle a_i|\Psi(t)\rangle$. Thus, the probability that the value a_i is obtained is given by

$$P_{a_i} = |\langle a_i|\Psi(t)\rangle|^2$$

Another useful and important property of hermitian operators is that their eigenvectors form a complete orthonormal basis of the Hilbert space, when the eigenvalue spectrum is non-degenerate. That is, they are linearly independent, span the space, satisfy the orthonormality condition

$$\langle a_i|a_j\rangle = \delta_{ij}$$

and thus any arbitrary vector $|\phi\rangle$ can be expanded as a linear combination of these vectors:

$$|\phi\rangle = \sum_i c_i|a_i\rangle$$

By multiplying both sides of this equation by $\langle a_j|$ and using the orthonormality condition, it can be seen that the expansion coefficients are

$$c_i = \langle a_i|\phi\rangle$$

The eigenvectors also satisfy a closure relation:

$$I = \sum_i |a_i\rangle\langle a_i|$$

where I is the identity operator.

Averaging over many individual measurements of A gives rise to an average value or expectation value for the observable A, which we denote $\langle A\rangle$ and is given by

$$\langle A\rangle = \langle\Psi(t)|A|\Psi(t)\rangle$$

That this is true can be seen by expanding the state vector $|\Psi(t)\rangle$ in the eigenvectors of A:

$$|\Psi(t)\rangle = \sum_i \alpha_i(t)|a_i\rangle$$

where a_i are the amplitudes for obtaining the eigenvalue a_i upon measuring A, i.e., $\alpha_i = \langle a_i|\Psi(t)\rangle$. Introducing this expansion into the expectation value expression gives

$$\begin{aligned}\langle A\rangle(t) &= \sum_{i,j} \alpha_i^*(t)\alpha_j(t)\langle a_i|A|a_i\rangle \\ &= \sum_{i,j} \alpha_i^*(t)\alpha_j a_i(t)\delta_{ij} \\ &= \sum_i a_i|\alpha_i(t)|^2\end{aligned}$$

The interpretation of the above result is that the expectation value of A is the sum over possible outcomes of a measurement of A weighted by the probability that each result is obtained. Since $|\alpha_i|^2 = |\langle a_i|\Psi(t)\rangle|^2$ is this probability, the equivalence of the expressions can be seen.

Two observables are said to be compatible if $AB = BA$. If this is true, then the observables can be diagonalized simultaneously to yield the same set of eigenvectors. To see this, consider the action of BA on an eigenvector $|a_i\rangle$ of A. $BA|a_i\rangle = a_i B|a_i\rangle$. But if this must equal $AB|a_i\rangle$, then the only way this can be true is if $B|a_i\rangle$ yields a vector proportional to $|a_i\rangle$ which means it must also be an eigenvector of B. The condition $AB = BA$ can be expressed as

$$AB - BA = 0$$

that is

$$[A, B] = 0$$

where, in the second line, the quantity $[A, B] \equiv AB - BA$ is know as the commutator between A and B. If $[A, B] = 0$, then A and B are said to commute with each other. That they can be simultaneously diagonalized implies that one can simultaneously predict the observables A and B with the same measurement.

As we have seen, classical observables are functions of position x and momentum P (for a one-particle system). Quantum analogs of classical observables are, therefore, functions of the operators X and P corresponding to position and momentum. Like other observables X and P are linear hermitian operators. The corresponding eigenvalues x and P and eigenvectors $|x\rangle$ and $|P\rangle$ satisfy the equations

$$X|x\rangle = x|x\rangle$$

$$P|p\rangle = p|p\rangle$$

which, in general, could constitute a *continuous* spectrum of eigenvalues and eigenvectors. The operators X and P are not compatible. In accordance with the Heisenberg uncertainty principle (to be discussed below), the commutator between X and P is given by

$$[X, P] = i\hbar I$$

and that the inner product between eigenvectors of X and P is

$$\langle x|p\rangle = \frac{1}{\sqrt{2\pi\hbar}} e^{ipx/\hbar}$$

Since, in general, the eigenvalues and eigenvectors of X and P form a continuous spectrum, we write the **orthonormality** and **closure relations** for the eigenvectors as:

$$\langle x|x'\rangle = \delta(x - x')$$

$$\langle p|p'\rangle = \delta(p - p')$$

$$|\phi\rangle = \int dx |x\rangle\langle x|\phi\rangle$$

$$|\phi\rangle = \int dp |p\rangle\langle p|\phi\rangle$$

$$I = \int dx |x\rangle\langle x|$$

$$I = \int dp |p\rangle\langle p|$$

The probability that a measurement of the operator X will yield an eigenvalue x in a region dx about some point is

$$P(x, t)dx = |\langle x|\Psi(t)\rangle|^2 dx$$

The object $\langle x|\Psi(t)\rangle$ is best represented by a continuous function $\Psi(x,t)$ often referred to as the *wave function*. It is a representation of the inner product between eigenvectors of X with the state vector. To determine the action of the operator X on the state vector in the basis set of the operator X, we compute

$$\langle x|X|\Psi(t)\rangle = x\Psi(x,t)$$

The action of P on the state vector in the basis of the X operator is consequential of the incompatibility of x and P and is given by

$$\langle x|P|\Psi(t)\rangle = \frac{\hbar}{i}\frac{\partial}{\partial x}\Psi(x,t)$$

Thus, in general, for any observable $A(X,P)$, its action on the state vector represented in the basis of X is

$$\langle x|A(X,P)|\Psi(t)\rangle = A\left(x,\frac{\hbar}{i}\frac{\partial}{\partial x}\right)\Psi(x,t)$$

9.2: Physical Observables

Physical observables are represented by linear, hermitian operators that act on the vectors of the Hilbert space. If A is such an operator, and $|\phi\rangle$ is an arbitrary vector in the Hilbert space, then A might act on $|\phi\rangle$ to produce a vector $|\phi'\rangle$, which we express as

$$A|\phi\rangle = |\phi'\rangle$$

Since $|\phi\rangle$ is representable as a column vector, A is representable as a matrix with components

$$A = \begin{pmatrix} A_{11} & A_{12} & A_{13} & \cdots \\ A_{21} & A_{22} & A_{23} & \cdots \\ \cdot & \cdot & \cdot & \cdots \end{pmatrix}$$

The condition that A must be hermitian means that

$$A^{\dagger} = A$$

or

$$A_{ij} = A^*_{ji}$$

9.3: The Fundamental Postulates of Quantum Mechanics

The fundamental postulates of quantum mechanics concern the following questions:

1. How is the physical state of a system described?
2. How are physical observables represented?
3. What are the results of measurements on quantum mechanical systems?
4. How does the physical state of a system evolve in time?
5. The uncertainty principle.

9.4: The Heisenberg Picture

In all of the above, notice that we have formulated the postulates of quantum mechanics such that the state vector $|\Psi(t)\rangle$ evolves in time, but the operators corresponding to observables are taken to be stationary. This formulation of quantum mechanics is known as the *Schrödinger picture*. However, there is another, completely equivalent, picture in which the state vector remains stationary and the operators evolve in time. This picture is known as the *Heisenberg picture*. This particular picture will prove particularly useful to us when we consider quantum time correlation functions.

The Heisenberg picture specifies an evolution equation for any operator A, known as the Heisenberg equation. It states that the time evolution of A is given by

$$\frac{dA}{dt} = \frac{1}{i\hbar}[A, H]$$

While this evolution equation must be regarded as a postulate, it has a very immediate connection to classical mechanics. Recall that any function of the phase space variables $A(x, p)$ evolves according to

$$\frac{dA}{dt} = \{A, H\}$$

where $\{\ldots, \ldots\}$ is the Poisson bracket. The suggestion is that in the classical limit ($\hbar$ small), the commutator goes over to the Poisson bracket. The Heisenberg equation can be solved in principle giving

$$\begin{aligned} A(t) &= e^{iHt/\hbar} A e^{-iHt/\hbar} \\ &= U^\dagger(t) A U(t) \end{aligned}$$

where A is the corresponding operator in the Schrödinger picture. Thus, the expectation value of A at any time t is computed from

$$\langle A(t)\rangle = \langle \Psi | A(t) | \Psi \rangle$$

where $|\Psi\rangle$ is the stationary state vector.

Let's look at the Heisenberg equations for the operators X and P. If H is given by

$$H = \frac{P^2}{2m} + U(X)$$

then Heisenberg's equations for X and P are

$$\begin{aligned} \frac{dX}{dt} &= \frac{1}{i\hbar}[X, H] \\ &= \frac{P}{m} \\ \frac{dP}{dt} &= \frac{1}{i\hbar}[P, H] \\ &= -\frac{\partial U}{\partial X} \end{aligned}$$

Thus, Heisenberg's equations for the operators X and P are just Hamilton's equations cast in operator form. Despite their innocent appearance, the solution of such equations, even for a one-particle system, is *highly* nontrivial and has been the subject of a considerable amount of research in physics and mathematics.

Note that any operator that satisfies $[A(t), H] = 0$ will not evolve in time. Such operators are known as constants of the motion. The Heisenberg picture shows explicitly that such operators do not evolve in time. However, there is an analog with the Schrödinger picture: Operators that commute with the Hamiltonian will have associated probabilities for obtaining different eigenvalues that do not evolve in time. For example, consider the Hamiltonian, itself, which it trivially a constant of the motion. According to the evolution equation of the state vector in the Schrödinger picture,

$$|\Psi(t)\rangle = \sum_i e^{-iE_i t/\hbar} |E_i\rangle\langle E_i|\Psi(0)\rangle$$

the amplitude for obtaining an energy eigenvalue E_j at time t upon measuring H will be

$$\begin{aligned}\langle E_j|\Psi(t)\rangle &= \sum_i e^{-iE_it/\hbar}\langle E_j|E_i\rangle\langle E_i|\Psi(0)\rangle \\ &= \sum_i e^{-iE_it/\hbar}\delta_{ij}\langle E_i|\Psi(0)\rangle \\ &= e^{-iE_jt/\hbar}\langle E_j|\Psi(0)\rangle\end{aligned}$$

Thus, the squared modulus of both sides yields the probability for obtaining E_j, which is

$$|\langle E_j|\Psi(t)\rangle|^2 = |\langle E_j|\Psi(0)\rangle|^2$$

Thus, the probabilities do not evolve in time. Since any operator that commutes with H can be diagonalized simultaneously with H and will have the same set of eigenvectors, the above arguments will hold for any such operator.

9.5: The Heisenberg Uncertainty Principle

Because the operators x and p are not compatible, $[\hat{X}, \hat{P}] \neq 0$, there is **no** measurement that can precisely determine both x and p simultaneously. Hence, there must be an uncertainty relation between them that specifies how uncertain we are about one quantity given a definite precision in the measurement of the other. Presumably, if one can be determined with infinite precision, then there will be an infinite uncertainty in the other. Recall that we had defined the uncertainty in a quantity by

$$\Delta A = \sqrt{\langle A^2 \rangle - \langle A \rangle^2} \tag{1}$$

Thus, for x and p, we have

$$\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} \tag{2a}$$

$$\Delta p = \sqrt{\langle p^2 \rangle - \langle p \rangle^2} \tag{2b}$$

These quantities can be expressed explicitly in terms of the wave function $\Psi(x,t)$ using the fact that

$$\langle x \rangle = \langle \Psi(t)|x|\Psi(t)\rangle = \int dx \langle \Psi(t)|x\rangle \langle |x|X|\Psi(t)\rangle = \int dx \Psi^*(x,t) x \Psi(x,t) \tag{3}$$

and

$$\langle x^2 \rangle = \langle \Psi(t)|x^2|\Psi(t)\rangle = \int \Psi^*(x,t) x^2 \Psi(x,t) \tag{4}$$

Similarly,

$$\langle p \rangle = \langle \Psi(t)|p|\Psi(t)\rangle = \int dx \langle \Psi(t)|x\rangle \langle |p|\Psi(t)\rangle = \int dx \Psi^*(x,t) \frac{\hbar}{i} \frac{\partial}{\partial x} \Psi(x,t) \tag{5}$$

and

$$\langle p^2 \rangle = \langle \Psi(t)|p^2|\Psi(t)\rangle = \int dx \Psi^*(x,t) \left(-\hbar^2 \frac{\partial^2}{\partial x^2}\right) \Psi(x,t) \tag{6}$$

Then, the Heisenberg uncertainty principle states that

$$\Delta x \Delta p \gtrsim \hbar \tag{7}$$

which essentially states that the greater certainty with which a measurement of x or p can be made, the greater will be the *uncertainty* in the other.

9.6: The Physical State of a Quantum System

The physical state of a quantum system is represented by a vector denoted $|\Psi(t)\rangle$ which is a column vector, whose components are *probability amplitudes* for different states in which the system might be found if a measurement were made on it.

A probability amplitude α is a complex number, the square modulus of which gives the corresponding probability P_α

$$P_\alpha = |\alpha|^2$$

The number of components of $|\Psi(t)\rangle$ is equal to the number of possible states in which the system might observed. The space that contains $|\Psi(t)\rangle$ is called a **Hilbert space** $\mathcal{H}$. The dimension of $\mathcal{H}$ is also equal $|\Psi(t)\rangle$ to the number of states in which the system might be observed. It could be finite or infinite (countable or not). $|\Psi(t)\rangle$ must be a unit vector. This means that the inner product:

$$\langle\Psi(t)|\Psi(t)\rangle = 1$$

In the above, if the vector $|\Psi(t)\rangle$, known as a Dirac "ket" vector, is given by the column

$$|\Psi(t)\rangle = \begin{pmatrix} \psi_1 \\ \psi_2 \\ \cdot \\ \cdot \\ \cdot \end{pmatrix}$$

then the vector $\langle\Psi(t)|$, known as a Dirac "bra" vector, is given by

$$\langle\Psi(t)| = (\psi_1^* \;\; \psi_2^* \;\; \cdots)$$

so that the inner product becomes

$$\langle\Psi(t)|\Psi(t)\rangle = \sum_i |\psi_i|^2 = 1$$

We can understand the meaning of this by noting that ψ_i, the components of the state vector, are probability amplitudes, and $|\psi_i|^2$ are the corresponding probabilities. The above condition then implies that the sum of all the probabilities of being in the various possible states is 1, which we know must be true for probabilities.

9.7: Time Evolution of the State Vector

The time evolution of the state vector is prescribed by the Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle = H|\Psi(t)\rangle$$

where H is the Hamiltonian operator. This equation can be solved, in principle, yielding

$$|\Psi(t)\rangle = e^{-iHt/\hbar}|\Psi(0)\rangle$$

where $|\Psi(0)\rangle$ is the initial state vector. The operator

$$U(t) = e^{-iHt\hbar}$$

is the **time evolution operator** or **quantum propagator**. Let us introduce the eigenvalues and eigenvectors of the Hamiltonian H that satisfy

$$H|E_i\rangle = E_i|E_i\rangle$$

The eigenvectors for an orthonormal basis on the Hilbert space and therefore, the state vector can be expanded in them according to

$$|\Psi(t)\rangle = \sum_i c_i(t)|E_i\rangle$$

where, of course, $c_i(t) = \langle E_i|\Psi(t)\rangle$, which is the amplitude for obtaining the value E_i at time t if a measurement of H is performed. Using this expansion, it is straightforward to show that the time evolution of the state vector can be written as an expansion:

$$\begin{aligned}|\Psi(t)\rangle &= e^{-iHt\hbar}|\Psi(0)\rangle \\ &= e^{-iHt/\hbar}\sum_i |E_i\rangle\langle E_i|\Psi(0)\rangle \\ &= \sum_i e^{-iE_it/\hbar}|E_i\rangle\langle E_i|\Psi(0)\rangle\end{aligned}$$

Thus, we need to compute all the initial amplitudes for obtaining the different eigenvalues E_i of H, apply to each the factor $\exp(-iE_it/\hbar)|E_i\rangle$ and then sum over all the eigenstates to obtain the state vector at time t.

If the Hamiltonian is obtained from a classical Hamiltonian $H(x,p)$, then, using the formula from the previous section for the action of an arbitrary operator $A(X,P)$ on the state vector in the coordinate basis, we can recast the Schrödiner equation as a partial differential equation. By multiplying both sides of the Schrödinger equation by $\langle x|$, we obtain

$$\begin{aligned}\langle x|H(X,P)|\Psi(t)\rangle &= i\hbar\frac{\partial}{\partial t}\langle x|\Psi(t)\rangle \\ H\left(x, \frac{\hbar}{i}\frac{\partial}{\partial x}\right)\Psi(x,t) &= i\hbar\frac{\partial}{\partial t}\Psi(x,t)\end{aligned}$$

If the classical Hamiltonian takes the form

$$H(x,p) = \frac{p^2}{2m} + U(x)$$

then the Schrödinger equation becomes

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U(x)\right]\Psi(x,t) = i\hbar\frac{\partial}{\partial t}\Psi(x,t)$$

which is known as the Schrödinger *wave equation* or the *time-dependent* Schrödinger equation. In a similar manner, the eigenvalue equation for H can be expressed as a differential equation by projecting it into the X basis:

$$\langle x|H|E_i\rangle = E_i\langle x|E_i\rangle$$

$$H\left(x,\frac{\hbar}{i}\frac{\partial}{\partial x}\right)\psi_i(x) = E_i\psi_i(x)$$

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+U(x)\right]\psi_i(x) = E_i\psi_i(x)$$

where $\psi_i(x) = \langle x|E_i\rangle$ is an eigenfunction of the Hamiltonian.

CHAPTER OVERVIEW

10: Fundamentals of quantum statistical mechanics

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10.1: Principles of quantum statistical mechanics

The problem of quantum statistical mechanics is the quantum mechanical treatment of an N-particle system. Suppose the corresponding N-particle classical system has Cartesian coordinates

$$q_1, \dots, q_{3N}$$

and momenta

$$p_1, \cdots, p_{3N}$$

and Hamiltonian

$$H = \sum_{i=1}^{3N} \frac{p_i^2}{2m_i} + U(q_1, \dots, q_{3N})$$

Then, as we have seen, the quantum mechanical problem consists of determining the state vector $|\Psi(t)\rangle$ from the Schrödinger equation

$$H|\Psi(t)\rangle = i\hbar \frac{\partial}{\partial t}|\Psi(t)\rangle$$

Denoting the corresponding operators, $Q_1, \cdots, Q_{3N}$ and $P_1, \cdots, P_{3N}$, we note that these operators satisfy the commutation relations:

$[Q_i, Q_j]$	$=$	$[P_i, P_j] = 0$
$[Q_i, P_j]$	$=$	$i\hbar I \delta_{ij}$

and the many-particle coordinate eigenstate $|q_1 \dots q_{3N}\rangle$ is a tensor product of the individual eigenstate $|q_1\rangle, \dots, |q_{3N}\rangle$:

$$|q_1 \dots q_{3N}\rangle = |q_1\rangle \cdots |q_{3N}\rangle$$

The Schrödinger equation can be cast as a partial differential equation by multiplying both sides by $\langle q_1 \dots q_{3N}|$:

$\langle q_1 \dots q_{3N}\|H\|\Psi(t)\rangle$	$=$	$\frac{\partial}{\partial t}\langle q_1 \dots q_{3N}\|\Psi(t)\rangle$	
$\left[-\sum_{i=1}^{3N} \frac{\hbar^2}{2m_i}\frac{\partial^2}{\partial q_i^2} + U(q_1, \dots, q_{3N})\right]$	$\Psi(q_1, \dots, q_{3N}, t)$	$i\hbar \frac{\partial}{\partial t}\Psi(q_1, \dots, q_{3N}, t)$	

where the many-particle wave function is $\Psi(q_1, \dots, q_{3N}, t) = \langle q_1 \dots q_{3N}|\Psi(t)\rangle$. Similarly, the expectation value of an operator $A = A(Q_1, \dots, Q_{3N}, P_1, \dots, P_{3N})$ is given by

$$\langle A\rangle = \int dq_1 \cdots dq_{3N} \Psi^*(q_1, \dots, q_{3N}) A\left(q_1, \cdots, q_{3N}, \frac{\hbar}{i}\frac{\partial}{\partial q_1}, \cdots, \frac{\hbar}{i}\frac{\partial}{\partial q_{3N}}\right) \Psi(q_1, \dots, q_{3N})$$

10.2: The Density Matrix and Density Operator

In general, the many-body wave function $\Psi(q_1, \dots, q_{3N}, t)$ is far too large to calculate for a macroscopic system. If we wish to represent it on a grid with just 10 points along each coordinate direction, then for $N = 10^{23}$, we would need $10^{10^{23}}$ total points, which is clearly enormous.

We wish, therefore, to use the concept of ensembles in order to express expectation values of observables $\langle A \rangle$ without requiring direct computation of the wavefunction. Let us, therefore, introduce an ensemble of systems, with a total of Z members, and each having a state vector $|\Psi^{(\alpha)}\rangle$, $\alpha = 1, \cdots, Z$. Furthermore, introduce an orthonormal set of vectors $\langle \phi_k | \phi_j \rangle = \delta_{ij}$) and expand the state vector for each member of the ensemble in this orthonormal set:

$$|\Psi^{(\alpha)}\rangle = \sum_k C_k^{(\alpha)} |\phi_k\rangle$$

The expectation value of an observable, averaged over the ensemble of systems is given by the average of the expectation value of the observable computed with respect to each member of the ensemble:

$$\langle A \rangle = \frac{1}{Z} \sum_{\alpha=1}^{Z} \langle \Psi^{(\alpha)} | A | \Psi^{(\alpha)} \rangle$$

Substituting in the expansion for $|\Psi^{(\alpha)}\rangle$, we obtain

$$\begin{aligned} \langle A \rangle &= \frac{1}{Z} \sum_{k,l} C_k^{(\alpha)^*} C_l^{(\alpha)} \langle \phi_k | A | \phi_l \rangle \\ &= \sum_{k,l} \left(\frac{1}{Z} \sum_{\alpha=1}^{Z} C_l^{(\alpha)} C_k^{(\alpha)^*} \right) \langle \phi_k | A | \phi_l \rangle \end{aligned}$$

Let us define a matrix

$$\rho_{lk} = \sum_{\alpha=1}^{Z} C_l^{(\alpha)} C_k^{(\alpha)^*}$$

and a similar matrix

$$\tilde{\rho}_{lk} = \frac{1}{Z} \sum_{\alpha=1}^{Z} C_l^{(\alpha)} C_k^{(\alpha)^*}$$

Thus, ρ_{lk} is a sum over the ensemble members of a product of expansion coefficients, while ρ_{lk} is an average over the ensemble of this product. Also, let $A_{kl} = \langle \phi_k | A | \phi_l \rangle$. Then, the expectation value can be written as follows:

$$\langle A \rangle = \frac{1}{Z} \sum_{k,l} \rho_{lk} A_{kl} = \frac{1}{Z} \sum_k (\rho A)_{kk} = \frac{1}{Z} \mathrm{Tr}(\rho A) = \mathrm{Tr}(\tilde{\rho} A)$$

where ρ and A represent the matrices with elements ρ_{lk} and A_{kl} in the basis of vectors $\{|\phi_k\rangle\}$. The matrix ρ_{lk} is known as the **density matrix**. There is an abstract operator corresponding to this matrix that is basis-independent. It can be seen that the operator

$$\rho = \sum_{\alpha=1}^{Z} |\Psi^{(\alpha)}\rangle \langle \Psi^{(\alpha)}|$$

and similarly

$$\tilde{\rho} = \frac{1}{Z} \sum_{\alpha=1}^{Z} |\Psi^{(\alpha)}\rangle \langle \Psi^{(\alpha)}|$$

have matrix elements ρ_{lk} when evaluated in the basis set of vectors $\{|\phi_k\rangle\}$.

$$
\begin{aligned}
\langle\phi_l|\rho|\phi_k\rangle &= \sum_{\alpha=1}^{Z}\langle\phi_l|\Psi^{(\alpha)}\rangle\langle\Psi^{(\alpha)}|\phi_k\rangle \\
&= \sum_{\alpha=1}^{Z} C_l^{(\alpha)} C_k^{(\alpha)^*} \\
&= \rho_{lk}
\end{aligned}
$$

Note that ρ is a hermitian operator

$$\rho^\dagger = \rho$$

so that its eigenvectors form a complete orthonormal set of vectors that span the Hilbert space. If w_k and $|w_k\rangle$ represent the eigenvalues and eigenvectors of the operator $\tilde{\rho}$, respectively, then several important properties they must satisfy can be deduced.

Firstly, let A be the identity operator I. Then, since $\langle I\rangle = 1$, it follows that

$$1 = \frac{1}{Z}\mathrm{Tr}(\rho) = \mathrm{Tr}(\tilde{\rho}) = \sum_k w_k$$

Thus, the eigenvalues of $\tilde{\rho}$ must sum to 1. Next, let A be a projector onto an eigenstate of $\tilde{\rho}$, $A = |w_k\rangle\langle w_k| \equiv P_k$. Then

$$\langle P_k\rangle = \mathrm{Tr}(\tilde{\rho}|w_k\rangle\langle w_k|)$$

But, since $\tilde{\rho}$ can be expressed as

$$\tilde{\rho} = \sum_k w_k |w_k\rangle\langle w_k|$$

and the trace, being basis set independent, can be therefore be evaluated in the basis of eigenvectors of $\tilde{\rho}$, the expectation value becomes

$$
\begin{aligned}
\langle P_k\rangle &= \sum_j \langle w_j|\sum_i w_i|w_i\rangle\langle w_i|w_k\rangle\langle w_k|w_j\rangle \\
&= \sum_{i,j} w_i\delta_{ij}\delta_{ik}\delta_{kj} \\
&= w_k
\end{aligned}
$$

However,

$$
\begin{aligned}
\langle P_k\rangle &= \frac{1}{Z}\sum_{\alpha=1}^{Z}\langle\Psi^{(\alpha)}|w_k\rangle\langle w_k|\Psi^{(\alpha)}\rangle \\
&= \frac{1}{Z}\sum_{\alpha=1}^{Z}|\langle\Psi^{(\alpha)}|w_k\rangle|^2 \geq 0
\end{aligned}
$$

Thus, $w_k \geq 0$. Combining these two results, we see that, since $\sum_k w_k = 1$ and $w_k \geq 0$, $0 \leq w_k \leq 1$, so that w_k satisfy the properties of probabilities.

With this in mind, we can develop a physical meaning for the density matrix. Let us now consider the expectation value of a projector $|a_i\rangle\langle a_i| \equiv \mathcal{P}_{a_i}$ onto one of the eigenstates of the operator A. The expectation value of this operator is given by

$$\begin{aligned}\langle \mathcal{P}_{a_i} \rangle &= \frac{1}{Z}\sum_{\alpha=1}^{Z} \langle \Psi^{(\alpha)} | P_{a_i} | \Psi^{(\alpha)} \rangle \\ &= \frac{1}{Z}\sum_{\alpha=1}^{Z} \langle \Psi^{(\alpha)} | a_i \rangle \langle a_i | \Psi^{(\alpha)} \rangle \\ &= \frac{1}{Z}\sum_{\alpha=1}^{Z} | \langle a_i | \Psi^{(\alpha)} \rangle |^2\end{aligned}$$

But $|\langle a_i|\Psi^{(\alpha)}\rangle|^2 \equiv P_{a_i}^{(\alpha)}$ is just probability that a measurement of the operator A in the α th member of the ensemble will yield the result a_i. Thus,

$$\langle \mathcal{P}_{a_i} \rangle = \frac{1}{Z}\sum_{\alpha=1}^{P} P_{a_i}^{(\alpha)}$$

or the expectation value of P_{a_i} is just the ensemble averaged probability of obtaining the value a_i in each member of the ensemble. However, note that the expectation value of P_{a_i} can also be written as

$$\begin{aligned}\langle \mathcal{P}_{a_i} \rangle &= \text{Tr}(\tilde{\rho}\mathcal{P}_{a_i}) \\ &= \text{Tr}(\sum_k w_k |w_k\rangle\langle w_k|a_i\rangle\langle a_i|) \\ &= \sum_{k,l} \langle w_l | w_k | w_k | w_k \rangle \langle w_k | a_i \rangle \langle a_i | w_l \rangle \\ &= \sum_{k,l} w_k \delta_{kl} \langle w_k a_i \rangle \langle a_i w_l \rangle \\ &= \sum_k w_k |\langle a_i | w_k \rangle|^2\end{aligned}$$

Equating the two expressions gives

$$\frac{1}{Z}\sum_{\alpha=1}^{Z} \langle P_{a_i}^{(\alpha)} \rangle = \sum_k w_k |\langle a_i | w_k \rangle|^2$$

The interpretation of this equation is that the ensemble averaged probability of obtaining the value a_i if A is measured is equal to the probability of obtaining the value a_i in a measurement of A if the state of the system under consideration were the state $|w_k\rangle$, weighted by the average probability w_k that the system in the ensemble is in that state. Therefore, the **density operator** ρ (or ρ) plays the same role in quantum systems that the phase space distribution function $f(\mathbf{\Gamma})$ plays in classical systems.

10.3: Time evolution of the density operator

The time evolution of the operator ρ can be predicted directly from the Schrödinger equation. Since $\rho(t)$ is given by

$$\rho(t)=\sum_{\alpha=1}^{Z}|\Psi^{(\alpha)}(t)\rangle\langle\Psi^{(\alpha)}(t)|$$

the time derivative is given by

$$\begin{aligned}\frac{\partial\rho}{\partial t}&=\sum_{\alpha=1}^{Z}\left[\left(\frac{\partial}{\partial t}|\Psi^{(\alpha)}(t)\rangle\right)\langle\Psi^{(\alpha)}(t)|+|\Psi^{(\alpha)}(t)\rangle\left(\frac{\partial}{\partial t}\langle\Psi^{(\alpha)}(t)|\right)\right]\\&=\frac{1}{i\hbar}\sum_{\alpha=1}^{Z}\left[\left(H|\Psi^{(\alpha)}(t)\rangle\right)\langle\Psi^{(\alpha)}(t)|-|\Psi^{(\alpha)}(t)\langle\left(\langle\Psi^{(\alpha)}(t)|H\right)\right]\\&=\frac{1}{i\hbar}(H\rho-\rho H)\\&=\frac{1}{i\hbar}[H,\rho]\end{aligned}$$

where the second line follows from the fact that the Schrödinger equation for the bra state vector $\langle\Psi^{(\alpha)}(t)|$ is

$$-i\hbar\frac{\partial}{\partial t}\langle\Psi^{(\alpha)}(t)|=\langle\Psi^{(\alpha)}(t)|H$$

Note that the equation of motion for $\rho(t)$ differs from the usual Heisenberg equation by a minus sign! Since $\rho(t)$ is constructed from state vectors, it is not an observable like other hermitian operators, so there is no reason to expect that its time evolution will be the same. The general solution to *its* equation of motion is

$$\begin{aligned}\rho(t)&=e^{-iHt/\hbar}\rho(0)e^{iHt/\hbar}\\&=U(t)\rho(0)U^{\dagger}(t)\end{aligned}$$

The equation of motion for $\rho(t)$ can be cast into a quantum Liouville equation by introducing an operator

$$iL=\frac{1}{i\hbar}[\dots,H]$$

In term of iL, it can be seen that $\rho(t)$ satisfies

$$\begin{aligned}\frac{\partial\rho}{\partial t}&=-iL\rho\\\rho(t)&=e^{-iLt}\rho(0)\end{aligned}$$

What kind of operator is iL ? It acts on an operator and returns another operator. Thus, it is not an operator in the ordinary sense, but is known as a *superoperator* or *tetradic operator* (see S. Mukamel, *Principles of Nonlinear Optical Spectroscopy*, Oxford University Press, New York (1995)).

Defining the evolution equation for ρ this way, we have a perfect analogy between the density matrix and the state vector. The two equations of motion are

$$\begin{aligned}\frac{\partial}{\partial t}|\Psi(t)\rangle&=-\frac{i}{\hbar}H|\Psi(t)\rangle\\\frac{\partial}{\partial t}\rho(t)&=-iL\rho(t)\end{aligned}$$

We also have an analogy with the evolution of the classical phase space distribution $f(\mathbf{\Gamma},t)$, which satisfies

$$\frac{\partial f}{\partial t}=-iLf$$

with $iL = \{\ldots, H\}$ being the classical Liouville operator. Again, we see that the limit of a commutator is the classical Poisson bracket.

10.4: A simple example - the quantum harmonic oscillator

As a simple example of the trace procedure, let us consider the quantum harmonic oscillator. The Hamiltonian is given by

$$H = \frac{P^2}{2m} + \frac{1}{2}m\omega^2 X^2$$

and the eigenvalues of H are

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega, \qquad n = 0, 1, 2, \dots$$

Thus, the canonical partition function is

$$Q(\beta) = \sum_{n=0}^{\infty} e^{-\beta(n+1/2)\hbar\omega} = e^{-\beta\hbar\omega/2} \sum_{n=0}^{\infty} \left(e^{-\beta\hbar\omega}\right)^n$$

This is a geometric series, which can be summed analytically, giving

$$Q(\beta) = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}} = \frac{1}{e^{\beta\hbar\omega/2} - e^{-\beta\hbar\omega/2}} = \frac{1}{2}csch(\beta\hbar\omega/2)$$

The thermodynamics derived from it as as follows:

1. **Free energy**:

   The free energy is

   $$A = -\frac{1}{\beta}\ln Q(\beta) = \frac{\hbar\omega}{2} + \frac{1}{\beta}\ln\left(1 - e^{-\beta\hbar\omega}\right)$$

2. **Average energy**:

   The average energy $E = \langle H \rangle$ is

   $$E = -\frac{\partial}{\partial\beta}\ln Q(\beta) = \frac{\hbar\omega}{2} + \hbar\omega e^{-\beta\hbar\omega} = \left(\frac{1}{2} + \langle n \rangle\right)\hbar\omega$$

3. **Entropy**

   The entropy is given by

   $$S = k\ln Q(\beta) + \frac{E}{T} = -k\ln\left(1 - e^{-\beta\hbar\omega}\right) + \frac{\hbar\omega}{T}\frac{e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}}$$

Now consider the classical expressions. Recall that the partition function is given by

$$Q(\beta) = \frac{1}{h}\int dpdxe^{-\beta\left(\frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2\right)} = \frac{1}{h}\left(\frac{2\pi m}{\beta}\right)^{1/2} = \frac{2\pi}{\beta\omega h} = \frac{1}{\beta\hbar\omega}$$

Thus, the classical free energy is

$$A_{\text{cl}} = \frac{1}{\beta}\ln(\beta\hbar\omega)$$

In the classical limit, we may take $\hbar$ to be small. Thus, the quantum expression for A becomes, approximately, in this limit:

$$A_{\text{Q}} \longrightarrow \frac{\hbar\omega}{2} + \frac{1}{\beta}\ln(\beta\hbar\omega)$$

and we see that

$$A_{\rm Q} - A_{\rm cl} \longrightarrow \frac{\hbar\omega}{2}$$

The residual $\frac{\hbar\omega}{2}$ (which truly vanishes when $\hbar \rightarrow 0$) is known as the quantum *zero point* energy. It is a pure quantum effect and is present because the lowest energy quantum mechanically is not $E = 0$ but the ground state energy $E = \frac{\hbar\omega}{2}$.

10.5: The quantum equilibrium ensembles

At equilibrium, the density operator does not evolve in time; thus, $\frac{\partial\rho}{\partial t} = 0$. Thus, from the equation of motion, if this holds, then $[H, \rho] = 0$, and $\rho(t)$ is a constant of the motion. This means that it can be simultaneously diagonalized with the Hamiltonian and can be expressed as a pure function of the Hamiltonian

$$\rho = f(H)$$

Therefore, the eigenstates of ρ, the vectors, we called $|w_k\rangle$ are the eigenvectors $|E_i\rangle$ of the Hamiltonian, and we can write H and ρ as

$$H = \sum_i E_i |E_i\rangle\langle E_i|$$

$$\rho = \sum_i f(E_i) |E_i\rangle\langle E_i|$$

The choice of the function f determines the ensemble.

10.5.1: The microcanonical ensemble

Although we will have practically no occasion to use the quantum microcanonical ensemble (we relied on it more heavily in classical statistical mechanics), for completeness, we define it here. The function f, for this ensemble, is

$$f(E_i)\delta E = \theta(E_i - (E + \delta E)) - \theta(E_i - E)$$

where $\theta(x)$ is the Heaviside step function. This says that $f(E_i)\delta E$ is 1 if $E < E_i < (E + \delta E)$ and 0 otherwise. The partition function for the ensemble is $\mathrm{Tr}(\rho)$, since the trace of ρ is the number of members in the ensemble:

$$\begin{aligned}\Omega(N,V,E) &= \mathrm{Tr}(\rho) \\ &= \sum_i \left[\theta(E_i - (E+\delta E)) - \theta(E_i - E)\right]\end{aligned}$$

The thermodynamics that are derived from this partition function are exactly the same as they are in the classical case:

$$\begin{aligned}S(N,V,E) &= -k\ln\Omega(N,V,E) \\ \frac{1}{T} &= -k\left(\frac{\partial \ln\Omega}{\partial E}\right)_{N,V}\end{aligned}$$

etc.

10.5.2: The canonical ensemble

In analogy to the classical canonical ensemble, the quantum canonical ensemble is defined by

$$\rho = e^{-\beta H}$$

$$f(E_i) = e^{-\beta E_i}$$

Thus, the quantum canonical partition function is given by

$$\begin{aligned} Q(N,V,T) &= \mathrm{Tr}(e^{-\beta H}) \\ &= \sum_i e^{-\beta E_i} \end{aligned}$$

and the thermodynamics derived from it are the same as in the classical case:

$$\begin{aligned} A(N,V,T) &= -\frac{1}{\beta} \ln Q(N,V,T) \\ E(N,V,T) &= -\frac{\partial}{\partial \beta} \ln Q(N,V,T) \\ P(N,V,T) &= \frac{1}{\beta} \frac{\partial}{\partial V} \ln Q(N,V,T) \end{aligned}$$

etc. Note that the expectation value of an observable A is

$$\langle A \rangle = \frac{1}{Q} \mathrm{Tr}(A e^{-\beta H})$$

Evaluating the trace in the basis of eigenvectors of H (and of ρ), we obtain

$$\begin{aligned} \langle A \rangle &= \frac{1}{Q} \sum_i \langle E_i | A e^{-\beta H} | E_i \rangle \\ &= \frac{1}{Q} \sum_i e^{-\beta E_i} \langle E_i | A | E_i \rangle \end{aligned}$$

The quantum canonical ensemble will be particularly useful to us in many things to come.

10.5.3: Isothermal-isobaric and grand canonical ensembles

Also useful are the isothermal-isobaric and grand canonical ensembles, which are defined just as they are for the classical cases:

- **isothermal-isobaric:**

$$\Delta(N,P,T)=\int_0^\infty dV e^{-\beta PV} Q(N,V,T)=\int_0^\infty dV \mathrm{Tr}(e^{-\beta(H+PV)})$$

- **grand canonical ensembles**

$$\mathcal{Z}(\mu,V,T)=\sum_{N=0}^{\infty} e^{\beta\mu N} Q(N,V,T)=\sum_{N=0}^{\infty}\mathrm{Tr}(e^{-\beta(H-\mu N)})$$

CHAPTER OVERVIEW

11: Introduction to path integrals in quantum mechanics and quantum statistical mechanics

SECTION OVERVIEW

11.1: Discretized and Continuous Path Integrals

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11.1.1: Derivation of the Discretized Path Integral

We begin our discussion of the Feynman path integral with the canonical ensemble. The expressions for the partition function and expectation value of an observable A are, respectively

$$Q(N,V,T) = \mathrm{Tr}(e^{-\beta H})$$

$$\langle A\rangle = \frac{1}{Q}\mathrm{Tr}(Ae^{-\beta H})$$

It is clear that we need to be able to evaluate traces of the type appearing in these expressions. We have already derived expressions for these in the basis of eigenvectors of H. However, since the trace is basis independent, let us explore carrying out these traces in the coordinate basis. We will begin with the partition function and treat expectation values later.

Consider the ensemble of a one-particle system. The partition function evaluated as a trace in the coordinate basis is

$$Q(\beta) = \int dx \langle x|e^{-\beta H}|x\rangle$$

We see that the trace involves the diagonal density matrix element $\langle x|e^{-\beta H}|x\rangle$. Let us solve the more general problem of *any* density matrix element $\langle x|e^{-\beta H}|x'\rangle$.

If the Hamiltonian takes the form

$$H = \frac{P^2}{2m} + U(X) \equiv K + U$$

then we cannot evaluate the operator $exp(-\beta H)$ explicitly because the operators for kinetic (T) and potential energies (U) do not commute with each other, being, respectively, functions of momentum and position, i.e.,

$$[K,U] \neq 0$$

In this instance, we will make use of the Trotter theorem, which states that given two operators A and B, such that $[A,B]\neq 0$, then for any number λ,

$$e^{\lambda(A+B)} = \lim_{P\to\infty}\left[e^{\lambda B/2P}e^{\lambda A/P}e^{\lambda B/2P}\right]^P$$

Thus, for the Boltzmann operator,

$$e^{-\beta(K+U)} = \lim_{P\to\infty}\left[e^{-\beta U/2P}e^{-\beta K/P}e^{-\beta U/2P}\right]^P$$

and the partition function becomes

$$Q(\beta) = \lim_{P\to\infty}\int dx\langle x|\left[e^{-\beta U/2P}e^{-\beta K/P}e^{-\beta U/2P}\right]^P|x\rangle$$

Define the operator in brackets to be Ω:

$$\Omega = e^{-\beta U/2P}e^{-\beta K/P}e^{-\beta U/2P}$$

Then,

$$Q(\beta) = \lim_{P\to\infty}\int dx\langle x|\Omega^P|x\rangle$$

In between each of the P factors of Ω, the coordinate space identity operator

$$I = \int dx |x\rangle\langle x|$$

is inserted. Since there are P factors, there will be $P-1$ such insertions. the integration variables will be labeled $x_2,\ldots,x_P$. Thus, the expression for the matrix element becomes

$$\langle x|\Omega|x'\rangle = \int dx_2 \cdots dx_P \langle x|\Omega|x_2\rangle\langle x_2|\Omega|x_3\rangle\langle x_3|\ldots|x_P\rangle\langle x_P|\Omega|x'\rangle$$

$$\int dx_2 \cdots dx_P \prod_{i=1}^{P} \langle x_i|\Omega|x_{i+1}\rangle|_{x_1=x, x_{P+1}=x'}$$

The next step clearly involves evaluating the matrix elementx

$$\langle x_i|\Omega|x_{i+1}\rangle = \langle x_i|e^{-\beta U(x)/2P} e^{-\beta P^2/2mP} e^{-\beta U(X)/2P}|x_{i+1}\rangle$$

Note that in the above expression, the operators involving the potential $U(X)$ act on their eigenvectors and can thus be replaced by the corresponding eigenvalues:

$$\langle x_i|\Omega|x_{i+1}\rangle = e^{-\beta(U(x_i)+U(x_{i+1})/2} \langle x_i|e^{-\beta P^2/2mP}|x_{i+1}\rangle$$

In order to evaluate the remaining matrix element, we introduce the momentum space identity operator

$$I = \int dp|p\rangle\langle p|$$

Letting $K = \frac{P^2}{2m}$, the matrix remaining matrix element becomes

$$\begin{aligned}\langle x_i|e^{-\beta K/P}|x_{i+1}\rangle &= \int dp\langle x_i|p\rangle\langle p|e^{-\beta P^2/2mP}|x_{i+1}\rangle \\ &= \int dp\langle x_i|p\rangle\langle p|x_{i+1}\rangle e^{-\beta p^2/2mP}\end{aligned}$$

Using the fact that

$$\langle x|p\rangle = \frac{1}{\sqrt{2\pi\hbar}} e^{ipx/\hbar}$$

it follows that

$$\langle x_i|e^{-\beta K/P}|x_{i+1}\rangle = \frac{1}{2\pi\hbar}\int dp e^{ip(x_i-x_{i+1})/\hbar} e^{-\beta p^2/2mP}$$

The remaining integral over P can be performed by completing the square, leading to the result

$$\langle x_i|e^{-\beta K/P}|x_{i+1}\rangle = \left(\frac{mP}{2\pi\beta\hbar^2}\right)^{1/2} \exp\left(-\frac{mP}{2\beta\hbar^2}(x_{i+1}-x_i)^2\right)$$

Collecting the pieces together, and introducing the $P \to \infty$ limit, we have for the density matrix

$$\langle x|e^{-\beta H}|x'\rangle = \lim_{P\to\infty}\left(\frac{mp}{2\pi\beta\hbar^2}\right)^{1/2}\int dx_2\cdots dx_P exp\left[-\sum_{i=1}^{P}\left(\frac{mP}{2\beta\hbar^2}(x_{i+1}-x_i)^2+\frac{\beta}{2P}(U(x_i)+U(x_{i+1})\right)\right]$$

$$|_{x_1=x, x_{P+1}=x'}$$

The partition function is obtained by setting $x = x'$, which is equivalent to setting $x_1 = x_{P+1}$ and integrating over x, or equivalently x_1. Thus, the expression for $Q(\beta)$ becomes

$$Q(\beta) = \lim_{P\to\infty}\left(\frac{mP}{2\pi\beta\hbar^2}\right)^{1/2}\int dx_1\cdots dx_P exp\left[-\beta\sum_{i=1}^{P}\left(\frac{1}{2}m\omega_P^2(x_{i+1}-x_i)^2+\frac{1}{P}U(x_i)\right)\right]|_{x_{P+1}=x_1}$$

where we have introduced a "frequency"

$$\omega_P = \frac{\sqrt{P}}{\beta\hbar}$$

When expressed in this way, the partition function, for a finite value of P, is *isomorphic* to a classical configuration integral for a P-particle system, that is a cyclic chain of particles, with harmonic nearest neighbor interactions and interacting with an *external* potential $\frac{U(x)}{P}$. That is, the partition function becomes

$$Q(\beta) \sim \int dx_1 \cdots dx_P e^{-\beta U_{\text{eff}}(x_1,\ldots,x_P)}$$

where

$$U_{\text{eff}}(x_1,\ldots,x_P) = \sum_{i=1}^{P} \left[\frac{1}{2} m\omega_P^2 (x_{i+1} - x_i)^2 + \frac{1}{P} U(x_i)\right]$$

Thus, for finite (if large) P the partition function in the discretized path integral representation can be treated as any ordinary classical configuration integral. Consider the integrand of $Q(\beta)$ in the limit that all P points on the cyclic chain are at the same location x. Then the harmonic nearest neighbor coupling (which is due to the quantum kinetic energy) vanishes and $(1/P)\sum_{i=1}^{P} U(x_i) \rightarrow U(x)$, and the integrand becomes

$$e^{-\beta U(x)}$$

which is just the true classical canonical position space distribution function. Therefore, the greater the spatial spread in the cyclic chain, the more "quantum" the system is, since this indicates a greater contribution from the quantum kinetic energy. The spatially localized it is, the more the system behaves like a classical system.

It remains formally to take the limit that $P \rightarrow \infty$. There we will see an elegant formulation for the density matrix and partition function emerges.

-

11.1.2: Doing the Path Integral - the Free Particle

The density matrix for the free particle

$$H = \frac{P^2}{2m}$$

will be calculated by doing the discrete path integral explicitly and taking the limit $P \rightarrow \infty$ at the end.

The density matrix expression is

$$\rho(x,x';\beta) = \lim_{P\rightarrow\infty}\left(\frac{mP}{2\pi\beta\hbar^2}\right)^{P/2}\int dx_2\cdots dx_P exp\left[-\frac{mP}{2\beta\hbar^2}\sum_{i=1}^{P}(x_{i+1}-x_i)^2\right]|_{x_1=x,x_{P+1}=x'}$$

Let us make a change of variables to

$$\begin{aligned} u_1 &= x_1 \\ u_k &= x_k - \tilde{x}_k \\ \tilde{x}_k &= \frac{(k-1)x_{k+1}+x_1}{k} \end{aligned} \tag{11.1.2.1}$$

The inverse of this transformation can be worked out explicitly, giving

$$x_1 = u_1$$

$$x_k = \sum_{l=1}^{P+1}\frac{k-1}{l-1}u_l + \frac{P-k+1}{P}u_1$$

The Jacobian of the transformation is simply

$$J = \det\begin{pmatrix} 1 & -1/2 & 0 & 0 & \cdots & \\ 0 & 1 & -2/3 & 0 & \cdots & \\ 0 & 0 & 1 & -3/4 & \cdots & \\ 0 & 0 & 0 & 1 & \cdots & \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdots \end{pmatrix} = 1$$

Let us see what the effect of this transformation is for the case $P = 3$. For $P = 3$, one must evaluate

$$(x_1-x_2)^2+(x_2-x_3)^2+(x_3-x_4)^2 = (x-x_2)^2+(x_2-x_3)^2+(x_3-x')^2$$

According to the inverse formula,

$$x_1 = u_1 \tag{11.1.2.2}$$

$$x_2 = u_2 + \frac{1}{2}u_3 + \frac{1}{3}x' + \frac{2}{3}x \tag{11.1.2.3}$$

$$x_3 = u_3 + \frac{2}{3}x' + \frac{1}{3}x \tag{11.1.2.4}$$

Thus, the sum of squares becomes

$$(x-x_2)^2+(x_2-x_3)^2+(x_3-x')^2 = (2u_2^2+\frac{3}{2}u_3^2+\frac{1}{3}(x-x')^2 = \frac{2}{2-1}u_2^2+\frac{3}{3-1}u_3^2+\frac{1}{3}(x-x')^2 \tag{11.1.2.5}$$

From this simple example, the general formula can be deduced:

$$\sum_{i=1}^{P}(x_{i+1}-x_i)^2 = \sum_{k=2}^{P}\frac{k}{k-1}u_k^2 + \frac{1}{P}(x-x')^2$$

Thus, substituting this transformation into the integral gives

$$\rho(x, x'; \beta) = \left(\frac{m}{2\pi\beta\hbar^2}\right)^{1/2} \prod_{k=2}^{P} \left(\frac{m_k P}{2\pi\beta\hbar^2}\right)^{1/2} \int du_2 \cdots du_P exp\left[-\sum_{k=2}^{P} \frac{m_k P}{2\beta\hbar^2} u_k^2\right] exp\left[-\frac{m}{2\beta\hbar^2}(x - x')^2\right]$$

where

$$m_k = \frac{k}{k-1} m$$

and the overall prefactor has been written as

$$\left(\frac{mP}{2\pi\beta\hbar^2}\right)^{P/2} = \left(\frac{m}{2\pi\beta\hbar^2}\right)^{1/2} \prod_{k=2}^{P} \left(\frac{m_k P}{2\pi\beta\hbar^2}\right)^{1/2}$$

Now each of the integrals over the u variables can be integrated over independently, yielding the final result

$$\rho(x, x'; \beta) = \left(\frac{m}{2\pi\beta\hbar^2}\right)^{1/2} \exp\left[-\frac{m}{2\beta\hbar^2}(x - x')^2\right]$$

In order to make connection with classical statistical mechanics, we note that the prefactor is just $\frac{1}{\lambda}$, where λ

$$\lambda = \left(\frac{2\pi\beta\hbar^2}{m}\right)^{1/2} = \left(\frac{\beta h^2}{2\pi m}\right)^{1/2}$$

is the kinetic prefactor that showed up also in the classical free particle case. In terms of λ, the free particle density matrix can be written as

$$\rho(x, x'; \beta) = \frac{1}{\lambda} e^{-\pi(x-x')^2/\lambda^2}$$

Thus, we see that λ represents the spatial width of a free particle at finite temperature, and is called the "**thermal de Broglie wavelength**."

11.1.3: Dominant Paths in the Propagator and Density Matrix

Let us first consider the real time quantum propagator. The quantity appearing in the exponential is an integral of

$$\frac{1}{2}m\dot{x}^2 - U(x) \equiv L(x, \dot{x})$$

which is known as the Lagrangian in classical mechanics. We can ask, which paths will contribute most to the integral

$$\int_0^t ds \left[\frac{m}{2}\dot{x}^2(s) - U(x(s))\right] = \int_0^t dsL(x(s), \dot{x}(s)) = S[x]$$

known as the *action integral*. Since we are integrating over a complex exponential $\exp(\frac{iS}{\hbar})$, which is oscillatory, those paths away from which small deviations cause no change in S (at least to first order) will give rise to the dominant contribution. Other paths that cause $\exp(\frac{iS}{\hbar})$ to oscillate rapidly as we change from one path to another will give rise to phase decoherence and will ultimately cancel when integrated over. Thus, we consider two paths $x(s)$ and a nearby one constructed from it $x(s) + \delta x(s)$ and demand that the change in S between these paths be 0

$$S[x + \delta x] - S[x] = 0$$

Note that, since $x(0) = x$ and $x(t) = x'$, $\delta x(0) = \delta x(t) = 0$, since *all* paths must begin at x and end at x'. The change in S is

$$\delta S = S[x + \delta x] - S[x] = \int_0^t dsL(x + \delta x, \dot{x} + \delta\dot{x}) - \int_0^t dsL(x, \dot{x})$$

Expanding the first term to first order in δx, we obtain

$$\delta S = \int_0^t ds \left[L(x, \dot{x}) + \frac{\partial L}{\partial \dot{x}}\delta\dot{x} + \frac{\partial L}{\partial x}\delta x\right] - \int_0^t L(x, \dot{x}) = \int_0^t ds \left[\frac{\partial L}{\partial \dot{x}}\delta\dot{x} + \frac{\partial L}{\partial x}\delta x\right]$$

The term proportional to $\delta\dot{x}$ can be handled by an integration by parts:

$$\int_0^t ds\frac{\partial L}{\partial \dot{x}}\delta\dot{x} = \int_0^t \frac{\partial L}{\partial \dot{x}}\frac{d}{dt}\delta x = \frac{\partial L}{\partial \dot{x}}\partial x|_0^t - \int_0^t ds\frac{d}{dt}\frac{\partial L}{\partial \dot{x}}\delta x$$

because δx vanishes at 0 and t, the surface term is 0, leaving us with

$$\delta S = \int_0^t ds \left[-\frac{d}{dt}\frac{\partial L}{\partial \dot{x}} + \frac{\partial L}{\partial x}\right]\delta x = 0$$

Since the variation itself is arbitrary, the only way the integral can vanish, in general, is if the term in brackets vanishes:

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{x}} - \frac{\partial L}{\partial x} = 0$$

This is known as the **Euler-Lagrange equation** in classical mechanics. For the case that $L = m\dot{x}/2 - U(x)$, they give

$$\frac{d}{dt}(m\dot{x}) + \frac{\partial U}{\partial x} = 0$$

$$m\ddot{x} = -\frac{\partial U}{\partial x}$$

which is just Newton's equation of motion, subject to the conditions that $x(0)$, $x(t) = x'$. Thus, the classical path and those near it contribute the most to the path integral.

The classical path condition was derived by requiring that $\delta S = 0$ to first order. This is known as an action *stationarity* principle. However, it turns out that there is also a **principle of least action,** which states that the classical path minimizes the action as well. This is an important consideration when deriving the dominant paths for the density matrix, which takes the form

$$\rho(x, x'; \beta) = \int_{x(0)=x}^{x(\beta\hbar=x'} \mathcal{D}x(\cdot)exp\left[-\frac{1}{\hbar}\int_0^{\beta\hbar} d\tau\left(\frac{m}{2}\dot{x}(\tau) + U(x(\tau))\right)\right]$$

The action appearing in this expression is

$$S_E[x] = \int_0^{\beta\hbar} d\tau \left[\frac{m}{2}\dot{x}^2 + U(x(\tau))\right] = \int_0^{\beta\hbar} d\tau H(x,\dot{x})$$

which is known as the **Euclidean action** and is just the integral over a path of the total energy or *Euclidean Lagrangian* $H(x,\dot{x})$. Here, we see that a minimum action principle is needed, since the smallest values of S_E will contribute most to the integral. Again, we require that to first order $S_E[x+\delta x] - S_E[x] = 0$. Applying the same logic as before, we obtain the condition

$$\frac{d}{d\tau}\frac{\partial H}{\partial \dot{x}} - \frac{\partial H}{\partial x} = 0$$

$$m\ddot{x} = \frac{\partial}{\partial x}U(x)$$

which is just Newton's equation of motion on the inverted potential surface $-U(x)$, subject to the conditions $x(0) = x$, $x(\beta\hbar) = x'$. For the partition function $Q(\beta)$, the same equation of motion must be solved, but subject to the conditions that $x(0) = x(\beta\hbar)$, i.e., periodic paths.

11.1.4: The Continuous Limit

In taking the limit $P \to \infty$, it will prove useful to define a parameter

$$\varepsilon = \frac{\beta\hbar}{P}$$

so that $P \to \infty$ implies $\varepsilon \to 0$. In terms of ε, the partition function becomes

$$Q(\beta) = \lim_{P\to\infty,\varepsilon\to 0} \left(\frac{m}{2\pi\varepsilon\hbar}\right)^{P/2} \int dx_1 \cdots dx_P exp\left[-\frac{\varepsilon}{\hbar}\sum_{i=1}^{P}\left(\frac{m}{2}\left(\frac{x_{i+1}-x_i}{\varepsilon}\right)^2 + U(x_i)\right)\right] |_{x_{P+1}=x_1}$$

We can think of the points $x_1, \ldots, x_P$ as specific points of a continuous functions $x(\tau)$, where

$$x_k = x(\tau = (k-1)\varepsilon)$$

such that $x(0) = x(\tau = P\varepsilon) = x(\tau = \beta\hbar)$:

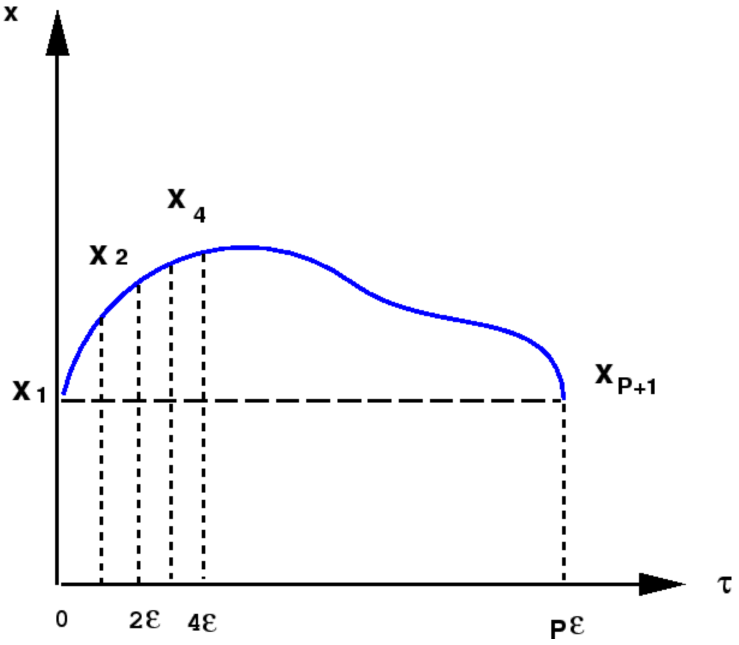


Figure 1:

Note that

$$\lim_{\varepsilon\to 0}\left(\frac{x_{k+1}-x_k}{\varepsilon}\right) = \lim_{\varepsilon\to 0}\left(\frac{x(k\varepsilon)-x((k-1)\varepsilon)}{\varepsilon}\right) = \frac{dx}{d\tau}$$

and that the limit

$$\lim_{P\to\infty,\varepsilon\to 0}\frac{\varepsilon}{\hbar}\sum_{i=1}^{P}\left[\frac{m}{2}\left(\frac{x_{i+1}-x_i}{\varepsilon}\right)^2 + U(x_i)\right]$$

is just a Riemann sum representation of the continuous integral

$$\frac{1}{\hbar}| \int_0^{\beta\hbar} d\tau \left[\frac{m}{2}\left(\frac{dx}{d\tau}\right)^2 + U(x(\tau))\right]$$

Finally, the measure

$$\lim_{P\to\infty,\varepsilon\to 0}\left(\frac{m}{2\pi\varepsilon\hbar^2}\right)^{P/2} dx_1 \cdots dx_P$$

represents an integral overa all values that the function $x(\tau)$ can take on between $\tau=0$ and $\tau=\beta\hbar$ such that $x(0)=x(\beta\hbar)$. We write this symbolically as $\mathcal{D}x(\cdot)$. Therefore, the $P\rightarrow\infty$ limit of the partition function can be written as

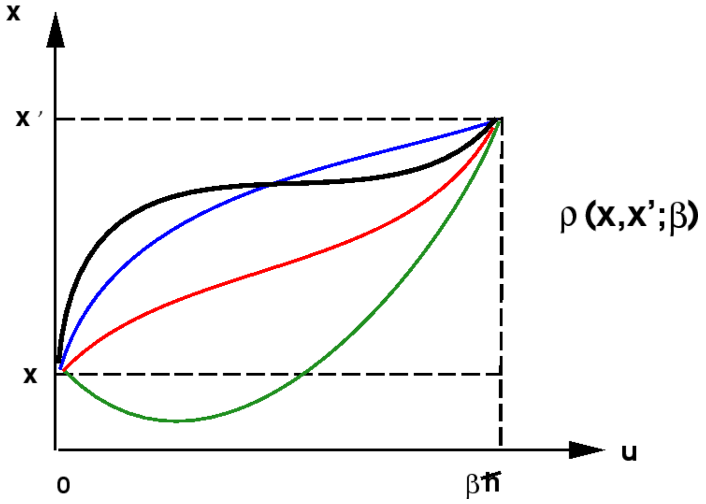
$$\begin{aligned} Q(\beta) &= \int dx \int_{x(0)=x}^{x(\beta\hbar)=x} \mathcal{D}x(\cdot) exp\left[-\frac{1}{\hbar}\int_0^{\beta\hbar} d\tau \left(\frac{m}{2}\dot{x}^2 + U(x(\tau))\right)\right] \\ &= \oint \mathcal{D}x(\cdot)\exp\left[-\frac{1}{\hbar}\int_0^{\beta\hbar} d\tau \left(\frac{m}{2}\dot{x}^2 + U(x(\tau))\right)\right] \end{aligned}$$

The above expression in known as a **functional integral**. It says that we must integrate over all functions (i.e., all values that an arbitrary function $x(\tau)$ may take on) between the values $\tau=0$ and $\tau=\beta\hbar$. It must really be viewed as the limit of the discretized integral introduced in the last lecture. The integral is also referred to as a *path integral* because it implies an integration over all paths that a particle might take between $\tau=0$ and $\tau=\beta\hbar$ such that $x(0)=x(\beta\hbar$, where the paths are parameterized by the variable τ (which is not time!). The second line in the above expression, which is equivalent to the first, indicates that the integration is taken over all paths that begin and end at the same point, plus a final integration over that point.

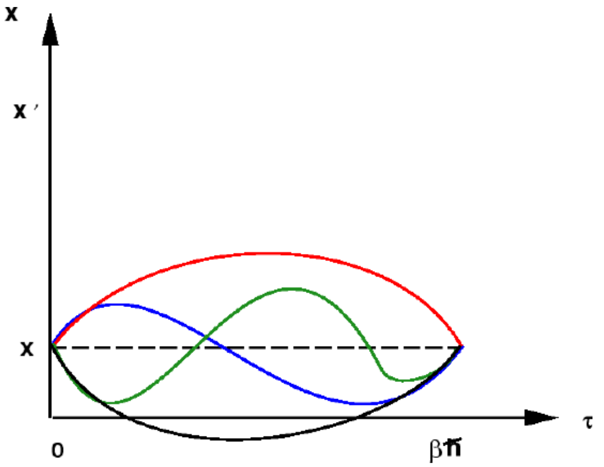
The above expression makes it clear how to represent a general density matrix element $\langle x|\exp(-\beta H)|x'\rangle$:

$$\langle x|e^{-\beta H}|x'\rangle = \int_{x(0)=x}^{x(\beta\hbar)=x'} \mathcal{D}x(\cdot) exp\left[-\frac{1}{\hbar}\int_0^{\beta\hbar} d\tau \left(\frac{m}{2}\dot{x}^2 + U(x(\tau))\right)\right]$$

which indicates that we must integrate over all functions $x(\tau)$ that begin at x at $\tau=0$ and end at x' at $\tau=\beta\hbar$:



Similarly, diagonal elements of the density matrix, used to compute the partition function, are calculated by integrating over all periodic paths that satisfy $x(0)=x(\beta\hbar)=x$:



Note that if we let $\beta=\frac{it}{\hbar}$, then the density matrix becomes

$$\rho(x,x';it/\hbar) = \langle x|e^{-iHt/\hbar}|x'\rangle = U(x,x';t)$$

which are the coordinate space matrix elements of the quantum time evolution operator. If we make a change of variables $\tau = is$ in the path integral expression for the density matrix, we find that the quantum propagator can also be expressed as a path integral:

$$U(x,x';t) = \langle x|e^{-iHt/\hbar}|x'\rangle = \int_{x(0)=x}^{x(t)=x'} \mathcal{D}x(\cdot) exp\left[\frac{i}{\hbar}\int_0^t ds\left(\frac{m}{2}\dot{x}(s) - U(x(s))\right)\right]$$

Such a variable transformation is known as a **Wick rotation**. This nomenclature comes about by viewing time as a complex quantity. The propagator involves real time, while the density matrix involves a transformation $t = -\beta\hbar$ to the imaginary time axis. It is because of this that the density matrix is sometimes referred to as an **imaginary time path integral**.

SECTION OVERVIEW

11.2: Calculation of observables from path integrals

Topic hierarchy

Template:HideTOC

-

11.2.1: Expectation values of observables

Recall the basic formula for the expectation value of an observable A:

$$\langle A\rangle = \frac{1}{Q(\beta)}\mathrm{Tr}(Ae^{-\beta H})$$

Two important cases pertaining to the evaluation of the trace in the coordinate basis for expectation values will be considered below:

Case 1: Functions only of position

If $A = A(X)$, i.e., a function of the operator X only, then the trace can be easily evaluated in the coordinate basis:

$$\langle A\rangle = \frac{1}{Q}\int dx\,\langle x|A(X)e^{-\beta H}|x\rangle$$

Since $A(X)$ acts to the left on one of its eigenstates, we have

$$\langle A\rangle = \frac{1}{Q}\int dx\,A(x)\langle x|e^{-\beta H}|x\rangle$$

which only involves a diagonal element of the density matrix. This can, therefore, be written as a path integral:

$$\langle A\rangle = \frac{1}{Q}\lim_{P\to\infty}\left(\frac{mP}{2\pi\beta\hbar^2}\right)^{P/2}\int dx_1\cdots dx_P\,A(x_1)exp\left[-\beta\sum_{i=1}^{P}\left(\frac{1}{2}m\omega_P^2(x_{i+1}-x_i)^2+\frac{1}{P}U(x_i)\right)\right]$$

However, since all points $x_1,\cdots,x_P$ are equivalent, due to the fact that they are all integrated over, we can make P equivalent cyclic renaming of the coordinates $x_1 \to x_2$, $x_2 \to x_3$ etc. and generate P equivalent integrals. In each, the function $A(x_1)$ or $A(x_2)$, etc. will appear. If we sum these P equivalent integrals and divide by P, we get an expression:

$$\langle A\rangle = \frac{1}{Q}\lim_{P\to\infty}\left(\frac{mP}{2\pi\beta\hbar^2}\right)^{P/2}\int dx_1\cdots dx_P\,A(x_1)exp\left[-\beta\sum_{i=1}^{P}\left(\frac{1}{2}m\omega_P^2(x_{i+1}-x_i)^2+\frac{1}{P}U(x_i)\right)\right]$$

This allows us to define an *estimator* for the observable A. Recall that an estimator is a function of the P variables $x_1,\cdots,x_P$ whose average over the ensemble yields the expectation value of A:

$$a_P(x_1,\ldots,x_P) = \frac{1}{P}\sum_{i=1}^{P}A(x_i)$$

Then

$$\langle A\rangle = \lim_{P\to\infty}\langle a_p\rangle_{x_1,\ldots,x_P}$$

where the average on the right is taken over many configurations of the P variables $x_1,\cdots,x_P$ (we will discuss, in the nex lecture, a way to generate these configurations).

The limit $P\to\infty$ can be taken in the same way that we did in the previous lecture, yielding a functional integral expression for the expectation value:

$$\langle A\rangle = \frac{1}{Q}\oint\mathcal{D}x(\tau)\left[\frac{1}{\beta\hbar}\int_0^{\beta\hbar}d\tau A(x(\tau))\right]exp\left[-\frac{1}{\hbar}\int_0^{\beta\hbar}d\tau\left(\frac{1}{2}m\dot{x}^2+U(x(\tau))\right)\right]$$

Case 2: Functions only of momentum

Suppose that $A = A(P)$, i.e., a function of the momentum operator. Then, the trace can still be evaluated in the coordinate basis:

$$\langle A\rangle = \frac{1}{Q}\int dx\,\langle x|A(P)e^{-\beta H}|x\rangle$$

However, $A(P)$ acting to the left does not act on an eigenvector. Let us insert a coordinate space identity $I = \int dx |x\rangle \langle x|$ between A and $exp(-\beta H)$:

$$\langle A \rangle = \frac{1}{Q} \int dx dx' \langle x|A(P)|x'\rangle \langle x|e^{-\beta H}|x\rangle$$

Now, we see that the expectation value can be obtained by evaluating *all* the coordinate space matrix elements of the operator and *all* the coordinate space matrix elements of the density matrix.

A particularly useful form for the expectation value can be obtained if a momentum space identity is inserted:

$$\langle A \rangle = \frac{1}{Q} \int dx dx' dp \langle x|A(P)|p\rangle \langle p|x'\rangle \langle x'|e^{-\beta H}|x\rangle$$

Now, we see that $A(P)$ acts on an eigenstate (at the price of introducing another integral). Thus, we have

$$\langle A \rangle = \frac{1}{Q} \int dp A(p) \int dx dx' \langle x|\rangle \langle p|x'\rangle \langle x'|e^{-\beta H}|x\rangle$$

Using the fact that $\langle x|p\rangle = (1/2\pi\hbar) \exp(ipx/\hbar)$, we find that

$$\langle A \rangle = \frac{1}{2\pi\hbar Q} \int dp A(p) \int dx dx' e^{ip(x-x')/\hbar} \langle x'|e^{-\beta H}|x\rangle$$

In the above expression, we introduce the change of variables

$$r = \frac{x+x'}{2} \qquad s = x - x'$$

Then

$$\langle A \rangle = \frac{1}{2\pi\hbar Q} \int dp A(p) \int dr ds e^{ips/\hbar} \langle r - \frac{s}{2}|e^{-\beta H}|r + \frac{s}{2}\rangle$$

Define a distribution function

$$\rho_{\rm W}(r,p) = \frac{1}{2\pi\hbar} \int ds e^{ips/\hbar} \langle r - \frac{s}{2}|e^{-\beta H}|r + \frac{s}{2}\rangle$$

Then, the expectation value can be written as

$$\langle A \rangle = \frac{1}{Q} \int dr dp A(p) \rho_{\rm W}(r,p)$$

which looks just like a classical phase space average using the "phase space" distribution function $\rho_{\rm W}(r,p)$. The distribution function $\rho_{\rm W}(r,p)$ is known as the Wigner density matrix and it has many interesting features. For one thing, its classical limit is

$$\rho_{\rm W}(r,p) = \exp\left[-\beta\left(\frac{p^2}{2m} + U(r)\right)\right]$$

which is the true classical phase space distribution function. There are various examples, in which the exact Wigner distribution function is the classical phase space distribution function, in particularly for quadratic Hamiltonians. Despite its compelling appearance, the evaluation of expectation values of functions of momentum are considerably more difficult than functions of position, due to the fact that the entire density matrix is required. However, there are a few quantities of interest, that are functions of momentum, that can be evaluated without resorting to the entire density matrix. These are thermodynamic quantities which will be discussed in the next section.

11.2.2: Path integrals for N-particle systems

If particle spin statistics must be treated in a given problem, the formulation of the path integral is more complicated, and we will not treat this subject here. The extension of path integrals to N-particle systems in which spin statistics can safely be ignored, however, is straightforward, and we will give the expressions below.

The partition function for an N-particle system in the canonical ensemble without spin statistics can be formulated essentially by analogy to the one-particle case. The partition function that one obtains is

$$Q(N,V,T) =$$
$$\lim_{P\to\infty}\left[\prod_{I=1}^{N}\left(\frac{m_I P}{2\pi\beta\hbar^2}\right)^{3P/2}\int d\mathbf{r}_I^{(1)}\cdots d\mathbf{r}_I^{(P)}\right] exp\left[-\beta\sum_{i=1}^{P}\left(\sum_{I=1}^{N}\frac{1}{2}m_I\omega_P^2(\mathbf{r}_I^{(i+1)}-\mathbf{r}_I^{(i)})^2+\frac{1}{P}U(\mathbf{r}_1^{(i)},\ldots,\mathbf{r}_N^{(i)})\right)\right]$$

Thus, it can be seen that the N-particle potential must be evaluated for each imaginary time discretization, however, there is no coupling between separate imaginary time slices due arising from the potential. Thus, interactions occur only between particles in the *same* time slice. From a computational point of view, this is advantageous, as it allows for easily parallelization over imaginary time slices.

The corresponding energy and pressure estimators for the N-particle path integral are given by

$\epsilon_P(\{\mathbf{r}^{(1)},\ldots,\mathbf{r}^{(P)}\})$	=	$\frac{3NP}{2\beta}-\sum_{i=1}^{P}\sum_{I=1}^{N}\frac{1}{2}m_I\omega_P^2\left(\mathbf{r}_I^{(i)}-\mathbf{r}_I^{(i+1)}\right)^2+\frac{1}{P}\sum_{i=1}^{P}U(\mathbf{r}_1^{(i)},\ldots,\mathbf{r}_N^{(i}$
$p_P(\{\mathbf{r}^{(1)},\ldots,\mathbf{r}^{(P)}\})$	=	$\frac{NP}{\beta V}-\frac{1}{3V}\sum_{i=1}^{P}\sum_{I=1}^{N}\left[m_I\omega_P^2\left(\mathbf{r}_I^{(i)}-\mathbf{r}_I^{(i+1)}\right)^2+\frac{1}{P}\mathbf{r}_I^{(i)}\cdot\nabla_{\mathbf{r}_I^{(i)}}U\right]$

11.2.3: Path integral molecular dynamics (optional reading)

Consider once again the path integral expression for the one-dimensional canonical partition function (for a finite but large value of P):

$$Q(\beta)=\left(\frac{mP}{2\pi\beta\hbar^2}\right)^{P/2}\int dx_1\cdots dx_P exp\left[-\beta\sum_{i=1}^{P}\left(\frac{1}{2}m\omega_P^2(x_{i+1}-x_i)^2+\frac{1}{P}U(x_i)\right)\right] \tag{1}$$

(the condition $x_{P+1}=x_1$ is understood). Recall that, according to the classical isomorphism, the path integral expression for the canonical partition function is isomorphic to the classical configuration integral for a certain P-particle system. We can carry this analogy one step further by introducing into the above expression a set of P momentum integrations:

$$Q(\beta)=\int dp_1\cdots dp_P\; dx_1\cdots dx_P exp\left[-\beta\sum_{i=1}^{P}\left(\frac{P_i^2}{2m'}+\frac{1}{2}m\omega_P^2(x_{i+1}-x_i)^2+\frac{1}{P}U(x_i)\right)\right] \tag{2}$$

Note that these momentum integrations are completely uncoupled from the position integrations, and if we were to carry out these momentum integrations, we would reproduce Eq. (1) apart from trivial constants. Written in the form Eq. (2), however, the path integral looks exactly like a phase space integral for a P-particle system. We know from our work in classical statistical mechanics that dynamical equations of motion can be constructed that will generate this partition function. In principle, one would start with the classical Hamiltonian

$$H=\sum_{i=1}^{P}\left[\frac{p_i^2}{2m'}+\frac{1}{2}m\omega_P^2(x_{i+1}-x_i)^2+\frac{1}{P}U(x_i)\right]$$

derive the corresponding classical equations of motion and then couple in thermostats. Such an approach has certainly been attempted with only limited success. The difficulty with this straightforward approach is that the more "quantum" a system is, the large the parameter P must be chosen in order to converge the path integral. However, if P is large, the above Hamiltonian describes a system with extremely stiff nearest-neighbor harmonic bonds interacting with a very weak potential U/P. It is, therefore, almost impossible for the system to deviate far harmonic oscillator solutions and explore the entire available phase space. The use of thermostats can help this problem, however, it is also exacerbated by the fact that all the harmonic interactions are coupled, leading to a wide variety of time scales associated with the motion of each variable in the Hamiltonian. In order to separate out all these time scales, one must somehow diagonalize this harmonic interaction. One way to do this is to use normal mode variables, and this is a perfectly valid approach. However, we will explore another, simpler approach here. It involves the use of a variable transformation of the formed used in previous lectures to do the path integral for the free-particle density matrix.

Consider a change of variables:

u_1	=	x_1
u_k	=	$x_k-\tilde{x}_k k=2,\cdots,P$

where

$$\tilde{x}_i=\frac{(k-1)x_{k+1}+x_1}{k}$$

The inverse of this transformation can be worked out in closed form:

x_1	=	u_1
x_k	=	$u_1+\sum_{l=k}^{P}\frac{(k-1)}{(l-1)}u_l$

and can also be expressed as a *recursive inverse*:

x_1	=	u_1
x_k	=	$u_1 + \sum_{l=k}^{P} \frac{(k-1)}{(l-1)} u_l$

The term $k = P$ here can be used to start the recursion. We have already seen that this transformation diagonalized the harmonic interaction. Thus, substituting the transformation into the path integral gives:

$$Q(\beta) = \int dp_1 \cdots dp_P \; du_1 \cdots du_P exp\left[-\beta \sum_{i=1}^{P} \left(\frac{P_i^2}{2m_i'} + \frac{1}{2} m_i \omega_P^2 u_i^2 + \frac{1}{P} U(x_i(u_1, \ldots, u_P)) \right) \right]$$

The parameters m_i are given by

m_1	=	0
m_i	=	$\frac{i}{i-1} m$

Note also that the momentum integrations have been changed slightly to involve a set of parameters m_i'. Introducing these parameters, again, only changes the partition function by trivial constant factors. How these should be chosen will become clear later in the discussion. The notation $x_i(u_1, \cdots, u_P)$ indicates that each variable x_i is a generally a function of all the new variables $u_1, \cdots, u_P$.

A dynamics scheme can now be derived using as an effective Hamiltonian:

$$H = \sum_{i=1}^{P} \left[\frac{p_i^2}{2m_i'} + \frac{1}{2} m_i \omega_P^2 u_i^2 + \frac{1}{P} U(x_i(u_1, \ldots, u_P)) \right]$$

which, when coupled to thermostats, yields a set of equations of motion

$m_i' \ddot{u}_i$	=	$-m_i \omega_P^2 u_i - \frac{1}{P} \frac{\partial U}{\partial u_i} - \dot{\eta}_i \dot{u}_i$	
$Q \ddot{\eta}_i$	=	$m_i \dot{u}_i^2 - \frac{1}{\beta}$	(3)

These equations have a conserved energy (which is not a Hamiltonian):

$$H' = \sum_{i=1}^{P} \left[\frac{1}{2} m_i' \dot{u}_i^2 + \frac{1}{2} m_i \omega_P^2 u_i^2 + \frac{1}{P} U(x_i(u_1, \cdots, u_P)) + \frac{1}{2} Q \dot{\eta}_i^2 + \frac{1}{\beta} \eta_i \right]$$

Notice that each variable is given its *own* thermostat. This is done to produce maximum ergodicity in the trajectories. In fact, in practice, the chain thermostats you have used in the computer labs are employed. Notice also that the time scale of each variable is now clear. It is just determined by the parameters $\{m_i\}$. Since the object of using such dynamical equations is not to produce real dynamics but to sample the phase space, we would really like each variable to move on the *same* time scale, so that there are no slow beads trailing behind the fast ones. This effect can be produced by choosing each parameter m_i' to be proportional to $m_i : m_i' = cm_i$ Finally, the forces on the u variables can be determined easily from the chain rule and the recursive inverse given above. The result is

$\frac{1}{P} \frac{\partial U}{\partial u_1}$	=	$\frac{1}{P} \sum_{i=1}^{P} \frac{\partial U}{\partial x_i}$
$\frac{1}{P} \frac{\partial U}{\partial u_i}$	=	$\frac{1}{P} \left[\frac{(k-2)}{(k-1)} \frac{\partial U}{\partial u_{k-1}} + \frac{\partial U}{\partial x_k} \right]$

where the first $(i = 1)$ of these expressions starts the recursion in the second equation.

Later on, when we discuss applications of path integrals, we will see why a formulation such as this for evaluating path integrals is advantageous.

11.2.4: Thermodynamics from path integrals

Although general functions of momentum are difficult (though not intractable) to evaluate by path integration, certain functions of momentum (and position) can be evaluated straightforwardly. These are thermodynamic quantities such as the energy and pressure, given respectively by

$$E=-\frac{\partial}{\partial\beta}\ln Q(\beta,V)$$

$$P=\frac{1}{\beta}\frac{\partial}{\partial V}\ln Q(\beta,V)$$

We shall derive estimators for these two quantities directly from the path integral expression for the partition function. However, let us work with the partition function for an ensemble of 1-particle systems in three dimensions, which is given by

$$Q(\beta,V)=\lim_{P\to\infty}\left(\frac{mP}{2\pi\beta\hbar^2}\right)^{3P/2}\int d\mathbf{r}_1\cdots d\mathbf{r}_P exp\left[-\beta\sum_{i=1}^{P}\left(\frac{1}{2}m\omega_P^2\mathbf{r}_{i+1}-\mathbf{r}_i)^2+\frac{1}{P}U(\mathbf{r}_i)\right)\right] \tag{11.2.4.1}$$

Using the above thermodynamic relation, the energy becomes

$$\begin{aligned}E&=-\frac{1}{Q}\frac{\partial Q}{\partial\beta}\\&=\frac{1}{Q}\lim_{P\to\infty}\left(\frac{mP}{2\pi\beta\hbar^2}\right)^{3P/2}\int d\mathbf{r}_1\cdots d\mathbf{r}_P exp\left[-\beta\sum_{i=1}^{P}\left(\frac{1}{2}m\omega_P^2(\mathbf{r}_{i+1}-\mathbf{r}_i)^2+\frac{1}{P}U(\mathbf{r}_i)\right)\right]\\&\qquad\times\left[\frac{3P}{2\beta}-\sum_{i=1}^{P}\frac{1}{2}m\omega_P^2(\mathbf{r}_{i+1}-\mathbf{r}_i)^2+\frac{1}{P}\sum_{i=1}^{P}U(\mathbf{r}_i)\right]\\&=\lim_{P\to\infty}\langle\varepsilon_P(\mathbf{r}_1,\ldots,\mathbf{r}_P)\rangle\end{aligned}$$

where

$$\varepsilon_P(\mathbf{r}_1,\ldots,\mathbf{r}_P)=\frac{3P}{2\beta}-\sum_{i=1}^{P}\frac{1}{2}m\omega_P^2(\mathbf{r}_{i+1}-\mathbf{r}_i)^2+\frac{1}{P}\sum_{i=1}^{P}U(\mathbf{r}_i)$$

is the thermodynamic estimator for the total energy. Similarly, an estimator for the internal pressure can be derived using $P=kT\partial\ln Q/\partial V$. As we have done in the past for classical systems, the volume dependence can be made explicitly by introducing the change of variables:

$$\mathbf{r}_k=V^{1/3}\mathbf{s}_k \tag{11.2.4.2}$$

In terms of the scaled variables s_k, the partition function expression reads:

$$Q(\beta,V)=\lim_{P\to\infty}\left(\frac{mP}{2\pi\beta\hbar^2}\right)^{3P/2}V^P\int ds_1\cdots ds_P exp\left[-\beta\sum_{i=1}^{P}\left(\frac{1}{2}m\omega_P^2V^{2/3}(\mathbf{s}_{i+1}-\mathbf{s}_i)^2+\frac{1}{P}U(V^{1/3}\mathbf{s}_i)\right)\right] \tag{11.2.4.3}$$

Evaluating the derivative with respect to volume gives the internal pressure:

$$\begin{aligned}
P &= \frac{1}{\beta Q}\frac{\partial Q}{\partial V} \\
&= \frac{1}{Q}\lim_{P\to\infty}\left(\frac{mP}{2\pi\beta\hbar^2}\right)^{3P/2} V^P \int ds_1\cdots ds_P exp\left[-\beta\sum_{i=1}^{P}\left(\frac{1}{2}m\omega_P^2 V^{2/3}(\mathbf{s}_{i+1}-\mathbf{s}_i)^2+\frac{1}{P}U(V^{1/3}\mathbf{s}_i)\right)\right] \\
&\qquad\qquad \times\left[\frac{P}{\beta V}-\frac{1}{3}m\omega_P^2 V^{-1/3}\sum_{i=1}^{P}(\mathbf{s}_{i+1}-\mathbf{s}_i)^2-\frac{1}{P}\sum_{i=1}^{P}\frac{\partial U}{\partial(V^{1/3}\mathbf{s}_i)}\cdot\frac{1}{3}V^{-2/3}\mathbf{s}_i\right] \\
&\qquad = \frac{1}{Q}\lim_{P\to\infty}\left(\frac{mP}{2\pi\beta\hbar^2}\right)^{3P/2}\int d\mathbf{r}_1\cdots d\mathbf{r}_P exp\left[-\beta\sum_{i=1}^{P}\left(\frac{1}{2}m\omega_P^2(\mathbf{r}_{i+1}-\mathbf{r}_i)^2+\frac{1}{P}U(\mathbf{r}_i)\right)\right] \\
&\qquad\qquad\qquad \times\left[\frac{P}{\beta V}-\frac{1}{3V}m\omega_P^2\sum_{i=1}^{P}\left(\mathbf{r}_{i+1}-\mathbf{r}_i\right)^2-\frac{1}{3VP}\sum_{i=1}^{P}\frac{\partial U}{\partial\mathbf{r}_i}\cdot\mathbf{s}_i\right] \\
&= \lim_{P\to\infty}\langle p_P(\mathbf{r}_1,\ldots,\mathbf{r}_P)\rangle
\end{aligned}$$

where

$$p_P(\mathbf{r}_1,\ldots,\mathbf{r}_P)=\frac{P}{\beta V}-\frac{1}{3V}\sum_{i=1}^{P}\left[m\omega_P^2(\mathbf{r}_{i+1}-\mathbf{r}_i)^2+\frac{1}{P}\mathbf{r}_i\cdot\frac{\partial U}{\partial\mathbf{r}_i}\right] \tag{11.2.4.4}$$

is the thermodynamic estimator for the pressure. Clearly, both the energy and pressure will be functions of the particle momenta, however, because they are related to the partition function by thermodynamic differentiation, estimators can be derived for them that do not require the off-diagonal elements of the density matrix.

SECTION OVERVIEW

11.3: Expansion about the classical path and stationary phase

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11.3.1: The harmonic Oscillator - Expansion about the Classical Path

It will be shown how to compute the density matrix for the harmonic oscillator:

$$H = \frac{P^2}{2m} + \frac{1}{2}m\omega^2 X^2$$

using the functional integral representation. The density matrix is given by

$$\rho(x,x';\beta) = \int_{x(0)=x}^{x(\beta\hbar)=x'} \mathcal{D}x(\tau) exp\left[-\frac{1}{\hbar}\int_0^{\beta\hbar} d\tau \left(\frac{1}{2}m\dot{x}^2 + \frac{1}{2}m\omega^2 x^2\right)\right]$$

As we saw in the last lecture, paths in the vicinity of the classical path on the inverted potential give rise to the dominant contribution to the functional integral. Thus, it proves useful to expand the path $x(\tau)$ about the classical path. We introduce a change of path variables from $x(\tau)$ to $y(\tau)$, where

$$x(\tau) = x_{\text{cl}}(\tau) + y(\tau)$$

where $x_{\text{cl}}(\tau)$ satisfies

$$m\ddot{x}_{\text{cl}} = m\omega^2 x_{\text{cl}}$$

subject to the conditions

$$x_{\text{cl}}(0) = x, \qquad x_{\text{cl}}(\beta\hbar) = x'$$

so that $y(0) = y(\beta\hbar) = 0$.

Substituting this change of variables into the action integral yields

$$\begin{aligned} S &= \int_0^{\beta\hbar} d\tau \left[\frac{1}{2}m\dot{x}^2 + \frac{1}{2}m\omega^2 x^2\right] \\ &= \int_0^{\beta\hbar} d\tau \left[\frac{1}{2}m(\dot{x}_{\text{cl}} + \dot{y})^2 + \frac{1}{2}m\omega^2 (x_{\text{cl}} + y)^2\right] \\ &= \int_0^{\beta\hbar} d\tau \left[\frac{1}{2}m\dot{x}_{\text{cl}}^2 + \frac{1}{2}m\omega^2 x_{cl}^2\right] + \int_0^{\beta\hbar} d\tau \left[\frac{1}{2}m\dot{y}^2 + \frac{1}{2}m\omega^2 y^2\right] + \int_0^{\beta\hbar} d\tau \left[m\dot{x}_{cl}\dot{y} + m\omega^2 x_{\text{cl}} y\right] \end{aligned}$$

An integration by parts makes the cross terms vanish:

$$\int_0^{\beta\hbar} d\tau \left[m\dot{x}_{\text{cl}}\dot{y} + m\omega^2 x_{cl} = m\dot{x}_{cl} y\right] = m\dot{x}_{cl} y|_0^{\beta\hbar} + \int_0^{\beta\hbar} dtau \left[-m\ddot{x}_{\text{cl}} + m\omega^2 xcl\right] y = 0$$

where the surface term vanishes because $y(0) = y(\beta\hbar) = 0$ and the second term vanishes because \(xcl\) satisfies the classical equation of motion.

The first term in the expression for S is the classical action, which we have seen is given by

$$\int_0^{\beta\hbar} d\tau \left[\frac{1}{2}m\dot{x}_{\text{cl}}^2 + \frac{1}{2}m\omega^2 x_{cl}^2\right] = \frac{m\omega}{2\sinh(2\beta\hbar\omega} \left[(x^2 + x'^2)\cosh(\beta\hbar\omega) - 2xx'\right]$$

Therefore, the density matrix for the harmonic oscillator becomes

$$\rho(x,x';\beta) = I[y] \exp\left[-\frac{m\omega}{2\sinh(\beta\hbar\omega)}\left((x^2 + x^2 + x'^2)\cosh(\beta\hbar\omega) - 2xx'\right)\right]$$

where $I(y)$ is the path integral

$$I[y] = \int_{y(0)=0}^{y(\beta\hbar)=0} \mathcal{D}y(\tau) exp\left[-\frac{1}{\hbar}\int_0^{\beta\hbar}\left(\frac{m}{2}\dot{y}^2 + \frac{m\omega^2}{2}y^2\right)\right]$$

Note that $I[y]$ does not depend on the points x and x' and therefore can only contribute an overall (temperature dependent) constant to the density matrix. This will affect the thermodynamics but not any averages of physical observables. Nevertheless, it is important to see how such a path integral is done.

To compute $I[y]$, we note that it is a functional integral over functions $y(\tau)$ that vanish at $\tau = 0$ and $\tau = \beta\hbar$. Thus, they are a special class of periodic functions and can be expanded in a Fourier sine series:

$$y(\tau) = \sum_{n=1}^{\infty} c_n \sin(\omega_n \tau)$$

where

$$\omega_n = \frac{n\pi}{\beta\hbar}$$

Thus, we wish to change from an integral over the functions $y(\tau)$ to an integral over the Fourier expansion coefficients c_n. The two integrations should be equivalent, as the coefficients uniquely determine the functions $y(\tau)$. Note that

$$\dot{y}(\tau) = \sum_{n=1}^{\infty} \omega_n c_n \cos(\omega_n \tau)$$

Thus, terms in the action are:

$$\int_0^{\beta\hbar} d\tau \frac{1}{m}\dot{y}^2 = \frac{m}{2}\sum_{n=1}^{\infty}\sum_{n'=1}^{\infty} c_n c_{n'} \omega_n \omega_{n'} \int_0^{\beta\hbar} d\tau \cos(\omega_n \tau)\cos(\omega_{n'}\tau)$$

Since the cosines are orthogonal between $\tau = 0$ and $\tau = \beta\hbar$, the integral becomes

$$\int_0^{\beta\hbar} d\tau \frac{1}{m}\dot{y}^2 = \frac{m}{2}\sum_{n=1}^{\infty} c_n^2 \omega_n^2 \int_0^{\beta\hbar} d\tau \cos^2(\omega_n \tau) = \frac{m}{2}\sum_{n=1}^{\infty} c_n^2 \omega_n^2 \int_0^{\beta\hbar} d\tau \left[\frac{1}{2} + \frac{1}{2}\cos(2\omega_n \tau)\right] = \frac{m\beta\hbar}{4}\sum_{n=1}^{\infty} c_n^2 \omega_n^2$$

similarly,

$$\int_0^{\beta\hbar} \frac{1}{2} m\omega^2 y^2 = \frac{m\beta\hbar}{4}\omega^2 \sum_{n=1}^{\infty} c_n^2$$

The measure becomes

$$\mathcal{D}y(t) \rightarrow \prod_{n=1}^{\infty} \frac{dc_n}{\sqrt{4\pi/m\beta\omega_n^2}}$$

which, is not an equivalent measure (since it is not derived from a determination of the Jacobian), but is chosen to give the correct free-particle ($\omega = 0$) limit, which can ultimately be corrected by attaching an overall factor of $\sqrt{m/2\pi\beta\hbar^2}$.

With this change of variables, $I[y]$ becomes

$$I[y] = \prod_{n=1}^{\infty} \int_{-\infty}^{\infty} \frac{dc_n}{\sqrt{4\pi/m\beta\omega_n^2}} exp\left[-\frac{m\beta}{4}(\omega^2 + \omega_n^2)c_n^2\right] = \prod_{n=1}^{\infty}\left[\frac{\omega_n^2}{\omega^2 + \omega_n^2}\right]^{1/2}$$

The infinite product can be written as

$$\prod_{n=1}^{\infty}\left[\frac{\pi^2 n^2/\beta^2\hbar^2}{\omega^2 + \pi^2 n^2/\beta^2\hbar^2}\right] = \left[\prod_{n=1}^{\infty}\left(\frac{\beta^2\hbar^2\omega^2}{\pi^2 n^2}\right)\right]^{-1}$$

the product in the square brackets is just the infinite product formula for $\sinh(\beta\hbar\omega)/(\beta\hbar\omega)$, so that $I[y]$ is just

$$I[y] = \sqrt{\frac{\beta\hbar\omega}{\sinh(\beta\hbar\omega)}}$$

Finally, attaching the free-particle factor $\sqrt{m/2\pi\beta\hbar^2}$, the harmonic oscillator density matrix becomes:

$$\rho(x,x';\beta) = \sqrt{\frac{m\omega}{2\pi\hbar \mathrm{sinh}(\beta\hbar\omega)}} exp\left[-\frac{m\omega}{2\sinh(\beta\hbar\omega)}\left(\left(x^2+x'^2\right)\cosh(\beta\hbar\omega) - 2xx'\right)\right]$$

Notice that in the free-particle limit $(\omega \to 0)$, $\sinh(\beta\hbar\omega) \approx \beta\hbar\omega$ and $\cosh(\beta\hbar\omega) \approx 1$, so that

$$\rho(x,x';\beta) \to \sqrt{\frac{m}{2\pi\beta\hbar^2}}\exp\left[-\frac{m}{2\beta\hbar^2}\left(x-x'\right)^2\right]$$

which is the expected free-particle density matrix.

11.3.2: The Stationary Phase Approximation

Consider the simple integral:

$$I = \lim_{\lambda\rightarrow\infty}\int_{-\infty}^{\infty} dx\ e^{-\lambda f(x)}$$

Assume $f(x)$ has a global minimum at $x = x_0$, such that $f'(x_0) = 0$. If this minimum is well separated from other minima of $f(x)$ and the value of $f(x)$ at the global minimum is significantly lower than it is at other minima, then the dominant contributions to the above integral, as $\lambda\rightarrow\infty$ will come from the integration region around x_0. Thus, we may expand $f(x)$ about this point:

$$f(x) = f(x_0) + f'(x_0)(x-x_0) + \frac{1}{2}f''(x_0)(x-x_0)^2 + \cdots$$

Since $f'(x_0) = 0$, this becomes:

$$f(x) \approx f(x_0) + \frac{1}{2}f''(x_0)(x-x_0)^2$$

Inserting the expansion into the expression for I gives

$$\begin{aligned} I &= \lim_{\lambda\rightarrow\infty} e^{-\lambda f(x_0)}\int_{-\infty}^{\infty} dx\ e^{-\frac{\lambda}{2}f''(x_0)(x-x_0)^2} \\ &= \lim_{\lambda\rightarrow\infty}\left[\frac{2\pi}{\lambda f''(x_0)}\right]^{1/2} e^{-\lambda f(x_0)} \end{aligned}$$

Corrections can be obtained by further expansion of higher order terms. For example, consider the expansion of $f(x)$ up to fourth order:

$$f(x) \approx f(x_0) + \frac{1}{2}f''(x_0)(x-x_0)^2 + \frac{1}{6}f'''(x_0)(x-x_0)^3 + \frac{1}{24}f^{(iv)}(x_0)(x-x_0)^4$$

Substituting this into the integrand and further expanding the exponential would give, as the lowest order nonvanishing correction:

$$I = \lim_{\lambda\rightarrow\infty} e^{-\lambda f(x_0)}\int_{-\infty}^{\infty} dx e^{\frac{-\lambda}{2}} f''(x_0)(x-x_0)^2\left[1 - \frac{\lambda}{24}f^{(iv)}(x_0)(x-x_0)^4\right]$$

This approximation is known as the *stationary phase* or *saddle point* approximation. The former may seem a little out-of-place, since there is no phase in the problem, but that is because we formulated it in such a way as to anticipate its application to the path integral. But this is only if λ is taken to be a real instead of an imaginary quantity.

The application to the path integral follows via a similar argument. Consider the path integral expression for the density matrix:

$$\rho(x,x';\beta) = \int_{x(0)=x}^{x(\beta\hbar)=x'}\mathcal{D}[x]e^{-S_{\rm E}[x]/\hbar}$$

We showed that the classical path satisfying

$$m\ddot{x}_{\rm cl} = \left.\frac{\partial U}{\partial x}\right|_{x=x_{\rm cl}} = x(0) = x \tag{11.3.2.1}$$

$$x(\beta\hbar) = x' \tag{11.3.2.2}$$

is a stationary point of the Euclidean action $S_{\rm E}[x]$, i.e., $\delta S_{\rm E}[x_{\rm cl}] = 0$. Thus, we can develop a stationary phase or saddle point approximation for the density matrix by introducing an expansion about the classical path according to

$$x(\tau) = x_{\rm cl}(\tau) + y(\tau) = x_{\rm cl}(\tau) + \sum_n c_n\phi_n(\tau) \tag{11.3.2.3}$$

where the correction $y(\tau)$, satisfying $y(0) = y(\beta\hbar) = 0$ has been expanded in a complete set of orthonormal functions $\{\phi_n(\tau)\}$, which are orthonormal on the interval $[0,\beta\hbar]$ and satisfy $\phi_n(0) = \phi_n(\beta\hbar) = 0$ as well as the orthogonality condition:

$$\int_0^{\beta\hbar} d\tau\ \phi_n(\tau)\phi_m(\tau) = \delta_{mn} \tag{11.3.2.4}$$

Setting all the expansion coefficients to 0 recovers the classical path. Thus, we may expand the action $S[x]$ (the "E" subscript will henceforth be dropped from this discussion) with respect to the expansion coefficients:

S[x] = S[x_{\rm cl}] + \sum_j \left.{\partial S \over \partial S \over \partial c_j c_k}\right\vert _{\{c\}=0}c_jc_k + \cdots

Since

$$S[x] = \int_0^{\beta\hbar} d\tau \left[\frac{1}{2}m\dot{x}^2 + U(x(\tau))\right] \tag{11.3.2.5}$$

the expansion can be worked out straightforwardly by substitution and subsequent differentiation:

$$S[x] = \int_0^{\beta\hbar} d\tau \left[\frac{1}{2}m\left(\dot{x}_{\rm cl} + \sum_n c_n\dot{\phi}_n\right)^2 + U(x_{\rm cl} + \sum_n c_n\phi_n)\right] \tag{11.3.2.6}$$

$$\frac{\partial S}{\partial c_j} = \int_0^{\beta\hbar} d\tau \left[m(\dot{x}_{\rm cl} + \sum_n c_n\dot{\phi}_n)\dot{\phi}_j + U'\left(x_{\rm cl} + \sum_n c_n\phi_n\right)\phi_j\right] \tag{11.3.2.7}$$

$$\left.\frac{\partial S}{\partial c_j}\right|_{\{c\}=0} = \int_0^{\beta\hbar} d\tau \left[m\dot{x}_{\rm cl}\dot{\phi}_j + U'(x_{\rm cl})\phi_j\right] = m\dot{x}_{\rm cl}\phi_j|_0^{\beta\hbar} + \int_0^{\beta\hbar} d\tau \left[-m\ddot{x}_{\rm cl} + U'(x_{\rm cl})\right]\phi_j = 0 \tag{11.3.2.8}$$

$$\frac{\partial^2 S}{\partial c_j \partial c_k} = \int_0^{\beta\hbar} \left[m\dot{\phi}_j\dot{\phi}_k + U''\left(x_{\rm cl} + \sum_n c_n\phi_n]\right)\phi_j\phi_k\right] \tag{11.3.2.9}$$

$$\left.\frac{\partial^2 S}{\partial c_j \partial c_k}\right|_{\{c\}=0} = \int_0^{\beta\hbar} d\tau \left[m\dot{\phi}_j\dot{\phi}_k + U''(x_{\rm cl})\phi_j\phi_k\right] = \int_0^{\beta\hbar} d\tau \left[-m\phi_j\ddot{\phi}_k + U''(x_{\rm cl}(\tau))\phi_j\phi_k\right] = \tag{11.3.2.10}$$

$$\int_0^{\beta\hbar} d\tau\phi_j(\tau)\left[-m\frac{d^2}{d\tau^2} + U''(x_{\rm cl}(\tau))\right]\phi_k(\tau)$$

where the fourth and eighth lines are obtained from an integration by parts. Let us write the integral in the last line in the suggestive form:

\left.{\partial^2 S \over \partial c_j\partial c_k}\right\vertical ... ...tau^2} + U"(x_{\rm cl}(\tau))\vert\phi_k\rangle = \Delta_{jk}

which emphasizes the fact that we have matrix elements of the operator $-md^2/d\tau^2 + U''(x_{\rm cl}(\tau))$ with respect to the basis functions. Thus, the expansion for S can be written as

$$S[x] = S[x_{\rm cl}] + \frac{1}{2}\sum_{j,k} c_j\Delta_{jk}c_k + \cdots \tag{11.3.2.11}$$

and the density matrix becomes

\rho(x,x';\beta) = {\cal N}\int \prod_j {dc_j \over \sqrt{2\... ...x,x';\beta)} e^{-{1 \over 2}\sum_{j,k}c_j\Delta_{jk}c_k/\hbar}

where $S_{\rm cl}(x, x'; \beta) = S[x_{\rm cl}]$. $\mathcal{N}$ is an overall normalization constant. The integral over the coefficients becomes a generalized Gaussian integral, which brings down a factor of $1/\sqrt{\det\Delta}$:

\[\rho(x,x';\beta) = {\cal N}e^{-S_{\rm cl}(x,x';\beta)}{1 \over \sqrt

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\) = \({\cal N}e^{-S_{\rm cl}(x,x';\beta)} {1 \over \sqrt

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\]

where the last line is the abstract representation of the determinant. The determinant is called the **Van Vleck-Pauli-Morette determinant**.

If we choose the basis functions $\phi_n(\tau)$ to be eigenfunctions of the operator appearing in the above expression, so that they satisfy

$$\left[-m\frac{d^2}{d\tau^2}+U''(x_{\rm cl}(\tau))\right]\phi_n(\tau)=\lambda_n\phi_n(\tau) \tag{11.3.2.12}$$

Then,

$$\Delta_{jk}=\lambda_j\delta_{jk}=\lambda_j(x,x';\beta)\delta_{jk} \tag{11.3.2.13}$$

and the determinant can be expressed as a product of the eigenvalues. Thus,

$$\rho(x,x';\beta)=\mathcal{N}e^{-S_{\rm cl}(x,x';\beta)}\prod_j\frac{1}{\sqrt{\lambda_j(x,x';\beta)}} \tag{11.3.2.14}$$

The product must exclude any 0-eigenvalues.

Incidentally, by performing a Wick rotation back to real time according to $\beta=-it/\hbar$, the saddle point or stationary phase approximation to the real-time propagator can be derived. The derivation is somewhat tedious and will not be given in detail here, but the result is

U(x,x';t) = e^{{i \over \hbar}S_{\rm cl}(x,x';t)} {1 \over \... ...-m{d^2 \over dt^2} - U"(x_{\rm cl}(t))\right)}}e^{-i\pi\nu/2}

where $x_{\rm cl}(t)$ satisfies

\] m\ddot{x}_{\rm cl} = -\left.{\partial U \over \partial x}\right\vert _{x=x_{\rm cl}}\)   \(x_{\rm cl}(0) = x\]

$$x_{\rm cl}(t)=x' \tag{11.3.2.15}$$

and ν is an integer that increases by 1 each time the determinant vanishes along the classical path. ν is called the **Maslov index**. It is important to note that because the classical paths satisfy an endpoint problem, rather than an initial value problem, there can be more than one solution. In this case, one must sum the result over classical paths:

\(U(x,x';t) = \sum_{\rm classical\ paths} e^

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\)

CHAPTER OVERVIEW

12: Time-dependent Processes - Classical case

12.1: Perturbative solution of the Liouville equation

As in the classical case, we assume a solution of the form

$$\rho(t) = \rho_0(H_0) + \Delta\rho(t)$$

where

$$[H_0, \rho_0] = 0 \qquad \Rightarrow \qquad \frac{\partial \rho_0}{\partial t} = 0$$

and we will assume

$$\rho_0(H_0) = \frac{e^{-\beta H_0}}{Q(N,V,T)}$$

Substituting into the Liouville equation and working to first order in small quantities, we find

$$\frac{\partial \Delta\rho}{\partial t} = \frac{1}{i\hbar}[H_0, \Delta\rho] - \frac{1}{i\hbar}[B, \rho_0]F_e(t)$$

which is a **first order inhomogeneous equation** that can be solved by using an integrating factor:

$$\Delta\rho(t) = -\frac{1}{i\hbar}\int_{-\infty}^{t} ds\ e^{-iH_0(t-s)/\hbar}[B, \rho_0]e^{iH_0(t-s)/\hbar}F_e(s)$$

(Note that we have chosen the origin in time to be $t = -\infty$, which is an arbitrary choice.)

For an observable A, the expectation value is

$$\langle A(t)\rangle = \mathrm{Tr}(\rho A) = \langle A\rangle_0 + \mathrm{Tr}(\Delta\rho(t)A)$$

when the solution for $\Delta\rho$ is substituted in, this becomes

$\langle A(t)\rangle$	$=$	$\langle A\rangle_0 - \frac{1}{i\hbar}\int_{-\infty}^{t}\ ds\ \mathrm{Tr}\ [Ae^{-iH_0(t-s)/hbar}\ [B, \rho_0]e^{iH_0(t-}$
	$=$	$\langle A\rangle_0 - \frac{1}{i\hbar}\int_{-\infty}^{t}\ ds\ \mathrm{Tr}\ [e^{iH_0(t-s)/\hbar}\ Ae^{-iH_0(t-s)/hbar}\ [B$
	$=$	$\langle A\rangle_0 - \frac{1}{i\hbar}ds\ \mathrm{Tr}\ [A(t-s)[B, \rho_0]]\ F_e(s)$

where the cyclic property of the trace has been used and the Heisenberg evolution for A has been substituted in. Expanding the commutator gives

$\langle A(t)\rangle$	$=$	$\langle A\rangle_0 - \frac{1}{i\hbar}\int_{-\infty}^{t}\ ds\ \mathrm{Tr}\ [A(t-s)B\rho_0 - A(t-s)\rho_0 B]$
	$=$	$\langle A\rangle_0 - \frac{1}{i\hbar}\int_{-\infty}^{t}\ ds\ \mathrm{Tr}\ [\rho_0\ (A(t-s)B - BA(t-s))]$
	$=$	$\langle A\rangle_0 - \frac{1}{i\hbar}\int_{-\infty}^{t}\ ds\ F_e(s)\langle[A(t-s), B(0)]_0\rangle$

where the cyclic property of the trace has been used again. Define a function

$$\Phi_{AB}(t) = \frac{i}{\hbar}\langle[A(t), B(0)]\rangle_0$$

called the *after effect function*. It is essentially the antisymmetric quantum time correlation function, which involves the commutator between $A(t)$ and $B(0)$. Then the linear response result can be written as

$$\langle A(t)\rangle = \langle A\rangle_0 + \int_{-\infty}^{t} dsF_e(s)\Phi_{AB}(t-s)$$

which is the starting point for the theory of quantum transport coefficients. If we choose to measure the operator B, then we find

$$\langle B(t)\rangle = \langle B\rangle_0 + \int_{-\infty}^{t} ds\ F_e(s)\Phi_{BB}(t-s)$$

12.2: Kubo Transform Expression for the Time Correlation Function

We shall derive the following expression for the quantum time correlation function

$$\Phi_{AB}(t) = \int_0^\beta d\lambda\ \langle \dot{B}(-i\hbar\lambda)A(t)\rangle_0$$

known as a **Kubo transform** relation. Since $\dot{B}$ is given by the Heisenberg equation:

$$\dot{B} = \frac{1}{i\hbar}[B, H_0]$$

it follows that

$$\dot{B}(t) = -\frac{1}{i\hbar}e^{iH_0t/\hbar}[H_0, B(0)]e^{-iH_0t/\hbar}$$

Evaluating the expression at $t = -i\hbar\lambda$ gives

$$\dot{B}(-i\hbar\lambda) = e^{\lambda H_0}\frac{1}{i\hbar}[B(0), H_0]e^{-\lambda H_0}$$

Thus,

$$\Phi_{AB}(t) = \int_0^\beta d\lambda \langle e^{\lambda H_0}\left(\frac{1}{i\hbar}[B(0), H_0]\right) e^{-\lambda H_0} A(t)\rangle_0$$

By performing the trace in the basis of eigenvectors of H_0, we obtain

$$\begin{aligned}
\Phi_{AB}(t) &= \frac{1}{Q}\int_0^\beta d\lambda \sum_n \langle n|e^{\lambda H_0}\left(\frac{1}{i\hbar}\right)[B(0), H_0]e^{-\lambda H_0} A(t)|n\rangle e^{-\beta E_n} \\
&= \frac{1}{Q}\int_0^\beta d\lambda \sum_{m,n} \langle n|e^{\lambda H_0}\left(\frac{1}{i\hbar}\right)[B(0), H_0]\, e^{-\lambda H_0}\,|m\rangle\langle m|A(t)|n\rangle e^{-\beta E_n} \\
&= \frac{1}{Q}\int_0^\beta d\lambda \sum_{m,n} e^{\lambda E_n} e^{-\lambda E_m}\frac{1}{i\hbar}\langle n|[B(0), H_0]|m\rangle\langle m|A(t)|n\rangle e^{-\beta E_n} \\
&= \frac{1}{Q}\sum_{m,n} e^{-\beta E_n}\frac{e^{\beta(E_n-E_m)}-1}{(E_n-E_m)}\frac{1}{i\hbar}\langle n|[B(0), H_0]|m\rangle\langle m|A(t)|n\rangle e^{-\beta E_n}
\end{aligned}$$

But

$$\langle n|[B(0), H_0]|m\rangle = \langle n|B(0)H_0 - H_0B(0)|m\rangle = (E_m - E_n)\langle n|B(0)|m\rangle$$

Therefore,

$$\begin{aligned}
\Phi_{AB}(t) &= -\frac{1}{i\hbar Q}\sum_{m,n}\left(e^{-\beta E_n} - e^{-\beta E_m}\right)\langle n|B(0)|m\rangle\langle m|A(t)|n\rangle \\
&= -\frac{1}{i\hbar Q}\left[\sum_{m,n} e^{-\beta E_m}\langle m|A(t)|n\rangle\langle n|B(0)|m\rangle - \sum_{m,n} e^{-\beta E_n}\langle n|B(0)|m\rangle\langle m|A(t)|n\rangle\right] \\
&= \frac{i}{\hbar}\langle[A(t), B(0)]\rangle_0
\end{aligned}$$

which proves the relation. The classical limit can be deduced easily from the Kubo transform relation:

$$\Phi_{AB}(t) \longrightarrow \beta\langle\dot{B}(0)A(t)\rangle_0$$

Note further, by using the cylic properties of the trace, that

$$\langle \dot{B}(-i\hbar\lambda)B(t)\rangle_0 = -\frac{d}{dt}\langle B(-i\hbar\lambda)B(t)\rangle_0$$

12.3: Generalized Equations of Motion

The most general way a system can be driven away from equilibrium by a forcing function $F_e(t)$ is according to the equations of motion:

$$\dot{q}_i = \frac{\partial H}{\partial p_i} + C_i(\mathrm{x})F_e(t)$$

$$\dot{P}_i = -\frac{\partial H}{\partial p_i} + D_i(\mathrm{x})F_e(t)$$

where the $3N$ functions C_i and D_i are required to satisfy the incompressibility condition

$$\sum_{i=1}^{3N}\left[\frac{\partial C_i}{\partial q_i} + \frac{\partial D_i}{\partial p_i}\right] = 0$$

in order to insure that the Liouville equation for $f(x,t)$ is still valid. These equations of motion will give rise to a distribution function $f(x,t)$ satisfying

$$\frac{\partial f}{\partial t} + iLf = 0$$

with $\partial f/\partial t \neq 0$. (We assume that f is normalized so that $\int d\mathrm{x} f(\mathrm{x},t) = 1$.)

What does the Liouville equation say about the nature of $f(x,t)$ in the limit that C_i and D_i are small, so that the displacement away from equilibrium is, itself, small? To examine this question, we propose to solve the Liouville equation perturbatively. Thus, let us assume a solution of the form

$$f(\mathrm{x},t) = f_0(H(\mathrm{x})) + \Delta f(\mathrm{x},t)$$

Note, also, that the equations of motion $\dot{x}$ take a perturbative form

$$\dot{\mathrm{x}}(t) = \dot{\mathrm{x}}_0 + \Delta\dot{\mathrm{x}}(t)$$

and as a result, the Liouville operator contains two pieces:

$$iL = \dot{\mathrm{x}}\cdot\nabla_{\mathrm{x}} = \dot{\mathrm{x}}_0\cdot\nabla_x + \Delta\dot{\mathrm{x}}\cdot\nabla_{\mathrm{x}} = iL_0 + i\Delta L$$

where $iL_0 = \{\dots, H\}$ and $f_0(H)$ is assumed to satisfy

$$iL_0 f_0(H(\mathrm{x})) = 0$$

$\dot{x}_0$ means the Hamiltonian part of the equations of motion

$$\dot{q}_i = \frac{\partial H}{\partial p_i}$$

$$\dot{P}_i = -\frac{\partial H}{\partial q_i}$$

For an observable $A(x)$, the ensemble average of A is a time-dependent quantity:

$$\langle A(t)\rangle = \int d\mathrm{x} A(\mathrm{x}) f(\mathrm{x},t)$$

which, when the assumed form for $f(x,t)$ is substituted in, gives

$$\langle A(t)\rangle = \int d\mathrm{x} A(\mathrm{x}) f_0(\mathrm{x}) + \int dx\, A(x)\Delta f(x,t) = \langle A\rangle_0 + \int d\mathrm{x} A(\mathrm{x})\Delta f(\mathrm{x},t)$$

where $\langle\cdot\rangle_0$ means average with respect to $f_0(x)$.

12.4: General Properties of Time Correlation Functions

Define a time correlation function between two quantities $A(x)$ and $B(x)$ by

$$\begin{aligned} C_{AB}(t) &= \langle A(0)B(t)\rangle \\ &= \int d\mathrm{x} f(\mathrm{x})A(\mathrm{x})e^{iLt}B(\mathrm{x}) \end{aligned}$$

The following properties follow immediately from the above definition:

Property 1

$$\langle A(0)B(t)\rangle = \langle A(-t)B(0)\rangle$$

Property 2

$$C_{AB}(0) = \langle A(\mathrm{x})B(\mathrm{x})\rangle$$

Thus, if $A = B$, then

$$C_{AA}(t) = \langle A(0)A(t)\rangle$$

known as the autocorrelation function of A, and

$$C_{AA}(0) = \langle A^2\rangle$$

If we define $\delta A = A - \langle A\rangle$, then

$$C_{\delta A\delta A}(0) = \langle(\delta A)^2\rangle = \langle(A-\langle A\rangle)^2\rangle = \langle A^2\rangle - \langle A\rangle^2$$

which just measures the fluctuations in the quantity A.

Property 3

A time correlation function may be evaluated as a time average, assuming the system is ergodic. In this case, the phase space average may be equated to a time average, and we have

$$C_{AB}(t) = \lim_{T\to\infty}\frac{1}{T-t}\int_0^{T-t} ds A(\mathrm{x}(s))B(\mathrm{x}(t+s))$$

which is valid for $t << T$. In molecular dynamics simulations, where the phase space trajectory is determined at discrete time steps, the integral is expressed as a sum

$$C_{AB}(k\Delta t) = \frac{1}{N-k}\sum_{j=1}^{N-k} A(\mathrm{x}_k)B(\mathrm{x}_{k+j}) \qquad k = 0, 1, 2, \dots, N_c$$

where N is the total number of time steps, Δt is the time step and $N_c << N$.

Property 4: Onsager regression hypothesis

In the long time limit, A and B eventually become uncorrelated from each other so that the time correlation function becomes

$$C_{AB}(t) = \langle A(0)B(t)\rangle \to \langle A\rangle\langle B\rangle$$

For the autocorrelation function of A, this becomes

$$C_{AA}(t) \to \langle A\rangle^2$$

Thus, $C_{AA}(t)$ decays from $\langle A^2\rangle$ at $t = 0$ to $\langle A^2\rangle$ as $t \to \infty$.

An example of a signal and its time correlation function appears in Figure $12.4.1$. In this case, the signal is the magnitude of the velocity along the bond of a diatomic molecule interacting with a Lennard-Jones bath. Its time correlation function is shown beneath the signal:

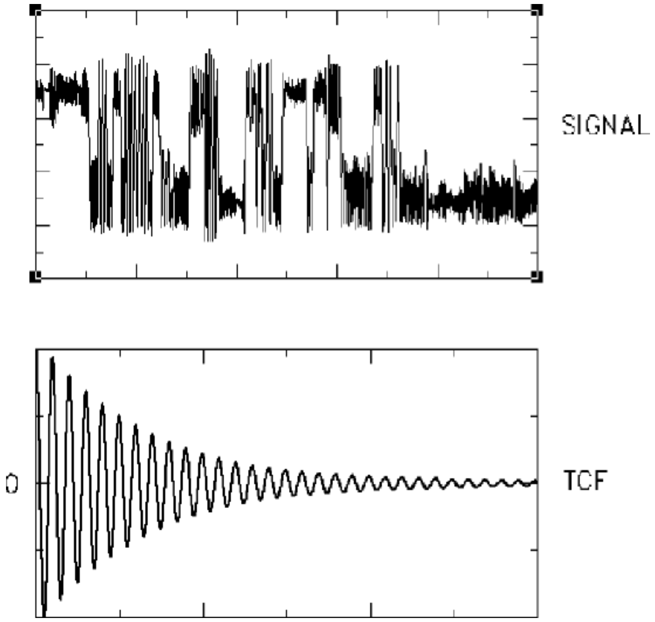


Figure 12.4.1

Over time, it can be seen that the property being autocorrelated eventually becomes uncorrelated with itself.

12.5: Perturbative solution of the Liouville equation

Substituting the perturbative form for $f(x,t)$ into the Liouville equation, one obtains

$$\frac{\partial}{\partial t}(f_0(\text{x})+\Delta f(\text{x},t))+(iL_0+i\Delta L(t))(f_0(\text{x})+\Delta f(\text{x},t))=0$$

Recall $\partial f_0/\partial t=0$. Thus, working to linear order in small quantities, one obtains the following equation for $\Delta f(\text{x},t)$:

$$\left(\frac{\partial}{\partial t}+iL_0\right)\Delta f(\text{x},t)=-i\Delta L f_0(\text{x})$$

which is just a first-order inhomogeneous differential equation. This can easily be solved using an integrating factor, and one obtains the result

$$\Delta f(\text{x},t)=-\int_0^t ds e^{-iL_0(t-s)}\,i\Delta L(s)f_0(\text{x})$$

Note that

$$i\Delta L f_0(\text{x})=iLf_0(\text{x})-iL_0f_0(\text{x})=iLf_0(\text{x})=\dot{\text{x}}\cdot\nabla_{\text{x}}f_0(\text{x})$$

But, using the chain rule, we have

$$\begin{aligned}\dot{\text{x}}\cdot\nabla_{\text{x}}f_0(\text{x}) &=\dot{\text{x}}\cdot\frac{\partial f_0}{\partial H}\frac{\partial H}{\partial \text{x}}\\ &=\frac{\partial f_0}{\partial H}\sum_{i=1}^{3N}\left[\dot{p}_i\frac{\partial H}{\partial p_i}+\dot{q}_i\frac{\partial H}{\partial q_i}\right]\\ &=\frac{\partial f_0}{\partial H}\sum_{i=1}^{3N}\left[\frac{\partial H}{\partial p_i}\left(-\frac{\partial H}{\partial q_i}+D_iF_e(t)\right)+\frac{\partial H}{\partial q_i}\left(\frac{\partial H}{\partial p_i}+C_iF_e(t)\right)\right]\\ &=\frac{\partial f_0}{\partial H}\sum_{i=1}^{3N}\left[D_i(\text{x})\frac{\partial H}{\partial p_i}+C_i(\text{x})\frac{\partial H}{\partial q_i}\right]F_e(t)\end{aligned}$$

Define

$$j(\text{x})=-\sum_{i=1}^{3N}\left[D_i(\text{x})\frac{\partial H}{\partial p_i}+C_i(\text{x})\frac{\partial H}{\partial q_i}\right]$$

which is known as the *dissipative flux*. Thus, for a Cartesian Hamiltonian

$$H=\sum_{i=1}^{N}\frac{\mathbf{p}_i^2}{2m_i}+U(\mathbf{r}_1,\ldots,\mathbf{r}_N)$$

where $\mathbf{F}_i(\mathbf{r}_1,\ldots,\mathbf{r}_N)=-\nabla_iU$ is the force on the i th particle, the dissipative flux becomes:

$$j(\text{x})=\sum_{i=1}^{N}\left[\mathbf{C}_i(\text{x})\cdot\mathbf{F}_i-\mathbf{D}_i(\text{x})\cdot\frac{\mathbf{p}_i}{m_i}\right]$$

In general,

$$\dot{\text{x}}\cdot\nabla_{\text{x}}f_0(\text{x})=-\frac{\partial f_0}{\partial H}j(\text{x})F_e(t)$$

Now, suppose $f_0(x)$ is a canonical distribution function

$$f_0(H(\text{x}))=\frac{1}{Q(N,V,T)}e^{-\beta H(\text{x})}$$

then

$$\frac{\partial f_0}{\partial H} = -\beta f_0(H)$$

so that

$$\dot{\mathrm{x}} \cdot \nabla_{\mathrm{x}} f_0(\mathrm{x}) = \beta f_0(\mathrm{x}) j(\mathrm{x}) F_e(t)$$

Thus, the solution for $\Delta f(x,t)$ is

$$\Delta f(\mathrm{x},t) = -\beta \int_0^t ds e^{-iL_0(t-s)} f_0(\mathrm{x}) j(\mathrm{x}) F_e(s)$$

The ensemble average of the observable $A(x)$ now becomes

$$\begin{aligned}\langle A(t)\rangle &= \langle A\rangle_0 - \beta \int d\mathrm{x} A(\mathrm{x}) \int_0^t ds e^{-iL_0(t-s)} f_0(\mathrm{x}) j(\mathrm{x}) F_e(s) \\ &= \langle A\rangle_0 - \beta \int_0^t ds \int d\mathrm{x} A(\mathrm{x}) e^{-iL_0(t-s)} f_0(\mathrm{x}) j(\mathrm{x}) F_e(s) \\ &= \langle A\rangle_0 - \beta \int_0^t ds \int d\mathrm{x} f_0(\mathrm{x}) A(\mathrm{x}) e^{-iL_0(t-s)} j(\mathrm{x}) F_e(s)\end{aligned}$$

Recall that the classical propagator is $exp(iLt)$. Thus the operator appearing in the above expression is a classical propagator of the unperturbed system for propagating backwards in time to $-(t-s)$. An observable $A(x)$ evolves in time according to

$$\frac{dA}{dt} = iLA$$

$$A(t) = e^{iLt} A(0)$$

$$A(-t) = e^{-iLt} A(0)$$

Now, if we take the complex conjugate of both sides, we find

$$A^*(t) = A^*(0) e^{-iLt}$$

where now the operator acts to the left on $A^*(0)$. However, since observables are real, we have

$$A(t) = A(0) e^{-iLt}$$

which implies that forward evolution in time can be achieved by acting to the left on an observable with the time reversed classical propagator. Thus, the ensemble average of A becomes

$$\begin{aligned}\langle A(t)\rangle &= \langle A\rangle_0 - \beta \int_0^t ds F_e(s) \int d\mathrm{x}_0 f_0(\mathrm{x}_0) A(\mathrm{x}_{t-s}(\mathrm{x}_0)) j(\mathrm{x}_0) \\ &= \langle A\rangle_0 - \beta \int_0^t ds F_e(s) \langle j(0) A(t-s)\rangle_0\end{aligned}$$

where the quantity on the last line is an object we have not encountered yet before. It is known as an **equilibrium time correlation function**. An equilibrium time correlation function is an ensemble average over the unperturbed (canonical) ensemble of the product of the dissipative flux at $t=0$ with an observable A evolved to a time $t-s$. Several things are worth noting:

1. The nonequilibrium average $\langle A(t)\rangle$, in the linear response regime, can be expressed solely in terms of equilibrium averages.
2. The propagator used to evolve $A(x)$ to $A(x,t-s)$ is the operator $exp(iL_0(t-s))$, which is the propagator for the unperturbed, Hamiltonian dynamics with $C_i = D_i = 0$. That is, it is just the dynamics determined by H.
3. Since $A(\mathrm{x}, t-s) = A(\mathrm{x}(t-s))$ is a function of the phase space variables evolved to a time $t-s$, we must now specify over which set of phase space variables the integration $\int dx$ is taken. The choice is actually arbitrary, and for convenience, we choose the initial conditions. Since $x(t)$ is a function of the initial conditions $x(0)$, we can write the time correlation function as

$$\langle j(0) A(t-s)\rangle_0 = \frac{1}{Q} \int d\mathrm{x}_0 e^{-\beta H(\mathrm{x}_0)} j(\mathrm{x}_0) A(\mathrm{x}_{t-s}(\mathrm{x}_0))$$

12.6: The Onsager Fluctuation Regression Theorem

Suppose that $F_e(t)$ is of the form

$$F_e(t) = F_0 e^{\epsilon t}\theta(-t)$$

which adiabatically induces a fluctuation in the system for $t < 0$ and the lets the system evolve in time according to the unperturbed Hamiltonian for $t > 0$. How will the induced fluctuation evolve in time? Combining the Kubo transform relation with the linear response result for $\langle B(t)\rangle$, we find that

$$\begin{aligned}\langle B(t)\rangle &= \int_{-\infty}^{0} ds\, e^{\epsilon s} \int_0^\beta d\lambda \langle \dot{B}(-i\hbar\lambda) B(t-s)\rangle_0 \\ &= -e^{\epsilon t}\int_0^\beta d\lambda \int_t^\infty du\, e^{-\epsilon u}\frac{d}{du}\langle B(-i\hbar\lambda)B(u)\rangle_0\end{aligned}$$

where the change of variables $u = t - s$ has been made. Taking the limit $\epsilon \to 0$, and performing the integral over u, we find

$$\langle B(t)\rangle = -\int_0^\beta d\lambda\, \left[\langle B(-i\hbar\lambda)B(\infty)\rangle_0 - \langle B(-i\hbar\lambda)B(t)\rangle_0\right]$$

Since we assumed that $\langle B\rangle_0 = 0$, we have $\langle B(-i\hbar\lambda)B(\infty)\rangle_0 = \langle B(-i\hbar\lambda)\rangle_0\langle B(\infty)\rangle_0 = 0$. Thus, dividing by $\langle B(0)\rangle$, we find

$$\frac{\langle B(t)\rangle}{\langle B(0)\rangle} = \frac{\int_0^\beta d\lambda B(-i\hbar\lambda)B(t)\rangle_0}{\int_0^\beta d\lambda B(-i\hbar\lambda)B(0)\rangle_0} \rightarrow_{\hbar\to 0} \frac{\langle B(0)B(t)\rangle_0}{\langle B(0)^2\rangle_0}$$

Thus at long times in the classical limit, the fluctuations decay to 0, indicting a complete *regression* or suppression of the induced fluctuation:

$$\frac{\langle B(t)\rangle}{\langle B(0)\rangle} \to 0$$

12.7: Relation to Spectra

Suppose that $F_e(t)$ is a monochromatic field

$$F_e(t) = F_\omega e^{i\omega t} e^{\epsilon t}$$

where the parameter ϵ insures that field goes to 0 at $t = -\infty$. We will take $\epsilon \rightarrow 0^+$ at the end of the calculation. The expectation value of B then becomes

$$\begin{aligned} \langle B(t) \rangle &= \langle B \rangle_0 + \int_{-\infty}^{t} ds\ \Phi_{BB}(t-s) F_\omega e^{i\omega s} e^{\epsilon s} \\ &= \langle B \rangle_0 + F_\omega e^{(i\omega+\epsilon)t} \int_0^\infty d\tau \Phi_{BB}(\tau) e^{-i(\omega - i\epsilon)\tau} \end{aligned}$$

where the change of integration variables $\tau = t - s$ has been made.

Define a frequency-dependent susceptibility by

$$\chi_{BB}(\omega - i\epsilon) = \int_0^\infty d\tau \Phi_{BB}(\tau) e^{-i(\omega - i\epsilon)\tau}$$

then

$$\langle B(t) \rangle = \langle B \rangle_0 + F_\omega e^{i\omega t} e^{\epsilon t} \chi_{BB}(\omega - i\epsilon)$$

If we let $z = \omega - i\epsilon$, then we see immediately that

$$\chi_{BB}(z) = \int_0^\infty d\tau\ \Phi_{BB}(\tau) e^{-iz\tau}$$

i.e., the susceptibility is just the Laplace transform of the after effect function or the time correlation function.

Recall that

$$\begin{aligned} \Phi_{AB}(t) &= \frac{i}{\hbar} \langle [A(t), B(0)] \rangle_0 \\ &= \frac{i}{\hbar} \langle [e^{iH_0 t/\hbar} A e^{-iH_0 t \hbar}, B] \rangle_0 \end{aligned}$$

Under time reversal, we have

$$\begin{aligned} \Phi_{AB}(-t) &= \frac{i}{\hbar} \langle \left[e^{-iH_0 t/\hbar} A e^{iH_0 t/\hbar}, B \right] \rangle_0 \\ &= \frac{i}{\hbar} \langle \left(e^{-iH_0 t/\hbar} A e^{iH_0 t/\hbar} B - B e^{-iH_0 t/\hbar} A e^{iH_0 t/\hbar} \right) \rangle_0 \\ &= \frac{i}{\hbar} \langle \left(A e^{iH_0 t/\hbar} B e^{-iH_0 t/\hbar} - e^{iH_0 t/\hbar} B e^{-iH_0 t/\hbar} A \right) \rangle_0 \\ &= \frac{i}{\hbar} \langle (AB(t) - B(t)A) \rangle_0 \\ &= -\frac{i}{\hbar} \langle [B(t), A] \rangle \\ &= -\Phi_{BA}(t) \end{aligned}$$

Thus,

$$\Phi_{AB}(-t) = -\Phi_{BA}(t)$$

and if $A = B$, then

$$\Phi_{BB}(-t) = -\Phi_{BB}(t)$$

Therefore

$$\begin{aligned}\chi_{BB}(\omega) &= \lim_{\epsilon\to 0^+}\int_0^\infty dt\ e^{-i(\omega-i\epsilon t)}\,\Phi_{BB}(t)\\ &= \lim_{\epsilon\to 0^+}\int_0^\infty dt\ e^{-\epsilon t}\left[\Phi_{BB}(t)\cos\omega t - i\Phi_{BB}(t)\sin\omega t\right]\\ &= \mathrm{Re}(\chi_{BB}(\omega)) - i\mathrm{Im}(\chi_{BB}(\omega))\end{aligned}$$

From the properties of $\Phi_{BB}(t)$ it follows that

$$\begin{aligned}\mathrm{Re}(\chi_{BB}(\omega) &= \mathrm{Re}(\chi_{BB}(-\omega)\\ \mathrm{Im}(\chi_{BB}(\omega) &= -\mathrm{Im}(\chi_{BB}(-\omega)\end{aligned}$$

so that $\mathrm{Im}(\chi_{BB}(\omega))$ is positive for $\omega > 0$ and negative for $\omega < 0$. It is a straightforward matter, now, to show that the energy difference $Q(\omega)$ derived in the lecture from the Fermi golden rule is related to the susceptibility by

$$Q(\omega) = 2\omega|F_\omega|^2\mathrm{Im}(\chi_{BB}(\omega))$$

SECTION OVERVIEW

12.8: Time Correlation Functions and Transport Coefficients

12.8.1: Shear Viscosity

The shear viscosity of a system measures is resistance to flow. A simple flow field can be established in a system by placing it between two plates and then pulling the plates apart in opposite directions. Such a force is called a *shear force*, and the rate at which the plates are pulled apart is the shear rate. A set of microscopic equations of motion for generating shear flow is

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i} + \gamma y_i \hat{\mathbf{x}}$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i + \gamma p_{y_i} \hat{\mathbf{x}}$$

where γ is a parameter known as the shear rate. These equations have the conserved quantity

$$H' = \sum_{i=1}^{N} \left(\mathbf{p}_i + m_i \gamma y_i \hat{\mathbf{x}}\right)^2 + U(\mathbf{r}_1, .., \mathbf{r}_N)$$

The physical picture of this dynamical system corresponds to the presence of a velocity flow field $\mathbf{v}(y) = \gamma y \hat{\mathbf{x}}$ shown in the figure.

The flow field points in the $\hat{\mathbf{x}}$ direction and increases with increasing y-value. Thus, layers of a fluid, for example, will slow past each other, creating an anisotropy in the system. From the conserved quantity, one can see that the momentum of a particle is the value of $\mathbf{p}_i$ plus the contribution from the field evaluated at the position of the particle

$$\mathbf{p}_i \rightarrow \mathbf{p}_i + m_i \mathbf{v}(y_i)$$

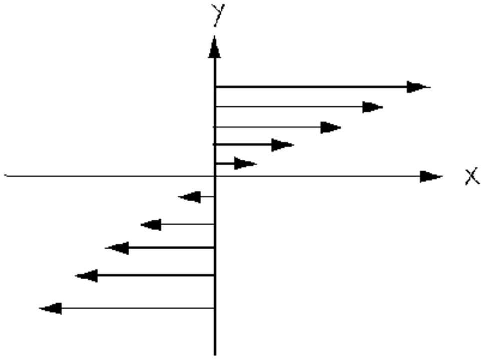


Figure 12.8.1.1

Such an applied external shearing force will create an asymmetry in the internal pressure. In order to describe this asymmetry, we need an analog of the internal pressure that contains a dependence on specific spatial directions. Such a quantity is known as the *pressure tensor* and can be defined analogously to the isotropic pressure P that we encountered earlier in the course. Recall that an estimator for the pressure was

$$p = \frac{1}{3V} \sum_{i=1}^{N} \left[\frac{\mathbf{p}_i^2}{m_i} + \mathbf{r}_i \cdot \mathbf{F}_i\right]$$

and $P = \langle p \rangle$ in equilibrium. Here, V is the volume of the system. By analogy, one can write down an estimator for the pressure tensor $p_{\alpha\beta}$:

$$p_{\alpha\beta} = \frac{1}{V} \sum_{i=1}^{N} \left[\frac{(\mathbf{p}_i \cdot \hat{e}_\alpha)(\mathbf{P}_i \cdot \hat{\mathbf{e}}_\beta)}{m_i} + (\mathbf{r}_i \cdot \hat{\mathbf{e}}_\alpha)(\mathbf{F}_i \cdot \hat{\mathbf{e}}_\beta)\right]$$

and

$$P_{\alpha\beta} = \langle p_{\alpha\beta} \rangle$$

where $\hat{\mathbf{e}}_\alpha$ is a unit vector in the α direction, $\alpha = x, y, z$. This (nine-component) pressure tensor gives information about spatial anisotropies in the system that give rise to off-diagonal pressure tensor components. The isotropic pressure can be recovered from

$$P = \frac{1}{3}\sum_{\alpha} P_{\alpha\alpha}$$

which is just 1/3 of the trace of the pressure tensor. While most systems have diagonal pressure tensors due to spatial isotropy, the application of a shear force according to the above scheme gives rise to a nonzero value for the xy component of the pressure tensor P_{xy}. In fact, P_{xy} is related to the velocity flow field by a relation of the form

$$P_{xy} = -\eta \frac{\partial v_x}{\partial y} = -\eta\gamma$$

where the coefficient η is known as the *shear viscosity* and is an example of a **transport coefficient**. Solving for η we find

$$\eta = -\frac{P_{xy}}{\gamma} = -\lim_{t\to\infty} \frac{\langle p_{xy}(t)\rangle}{\gamma}$$

where $\langle p_{xy}(t)\rangle$ is the nonequilibrium average of the pressure tensor estimator using the above dynamical equations of motion.

Let us apply the linear response formula to the calculation of the nonequilibrium average of the xy component of the pressure tensor. We make the following identifications:

$$F_e(t) = 1 \qquad \mathbf{C}_i(\mathrm{x}) = \gamma y_i \hat{\mathbf{x}} \qquad \mathbf{D}_i(\mathrm{x}) = -\gamma p_{y_i} \hat{\mathbf{x}}$$

Thus, the dissipative flux $j(\mathrm{x})$ becomes

$$\begin{aligned} j(\mathrm{x}) &= \sum_{i=1}^{N} \left[\mathbf{C}_i \cdot \mathbf{F}_i - \mathbf{D}_i \cdot \frac{\mathbf{p}_i}{m_i} \right] \\ &= \sum_{i=1}^{N} \left[\gamma y_i (\mathbf{F}_i \cdot \hat{\mathbf{x}}) + \gamma p_{y_i} \frac{\mathbf{p}_i \cdot \hat{\mathbf{x}}}{m_i} \right] \\ &= \gamma \sum_{i=1}^{N} \left[\frac{(\mathbf{p}_i \cdot \hat{\mathbf{y}})(\mathbf{p}_i \cdot \hat{\mathbf{x}})}{m_i} + (\mathbf{r}_i \cdot \hat{\mathbf{y}})(\mathbf{F}_i \cdot \hat{\mathbf{x}}) \right] \\ &= \gamma V p_{xy} \end{aligned}$$

According to the linear response formula,

$$\langle p_{xy}(t)\rangle = \langle p_{xy}\rangle_0 - \beta\gamma V \int_0^t ds \langle p_{xy}(0) p_{xy}(t-s)\rangle_0$$

so that the shear viscosity becomes

$$\eta = \lim_{t\to\infty} \left[-\frac{\langle p_{xy}\rangle_0}{\gamma} + \beta V \int_0^t ds \langle p_{xy}(0) p_{xy}(t)\rangle_0 \right]$$

Recall that $\langle\cdots\rangle_0$ means average of a canonical distribution with $\gamma = 0$. It is straightforward to show that $\langle p_{xy}\rangle_0 = 0$ for an equilibrium canonical distribution function. Finally, taking the limit that $t \to \infty$ in the above expression gives the result

$$\eta = \frac{V}{kT} \int_0^\infty dt \langle p_{xy}(0) p_{xy}(t)\rangle_0$$

which is a relation between a transport coefficient, in this case, the shear viscosity coefficient, and the integral of an equilibrium time correlation function. Relations of this type are known as *Green-Kubo* relations. Thus, we have expressed a new kind of thermodynamic quantity to an equilibrium time correlation function, which, in this case, is an autocorrelation function of the xy component of the pressure tensor.

12.8.2: The Diffusion Constant

The diffusive flow of particles can be studied by applying a constant force f to a system using the microscopic equations of motion

$$\begin{aligned} \dot{\mathbf{r}}_i &= \frac{\mathbf{p}_i}{m_i} \\ \dot{\mathbf{p}}_i &= \mathbf{F}_i(\mathbf{q}_1, .., \mathbf{q}_N) + f\hat{\mathbf{x}} \end{aligned}$$

which have the conserved energy

$$H' = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i} + U(\mathbf{q}_1, \ldots, \mathbf{q}_N) - f\sum_{i=1}^N x_i$$

Since the force is applied in the $\hat{\mathbf{x}}$ direction, there will be a net flow of particles in this direction, i.e., a current J_x. Since this current is a thermodynamic quantity, there is an estimator for it:

$$u_x = \sum_{i=1}^N \dot{x}_i$$

and $J_x = \langle u_x \rangle$. The constant force can be considered as arising from a potential field

$$\phi(x) = -xf$$

The potential gradient $\partial\phi/\partial x$ will give rise to a concentration gradient $\partial c/\partial x$ which is opposite to the potential gradient and related to it by

$$\frac{\partial c}{\partial x} = -\frac{1}{kT}\frac{\partial \phi}{\partial x}$$

However, Fick's law tells how to relate the particle current J_x to the concentration gradient

$$\begin{aligned} J_x &= D\frac{\partial c}{\partial x} \\ &= -\frac{D}{kT}\frac{\partial\phi}{\partial x} \\ &= \frac{D}{kT}f \end{aligned}$$

where D is the **diffusion constant**. Solving for D gives

$$\begin{aligned} D &= kT\frac{J_x}{f} \\ &= kT\lim_{t\to\infty}\frac{\langle u_x(t)\rangle}{f} \end{aligned}$$

Let us apply the linear response formula again to the above nonequilibrium average. Again, we make the identification:

$$F_e(t) = 1 \qquad \mathbf{D}_i = f\hat{\mathbf{x}} \qquad \mathbf{C}_i = 0$$

Thus,

$$\begin{aligned} \langle u_x(t)\rangle &= \langle u_x\rangle_0 + \beta\int_0^t ds f \langle \left(\sum_{i=1}^N \dot{x}_i(0)\right)\left(\sum_{i=1}^N \dot{x}_i(t-s)\right)\rangle_0 \\ &= \langle u_x\rangle_0 + \beta f\int_0^t ds \sum_{i,j}\langle \dot{x}_i(0)\dot{x}_j(t-s)\rangle_0 \end{aligned}$$

In equilibrium, it can be shown that there are no cross correlations between different particles. Consider the initial value of the correlation function. From the virial theorem, we have

$$\langle \dot{x}_i \dot{x}_j \rangle_0 = \delta_{ij} \langle \dot{x}_i^2 \rangle_0$$

which vanishes for $i \neq j$. In general,

$$\langle \dot{x}_i(0) \dot{x}_j(t) \rangle_0 = \delta_{ij} \langle \dot{x}_i(0) \dot{x}_i(t-s) \rangle_0$$

Thus,

$$\langle u_x(t) \rangle = \langle u_x \rangle_0 + \beta f \int_0^t ds \sum_{i=1}^N \dot{x}_i(0) \dot{x}_i(t-s) \rangle_0$$

In equilibrium, $\langle u_x \rangle_0 = 0$ being linear in the velocities (hence momenta). Thus, the diffusion constant is given by, when the limit $t \to \infty$ is taken,

$$D = \int_0^\infty \sum_{i=1}^N \langle \dot{x}_i(0) \dot{x}_i(t) \rangle_0$$

However, since no spatial direction is preferred, we could also choose to apply the external force in the y or z directions and average the result over the these three. This would give a diffusion constant

$$D = \frac{1}{3} \int_0^\infty dt \sum_{i=1}^N \langle \dot{\mathbf{r}}_i(0) \cdot \dot{\mathbf{r}}_i(t) \rangle_0$$

The quantity

$$\sum_{i=1}^N \langle \dot{\mathbf{r}}_i(0) \cdot \dot{\mathbf{r}}_i(t) \rangle_0$$

is known as the **velocity autocorrelation function**, a quantity we will encounter again in other contexts.

CHAPTER OVERVIEW

13: Time-dependent Processes - Quantum Case

SECTION OVERVIEW

13.1: Calculation of spectra from perturbation theory

Template:HideTOC

13.1.1: The Hamiltonian

Consider a quantum system with a Hamiltonian H_0. Suppose this system is subject to an external driving force $F_e(t)$ such that the full Hamiltonian takes the form

$$H = H_0 - BF_e(t) = H_0 + H'$$

where B is an operator through which this coupling occurs. This is the situation, for example, when the infrared spectrum is measured experimentally - the external force $F_e(t)$ is identified with an electric field $E(t)$ and B is identified with the electric dipole moment operator. If the field $F_e(t)$ is inhomogeneous, then H takes the more general form

$$\begin{aligned} H &= H_0 - \int d^3x \; B(\mathbf{x})F_e(\mathbf{x},t) \\ &= H_0 - \sum_{\mathbf{k}} B_{\mathbf{k}}F_{e,\mathbf{k}}(t) \end{aligned}$$

where the sum is taken over Fourier modes. Often, B is an operator such that, if $F_e(t) = 0$, then

$$\langle B \rangle = \frac{\mathrm{Tr}\left(Be^{-\beta H}\right)}{\mathrm{Tr}\left(e^{-\beta H}\right)}$$

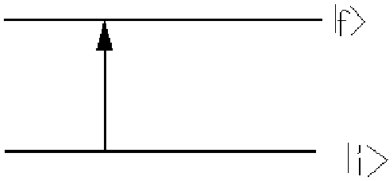
Suppose we take $F_e(t)$ to be a *monochromatic* field of the form

$$F_e(t) = F_\omega e^{i\omega t}$$

Generally, the external field can induce transitions between eigenstates of H_0 in the system. Consider such a transition between an initial state $|i\rangle$ and a final state $|f\rangle$, with energies E_i and E_f, respectively:

$$\begin{aligned} H_0|i\rangle &= E_i|i\rangle \\ H_0|f\rangle &= E_f|f\rangle \end{aligned}$$

(see figure below).



This transition can only occur if

$$E_f = E_i + \hbar\omega$$

13.1.2: The Transition Rate

In the next lecture, we will solve the quantum Liouville equation

$$i\hbar \frac{\partial \rho}{\partial t} = [H, \rho]$$

perturbatively and derive quantum linear response theory. However, the transition rate can actually be determined directly within perturbation theory using the Fermi Golden Rule approximation, which states that the probability of a transition's occurring per unit time, $R_{i \to f}$, is given by

$$R_{i\to f}(\omega) = \frac{2\pi}{\hbar} |\langle f|B|i\rangle|^2 \delta(E_f - E_i - \hbar\omega)$$

The δ-function expresses the fact that energy is conserved. This describes the rate of transitions between specific states $|i\rangle$ and $|f\rangle$. The transition rate between any initial and final states can be obtained by summing over both i and f and weighting the sum by the probability that the system is found in the initial state $|i\rangle$:

$$P(\omega) = \sum_{i,f} R_{i\to f}(\omega) w_i$$

where w_i is an eigenvalue of the density matrix, which we will take to be the canonical density matrix:

$$w_i = \frac{e^{-\beta E_i}}{\text{Tr}\,(e^{-\beta H})}$$

Using the expression for $R_{i\to f}(\omega)$, we find

$$P(\omega) = \frac{2\pi}{\hbar} |F_\omega|^2 \sum_{i,f} w_i |\langle i|B|f\rangle|^2 \delta(E_f - E_i - \hbar\omega)$$

Note that

$$P(-\omega) = \frac{2\pi}{\hbar} |F_\omega|^2 \sum_{i,f} w_i |\langle i|B|f\rangle|^2 \delta(E_f - E_i + \hbar\omega)$$

This quantity corresponds to a time-reversed analog of the absorption process. Thus, it describes an emission event $|i\rangle \to |f\rangle$ with $E_f = E_i - \hbar\omega$, i.e., emission of a photon with energy $\hbar\omega$. If can also be expressed as a process $|f\rangle \to |i\rangle$ by recognizing that

$$w_f = \frac{e^{-\beta E_f}}{\text{Tr}\,(e^{-\beta H})} = \frac{e^{\beta(E_i - \hbar\omega)}}{\text{Tr}\,(e^{-\beta H})}$$

or

$$w_f = e^{\beta\hbar\omega} w_i \quad \Rightarrow \quad w_i = e^{-\beta\hbar\omega} w_f$$

Therefore

$$P(-\omega) = \frac{2\pi}{\hbar} |F_\omega|^2 e^{-\beta\hbar\omega} \sum_{i,f} w_f |\langle i|B|f\rangle|^2 \delta(E_f - E_i + \hbar\omega)$$

If we now interchange the summation indices, we find

$$\begin{aligned} P(-\omega) &= \frac{2\pi}{\hbar} |F_\omega|^2 e^{-\beta\hbar\omega} \sum_{i,f} w_i |\langle i|B|f\rangle|^2 \delta(E_i - E_f + \hbar\omega) \\ &= \frac{2\pi}{\hbar} |F_\omega|^2 \sum_{i,f} w_i |\langle i|B|f\rangle|^2 e^{-\beta\hbar\omega} \delta(E_i - E_f - \hbar\omega) \end{aligned}$$

where the fact that $\delta(x) = \delta(-x)$ has been used. Comparing this expression for $P(-\omega)$ to that for $P(\omega)$, we find

$$P(-\omega) = e^{-\beta\hbar\omega} P(\omega)$$

which is the equation of **detailed balance**. We see from it that the probability of emission is less than that for absorption. The reason for this is that it is less likely to find the system in an excited state $|f\rangle$ initially, when it is in contact with a heat bath and hence thermally equilibrated. However, we must remember that the microscopic laws of motion (Newton's equations for classical systems and the Schrödinger equation for quantum systems) are reversible. This means that

$$R_{i\to f}(\omega) = R_{f\to i}(-\omega)$$

The conclusion is that, since $P(\omega) > P(-\omega)$, reversibility is lost when the system is placed in contact with a heat bath, i.e., the system is being driven irreversibly in time.

Define

$$\begin{aligned} C_>(\omega) &= \sum_{i,f} w_i |\langle i|B|f\rangle|^2 \delta(E_f - E_i - \hbar\omega) \\ C_<(\omega) &= \sum_{i,f} w_i |\langle i|B|f\rangle|^2 \delta(E_f - E_i + \hbar\omega) \end{aligned}$$

then

$$C_<(\omega) = e^{-\beta\hbar\omega} C_>(\omega)$$

Now using the fact that the δ-function can be written as

$$\delta(E) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt e^{-iEt}$$

$C_>(\omega)$ becomes

$$\begin{aligned} C_>(\omega) &= \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} dt \sum_{i,f} w_i |\langle i|B|f\rangle|^2 e^{-i(E_f - E_i - \hbar\omega)t/\hbar} \\ &= \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} dt\ e^{i\omega t} \sum_{i,f} w_i |\langle i|B|f\rangle|^2 e^{-i(E_f - E_i)t/\hbar} \\ &= \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} dt\ e^{i\omega t} \sum_{i,f} w_i \langle i|B|f\rangle\langle f|B|i\rangle e^{-iE_f t/\hbar} e^{iE_i t/\hbar} \\ &= \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} dt\ e^{i\omega t} \sum_{i,f} w_i \langle i|e^{iH_0 t/\hbar} B e^{-iH_0 t/\hbar}|f\rangle\langle f|B|i\rangle \end{aligned}$$

Recall that the evolution of an operator in the Heisenberg picture is given by

$$B(t) = e^{iH_0 t/\hbar} B e^{-iH_0 t/\hbar}$$

if the evolution is determined solely by H_0. Thus, the expression for $C > (\omega)$ becomes

$$\begin{aligned} C_>(\omega) &= \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} dt\ e^{i\omega t} \sum_{i,f} w_i \langle i|B(t)|f\rangle\langle f|B|i\rangle \\ &= \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} dt\ e^{i\omega t} \sum_{i} w_i \langle i|B(t)B(0)|i\rangle \\ &= \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} e^{i\omega t} \mathrm{Tr}\left[\rho B(t)B(0)\right] \\ &= \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} e^{i\omega t} \langle B(t)B(0)\rangle \end{aligned}$$

which involves the quantum autocorrelation function $\langle B(t)B(0)\rangle$.

In general, a quantum time correlation function in the canonical ensemble is defined by

$$C_{AB}(t) = \frac{\text{Tr}\left[A(t)B(0)e^{-\beta H}\right]}{\text{Tr}\left[e^{-\beta H}\right]}$$

In a similar manner, we can show that

$$C_<(\omega) = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} dt\ e^{i\omega t}\langle B(0)B(t)\rangle \neq C_>(\omega)$$

since

$$[B(0), B(t)] \neq 0$$

in general. Also, the product $B(0)B(t)$ is not Hermitian. However, a hermitian combination occurs if we consider the energy difference between absorption and emission. The energy absorbed per unit of time by the system is $P(\omega)\hbar\omega$, while the emitted into the bath by the system per unit of time is $P(-\omega)\hbar\omega$. The energy difference $Q(\omega)$ is just

$$\begin{aligned} Q(\omega) &= [P(\omega) - P(-\omega)]\hbar\omega \\ &= P(\omega)[1 - e^{-\beta\hbar\omega}]\hbar\omega \\ &= 2\pi\omega|F_\omega|^2 C_>(\omega)[1 - e^{-\beta\hbar\omega}] \end{aligned}$$

But since

$$C_<(\omega) = e^{-\beta\hbar\omega}C_>(\omega)$$

it follows that

$$C_>(\omega) + C_<(\omega) = \left(1 + e^{-\beta\hbar\omega}\right)C_>(\omega)$$

or

$$C_>(\omega) = \frac{C_>(\omega) + C_<(\omega)}{1 + e^{-\beta\hbar\omega}}$$

Note, however, that

$$\begin{aligned} C_>(\omega) + C_<(\omega) &= \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} dt e^{i\omega t}\langle B(t)B(0) + B(0)B(t)\rangle \\ &= \frac{1}{\pi\hbar} dt\ e^{i\omega t}\langle \frac{1}{2}[B(0), B(t)]_+\rangle \end{aligned}$$

where $[\ldots,\ldots]_+$ is known as the **anticommutator**:

$$[A, B]_+ = AB + BA. \tag{13.1.2.1}$$

The anticommutator between two operators is, itself, hermitian. Therefore, the energy difference is

$$\begin{aligned} Q(\omega) &= \frac{2\omega}{\hbar}|F_\omega|^2 \frac{1 - e^{-\beta\hbar\omega}}{1 + e^{-\beta\hbar\omega}}\int_{-\infty}^{\infty} dt\ e^{i\omega t}\langle [B(0), B(t)]_+\rangle \\ &= \frac{2\omega}{\hbar}|F_\omega|^2 \tanh(\beta\hbar\omega/2)\int_{-\infty}^{\infty} dt\ e^{i\omega t}\langle [B(0), B(t)]_+\rangle \end{aligned}$$

The quantity $\langle [B(0), B(t)]_+\rangle$ is the symmetrized quantum autocorrelation function. The classical limit is now manifest ($\tanh(\beta\hbar\omega/2) \rightarrow \beta\hbar\omega/2$):

$$Q(\omega) \rightarrow |F_\omega|^2 \int_{-\infty}^{\infty} dt\ e^{i\omega t}\langle B(0)B(t)\rangle$$

The classically, the energy spectrum $Q(\omega)$ is directly related to the Fourier transform of a time correlation function.

13.1.3: Examples

Define

$$G(\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{i\omega t}\langle\frac{1}{2}[B(0),B(t)]_+\rangle$$

which is just the frequency spectrum corresponding to the autocorrelation function of B. For different choices of B, $G(\omega)$ corresponds to different experimental measurements. Consider the example of a molecule with a transition dipole moment vector μ. If an electric field $\mathbf{E}(t)$ is applied, then the Hamiltonian H' becomes

$$H'=-\mu\cdot\mathbf{E}(t)$$

If we take $\mathbf{E}(t)=E(t)\hat{\mathbf{z}}$, then

$$H'=-\mu_z E(t)$$

Identifying $B=\mu_z$, the spectrum becomes

$$G(\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{i\omega t}\langle\frac{1}{2}[\mu_z(0),\mu_z(t)]_+\rangle$$

or for a general electric field, the result becomes

$$G(\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{i\omega t}\langle\frac{1}{2}(\mu(0)\cdot\mu(t)+\mu(t)\cdot\mu(0))\rangle$$

These spectra are the *infrared* spectra.

As another example, consider a block of material placed in a magnetic field $\mathcal{H}(t)$ in the z direction. The spin S_z of each particle will couple to the magnetic field giving a Hamiltonian H'

$$H'=-\sum_{i=1}^{N} S_{i,z}\mathcal{H}(t)$$

The net magnetization created by the field m_z is given by

$$m_z=\frac{1}{N}\sum_{i=1}^{N} S_{i,z}$$

so that

$$H'=-Nm_z\mathcal{H}(t)$$

Identify $B=m_z$ (the extra factor of N just expresses the fact that H' is extensive). Then the spectrum is

$$G(\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{i\omega t}\langle\frac{1}{2}[m_z(0),m_z(t)]_+\rangle$$

which is just the NMR spectrum. In general for each correlation function there is a corresponding experiment that measures its frequency spectrum.

To see what some specific lineshapes look like, consider as an ansatz a pure exponential decay for the correlation function $C_{BB}(t)$:

$$C_{BB}(t)=\langle B^2\rangle e^{-\Gamma|t|}$$

The spectrum corresponding to this time correlation function is

$$G(\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty} dte^{i\omega t}C_{BB}(t)$$

and doing the integral gives

$$G(\omega) = \frac{\langle B^2 \rangle}{\pi} \frac{\Gamma}{\omega^2 + \Gamma^2}$$

which is shown in the figure below:

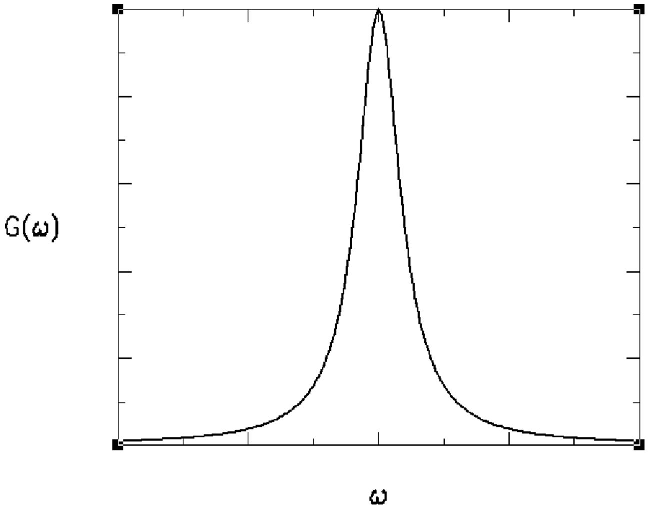


Figure 13.1.3.1: Copy and Paste Caption here. (Copyright; author via source)

We see that the lineshape is a Lorentzian with a width Γ. As a further example, suppose $C_{BB}(t)$ is a decaying oscillatory function:

$$C_{BB}(t) = \langle B^2 \rangle e^{-\Gamma|t|} \cos \omega_0 t$$

which describes well the behavior of a harmonic diatomic coupled to a bath. The spectrum can be shown to be

$$G(\omega) = \frac{\langle B^2 \rangle \Gamma}{\pi} \left[\frac{\Gamma^2 + \omega^2 + \omega_0^2}{(\Gamma^2 + (\omega - \omega_0)^2)(\Gamma^2 + (\omega + \omega_0)^2)} \right]$$

which contains two peaks at $\omega = \pm\sqrt{\omega_0^2 - \Gamma^2}$ as shown in the figure below:

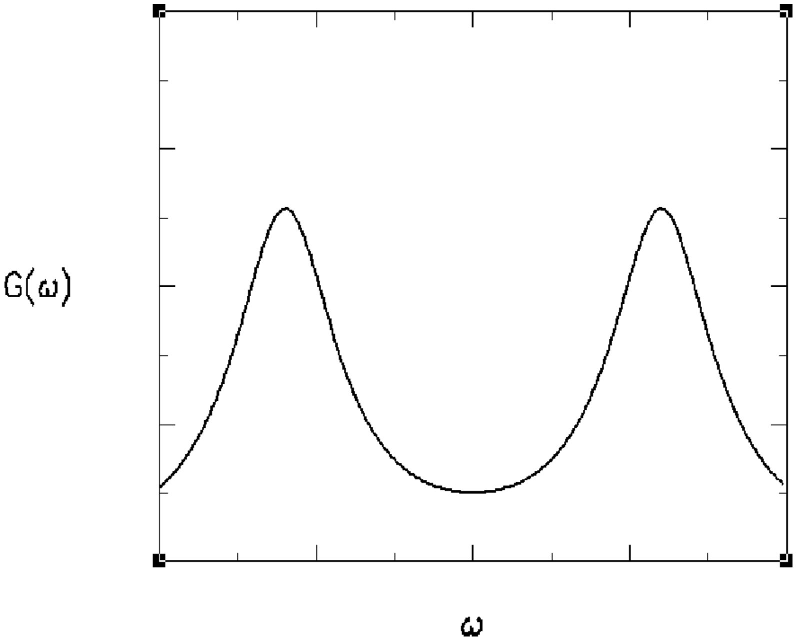


Figure 13.1.3.2: Copy and Paste Caption here. (Copyright; author via source)

13.2: Iterative solution for the interaction-picture state vector

The solution to Equation ??? can be expressed in terms of a unitary propagator $U_I(t;t_0)$, the interaction-picture propagator, which evolves the initial state $|\Phi(t_0)\rangle$ according to

$$|\Phi(t)\rangle = U_I(t;t_0)|\Phi(t_0)\rangle = U_I(t;t_0)|\Psi(t_0)\rangle \tag{13.2.1}$$

Substitution of Equation 13.2.1 into Equation ??? yields an evolution equation for the propagator $U_I(t;t_0)$:

$$H_I(t)U_I(t;t_0) = i\hbar\frac{\partial}{\partial t}U_I(t;t_0) \tag{13.2.2}$$

The initial condition on Equation 13.2.2 is $U_I(t_0;t_0) = I$. In developing a solution to Equation 13.2.2, we assume that $H_I(t)$ is a small perturbation, so that the solution can take the form of a sum of powers of $H_I(t)$.

A solution of this form can be generated by recognizing that Equation 13.2.2 can be solved formally in terms of an integral equation:

$$U_I(t;t_0) = U_I(t_0;t_0) - \frac{i}{\hbar}\int_{t_0}^{t} dt'\ H_I(t')U_I(t';t_0) = I - \frac{i}{\hbar}\int_{t_0}^{t} dt'\ H_I(t')U_I(t';t_0) \tag{13.2.3}$$

It is straightforward to verify this form solution for $U_I(t;t_0)$. Computing the time derivative of both sides gives

$$i\hbar\frac{\partial}{\partial t}U_I(t;t_0) = -i\hbar\frac{i}{\hbar}\frac{\partial}{\partial t}\int_{t_0}^{t} dt'\ H_I(t')U_I(t';t_0) = H_I(t)U_I(t;t_0) \tag{13.2.4}$$

Thus, Equation 13.2.3 is a valid expression of the solution. The implicit nature of the integral equation means that an iterative procedure based on the assumption that $H_I(t)$ is a small perturbation can be easily developed. We start with a zeroth-order solution by setting $H_I(t) = 0$ in Equation 13.2.3, which gives the trivial result

$$U_I^{(0)}(t;t_0) = I \tag{13.2.5}$$

This solution is now fed back into the right side of Equation 13.2.3 to develop a first-order solution:

$$U^{(1)}(t;t_0) = I - \frac{i}{\hbar}\int_{t_0}^{t} dt'\ H_I(t')U_I^{(0)}(t';t_0) \tag{13.2.6}$$

$$= I - \frac{i}{\hbar}\int_{t_0}^{t} dt'\ H_I(t') \tag{13.2.7}$$

The first order solution is fed back into the right side of Equation 13.2.3 to develop a second-order solution:

$$U^{(2)}(t;t_0) = I - \frac{i}{\hbar}\int_{t_0}^{t} dt'\ H_I(t')U_I^{(1)}(t';t_0) = I - \frac{i}{\hbar}\int_{t_0}^{t} dt'\ H_I(t') + \left(\frac{i}{\hbar}\right)^2\int_{t_0}^{t} dt'\int_{t_0}^{t'} dt''\ H_I(t')H_I(t'') \tag{13.2.8}$$

and so forth, such that the k th-order solution is always generated from the $(k-1)$ st-order solution according to the recursion formula:

$$U^{(k)}(t;t_0) = I - \frac{i}{\hbar}\int_{t_0}^{t} dt'\ H_I(t')U_I^{(k-1)}(t';t_0) \tag{13.2.9}$$

Thus, the third-order solution is given by

$$U^{(2)}(t;t_0) = I - \frac{i}{\hbar}\int_{t_0}^{t} dt'\ H_I(t') + \left(\frac{i}{\hbar}\right)^2\int_{t_0}^{t} dt'\int_{t_0}^{t'} dt''\ H_I(t')H_I(t'') - \left(\frac{i}{\hbar}\right)^3\int_{t_0}^{t} dt'\int_{t_0}^{t'} dt''\int_{t_0}^{t''} dt'''\ H_I(t')H_I(t'')H_I(t''') \tag{13.2.10}$$

The exact solution is then just a sum of the solutions obtained at each order:

$$U_I(t;t_0) = \sum_{k=0}^{\infty}(-1)^k\left(\frac{i}{\hbar}\right)^k\int_{t_0}^{t} dt'\int_{t_0}^{t'} dt''\cdots\int_{t_0}^{t^{(k-1)}} dt^{(k)}\ H_I(t')H_I(t'')\cdots H_I(t^{(k)}) \tag{13.2.11}$$

Having seen how to generate a solution for the propagator in the interaction picture to arbitrarily high orders in the perturbation, the time evolution of the state vector $|\Phi(t)\rangle$ in the interaction picture can be determined from

$$|\Phi(t)\rangle = U_I(t;t_0)|\Phi(t_0)\rangle \tag{13.2.12}$$

and from this expression, the time evolution of the original state vector $|\Phi(t)\rangle$ in the Schrödinger picture can be determined

$$|\Phi(t)\rangle = e^{-iH_0(t-t_0)/\hbar}|\Phi(t)\rangle = e^{-iH_0(t-t_0)/\hbar}U_I(t;t_0)|\Phi(t_0)\rangle = e^{-iH_0(t-t_0)/\hbar}U_I(t;t_0)|\Psi(t_0)\rangle \equiv U(t;t_0)|\Psi(t_0)\rangle \tag{13.2.13}$$

where we have used the fact that $|\Phi(t_0)\rangle = |\Psi(t_0)\rangle$ and, in the last line, the full propagator in the Schrödinger picture is identified as

$$U(t;t_0) = e^{-iH_0(t-t_0)/\hbar} U_I(t;t_0) \tag{13.2.14}$$

From Equation 13.2.14, the structure of the full propagator for the time-dependent system reveals itself. Let us use Equation 13.2.14 to generate the first few lowest order terms in the propagator. Substituting Equation 13.2.5 into Equation 13.2.14 yields the lowest order contribution to $U(t;t_0)$:

$$U^{(0)}(t;t_0) = e^{-iH_0(t-t_0)/\hbar} = U_0(t;t_0) \tag{13.2.15}$$

Thus, at zeroth order, Equation 13.2.15 implies that the system is to be propagated using the unperturbed propagator $U_0(t;t_0)$ as if the perturbation did not exist. At first order, we obtain

$$\begin{aligned} U^{(1)}(t;t_0) &= e^{-iH_0(t-t_0)/\hbar} - \frac{i}{\hbar} e^{-iH_0(t-t_0)/\hbar} \int_{t_0}^{t} dt'\ H_I(t') && (13.2.16) \\ &= e^{-iH_0(t-t_0)/\hbar} - \frac{i}{\hbar} e^{-iH_0(t-t_0)/\hbar} \int_{t_0}^{t} dt' e^{-iH_0(t'-t_0)/\hbar} \mathrm{H}_1(t') e^{-iH_0(t'-t_0)/\hbar} && (13.2.17) \\ &= e^{-iH_0(t-t_0)/\hbar} - \frac{i}{\hbar} \int_{t_0}^{t} dt'\ e^{-iH_0(t-t')/\hbar} \mathrm{H}_1(t') e^{-iH_0(t'-t_0)/\hbar} && (13.2.18) \\ &= U_0(t;t_0) - \frac{i}{\hbar} \int_{t_0}^{t} dt'\ U_0(t;t') \mathrm{H}_1(t') U_0(t';t_0) && (13.2.19) \end{aligned}$$

where, in the second line, the definition of $H_I(t)$ in terms of the original perturbation Hamiltonian $H_1(t)$ has been used. What Equation 13.2.19 says is that at first order, the propagator is composed of two terms. The first term is simply the unperturbed propagation from t_0 to t. In the second term, the system undergoes unperturbed propagation from t_0 to t' and at t', the perturbation $H_1(t')$ is allowed to act. From t' to t, the system undergoes unperturbed propagation. Finally, we need to integrate over all possible intermediate times t'.

In a similar manner, it can be shown that up to second order, the full propagator is given by

$$\begin{gathered} U^{(2)}(t;t_0) = U_0(t;t_0) - \frac{i}{\hbar} \int_{t_0}^{t} d'\ U_0(t;t') \mathrm{H}_1(t') U_0(t';t_0) + \left(\frac{i}{\hbar}\right)^2 \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' \\ U_0(t;t') \mathrm{H}_1(t') U_0(t';t'') \mathrm{H}_1(t'') U_0(t'';t_0) \end{gathered} \tag{13.2.20}$$

Thus, at second order, the new term involves unperturbed propagation from t_0 to t'', action of $H_1(t'')$ at t'', unperturbed propagation from t'' to t', action of $H_1(t')$ at t' and, finally, unperturbed propagation from t' to t. Again, the intermediate times t' and t'' must be integrated over. The picture on the left side of the equation indicates that the perturbation causes the system to undergo some undetermined dynamical process between t_0 and t. The terms on the right show how that process is broken down in terms of the action of the perturbation H_1 at specific intermediate times. At the k th order, the perturbation Hamiltonian H_1 acts on the system at k specific instances in time. Because of the limits of integration, these time instances are ordered chronologically.

The specific ordering of the instances in time when H_1 acts on the unperturbed system raises an important point. At each order the expansion for $U_I(t;t_0)$, the order in which the operators $H_I(t')$, $H_I(t'')$, etc. are multiplied is important. The reason for this is that the operator $H_I(t)$ does not commute with itself at different instances in time

$$[H_I(t), H_I(t')] \neq 0 \tag{13.2.21}$$

Thus, in order to remove any possible ambiguity when specifying the order in which operators are to be applied in a time series, we introduce the *time-ordering operator*, T. The purpose of T is to take a product string of time-dependent operators $A(t_1)B(t_2)C(t_3)\cdots D(t_n)$ which act at different instances in time $t_1, t_2, \cdots, t_n$ and order the operators in the product such that they act chronologically in time from the earliest time to the latest time. For example, the action of T on two operators $A(t_1)$ and $B(t_2)$ is

$$T\left(A(t_1)B(t_2)\right) = \begin{cases} A(t_1)B(t_2) & t_2 < t_1 \\ B(t_2)A(t_1) & t_1 < t_2 \end{cases} \tag{13.2.22}$$

Let us now apply the time-ordering operator to the second-order term. First write the double integral as a sum of two terms generated simply interchanging the names of the dummy variables t' and t'':

$$\int_{t_0}^{t} dt' \int_{t_0}^{t'} dt''\ H_I(t')H_I(t'') = \frac{1}{2}\left[\int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' H_I(t')H_I(t'') + \int_{t_0}^{t} dt'' \int_{t_0}^{t''} dt'\ H_I(t'')H_I(t')\right] \tag{13.2.23}$$

The same region can be covered by choosing $t' \in [t_0, t]$ and $t'' \in [t_0, t]$. With this choice, Equation 13.2.23 becomes

$$\int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' H_I(t')H_I(t'') = \frac{1}{2}\left[\int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' H_I(t')H_I(t'') + \int_{t_0}^{t} dt' \int_{t'}^{t} dt''\ H_I(t'')H_I(t')\right] \tag{13.2.24}$$

In the first term on the right side of Equation 13.2.24, $t'' < t'$ and $H_I(t'')$ acts first, followed by $H_I(t')$. In the second term, $t' < t''$ and $H_I(t')$ acts first followed by $H_I(t'')$. The two terms can, thus, be combined with both t' and t'' lying in the interval $[t_0, t]$ if the time-ordering operator is applied:

$$\int_{t_0}^{t} dt' \int_{t_0}^{t'} dt''\ H_I(t')H_I(t'') = \frac{1}{2}\int_{t_0}^{t} dt' \int_{t_0}^{t} dt''\ T\left(H_I(t')H_I(t'')\right) \tag{13.2.25}$$

The same analysis can be applied to each order in Equation 13.2.11, recognizing that the number of possible time orderings of a product of k operators is $k!$. Thus, Equation 13.2.11can be rewritten in terms of the time-ordering operator as

$$U_I(t;t_0) = \sum_{k=0}^{\infty}(-1)^k\left(\frac{i}{\hbar}\right)^k \frac{1}{k!}\int_{t_0}^{t} dt_1 \int_{t_0}^{t} dt_2 \cdots \int_{t_0}^{t} dt_k T\left(H_I(t_1)H_I(t_2)\cdots H_I(t_k)\right) \tag{13.2.26}$$

The sum in Equation 13.2.26resembles the power-series expansion of an exponential, and, indeed, we can write the sum symbolically as

$$U_I(t;t_0) = T\left[\exp\left(-\frac{i}{\hbar}\int_{t_0}^{t} dt'\ H_I(t')\right)\right] \tag{13.2.27}$$

which is known as a *time-ordered exponential*. Equation 13.2.27 is really a symbolic representation of Equation 13.2.26, in which it is understood that the time-ordering operator acts to order the operators in each term of the expansion of the exponential.

Given the formalism of time-dependent perturbation theory, we now seek to answer the following question: If the system is initially in an eigenstate of H_0 with energy E_i, what is the probability as a function of time t that the system will undergo a transition to a new eigenstate of H_0 with energy E_f? From the statement of the question, it is clear that the initial state vector $|\Psi(t_0)\rangle$ is simply the eigenstate of H_0 with energy E_i

$$|\Psi(t_0)\rangle = |E_i\rangle \tag{13.2.28}$$

The amplitude as a function of time that the system will undergo a transition to the eigenstate $|E_f\rangle$ is obtained by propagating this initial state out to time t with the propagator $U(t;t_0)$ and then taking the overlap of the resultant state with the eigenstate $|E_f\rangle$:

$$A_{fi}(t) = \langle E_f|U(t;t_0)|E_i\rangle \tag{13.2.29}$$

and the probability is just the square magnitude of this complex amplitude:

$$P_{fi}(t) = |\langle E_f|U(t;t_0)|E_i\rangle|^2 \tag{13.2.30}$$

Consider, first, the amplitude at zeroth order in perturbation theory. At this order, $U(t;t_0) = U_0(t;t_0)$, and the amplitude is simply

$$A_{fi}^{(0)}(t) = \langle E_f|e^{-iH_0(t-t_0)/\hbar}|E_i\rangle \tag{13.2.31}$$

$$= e^{-iE_i(t-t_0)/\hbar}\langle E_f|E_i\rangle \tag{13.2.32}$$

which clearly vanishes if $E_i \neq E_f$. Thus, at zeroth order, the only possibility is the trivial one in which no transition occurs.

The lowest nontrivial order is first order, where the transition amplitude is given by

$$A_{fi}^{(1)}(t) = \langle E_f|U^{(1)}(t;t_0)|E_i\rangle = -\frac{i}{\hbar}\int_{t_0}^{t} dt'\ \langle E_f|U_0(t;t')\mathrm{H}_1(t')U_0(t';t_0)|E_i\rangle \tag{13.2.33}$$

$$= -\frac{i}{\hbar}\int_{t_0}^{t} dt\ \langle E_f|e^{-iH_0(t-t')/\hbar}\mathrm{H}_1(t')e^{-iH_0(t'-t_0)/\hbar}|E_i\rangle \tag{13.2.34}$$

$$= -\frac{i}{\hbar}\int_{t_0}^{t} dt'\ e^{-iE_f(t-t')/\hbar}e^{-iE_i(t'-t_0)/\hbar}\langle E_f|\mathrm{H}_1(t')|E_i\rangle \tag{13.2.35}$$

$$= -\frac{i}{\hbar}e^{-iE_ft/\hbar}e^{iE_it_0/\hbar}\int_{t_0}^{t} dt'\ e^{i(E_f-E_i)t'/\hbar}\langle E_f|\mathrm{H}_1(t')|E_i\rangle \tag{13.2.36}$$

Define a transition frequency ω_{fi} by

$$\omega_{fi} = \frac{E_f - E_i}{\hbar} \tag{13.2.37}$$

Then, taking the absolute square of the last line of Equation 13.2.36, we obtain the probability at first-order

$$P_{fi}^{(1)}(t) = \frac{1}{\hbar^2}\left|\int_{t_0}^{t} dt' e^{i\omega_{fi}t'} \langle E_f|\mathrm{H}_1(t')|E_i\rangle\right|^2 \tag{13.2.38}$$

At first order, the probability depends on the matrix element of the perturbation between the initial and final eigenstates. Thus far, the formalism we have derived is valid for any perturbation Hamiltonian $H_1(t)$. If we consider the use of an external perturbation to probe the eigenvalue spectrum of H_0, then the specific type of probe determines the form of $H_1(t)$, as we saw in the first section and will explore in the next subsection.

13.3: The Interaction Picture

Consider a quantum system described by a time-dependent Hamiltonian of the form

$$H(t) = H_0 + H_1(t)$$

In the language of perturbation theory, H_0 is known as the unperturbed Hamiltonian and describes a system of interest such as a molecule or a condensed-phase sample such as a pure liquid or solid or a solution. $H_1(t)$ is known as the perturbation, and it often describes an external system, such as a laser field, that will be used to probe the energy levels and other properties of H_0.

We now seek a solution to the time-dependent Schrödinger equation

$$\mathrm{H}(t)|\Psi(t)\rangle = (\mathrm{H}_0 + \mathrm{H}_1(t))\,|\Psi(t)\rangle = i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle \tag{13.3.1}$$

subject to an initial state vector $|\Psi(t_0)\rangle$. In order to solve the equation, we introduce a new state vector $|\Phi(t)\rangle$ related to $|\Psi(t)\rangle$ by

$$|\Psi(t)\rangle = e^{-i\mathrm{H}_0(t-t_0)}\,|\Phi(t)\rangle \tag{13.3.2}$$

The new state vector $|\Phi(t)\rangle$ is an equally valid representation of the state of the system. In Chapter 10, we introduced the concept of *pictures* in quantum mechanics and discussed the difference between the Schrödinger and Heisenberg pictures. Equation 13.3.2 represents yet another picture of quantum mechanics, namely the **interaction picture**. Like the Schrödinger and Heisenberg pictures, the interaction picture is a perfectly valid way of representing a quantum mechanical system. The interaction picture can be considered as "intermediate" between the Schrödinger picture, where the state *evolves in time* and the operators are *static*, and the Heisenberg picture, where the state vector is *static* and the operators *evolve*.

However, as we will see shortly, in the interaction picture, both the state vector and the operators evolve in time, however, the time-evolution is determined by the perturbation $H_1(t)$. Equation 13.3.2 specifies how to transform between the Schrödinger and interaction picture state vectors. The transformation of operators proceeds in an analogous fashion. If A denotes an operator in the Schrödinger picture, its representation in the interaction picture is given by

$$\mathrm{A}_I(t) = e^{i\mathrm{H}_0(t-t_0)/\hbar}\,\mathrm{A}\,e^{-i\mathrm{H}_0(t-t_0)/\hbar} \tag{13.3.3}$$

which is equivalent to an equation of motion of the form

$$\frac{d\mathrm{A}_I(t)}{dt} = \frac{1}{i\hbar}[\mathrm{A}_I(t), \mathrm{H}_0] \tag{13.3.4}$$

Substitution of Equation 13.3.2 into the time-dependent Schrödinger equation yields

$$(\mathrm{H}_0 + \mathrm{H}_1(t))\,e^{-i\mathrm{H}_0(t-t_0)/\hbar}|\Phi(t)\rangle = \mathrm{H}_0 e^{-i\mathrm{H}_0(t-t_0)/\hbar}|\Phi(t)\rangle + e^{-i\mathrm{H}_0(t-t_0)/\hbar}i\hbar\frac{\partial}{\partial t}|\Phi(t)\rangle \tag{13.3.5}$$

$$\mathrm{H}_1(t)e^{-iH_0(t-t_0)/\hbar}|\Phi(t)\rangle = e^{-iH_0(t-t_0)/\hbar}i\hbar\frac{\partial}{\partial t}|\Phi(t)\rangle \tag{13.3.6}$$

$$e^{iH_0(t-t_0)/\hbar}\mathrm{H}_1(t)e^{-iH_0(t-t_0)/\hbar}|\Phi(t)\rangle = i\hbar\frac{\partial}{\partial t}|\Phi(t)\rangle \tag{13.3.7}$$

According to Equation 13.3.3, the $\exp[i\mathrm{H}_0(t-t_0)/\hbar]\mathrm{H}_1(t)\exp[-i\mathrm{H}_0(t-t_0)/\hbar]$ is the interaction-picture representation of the perturbation Hamiltonian, and we will denote this operator as $H_I(t)$. Thus, the time-evolution of the state vector in the interaction picture is given a Schrödinger equation of the form

$$H_I(t)|\Phi(t)\rangle = i\hbar\frac{\partial}{\partial t}|\Phi(t)\rangle \tag{13.3.8}$$

The initial condition to Equation 13.3.8, $|\Phi(t_0)\rangle$ is, according to Equation 13.3.2, also $|\Phi(t_0)\rangle$. In the next section, we will develop an iterative solution to Equation 13.3.8, which will reveal a rich structure of the propagator for time-dependent systems.

13.4: Fermi's Golden Rule

In the first section, we saw how to formulate the Hamiltonian of a material system coupled to an external electromagnetic field. Moreover, we obtained solutions for the electromagnetic field in the absence of sources or physical boundaries, namely, solutions of the free-field wave equations. In this chapter, we will focus primarily on weak fields. We will also focus on a class of experiments in which the wavelength of electromagnetic radiation is taken to be long compared to the size of the sample under investigation. In this case, the spatial dependence of the electromagnetic field can also be neglected, since

$$\cos(\mathbf{k}\cdot\mathbf{r}-\omega t+\varphi_0)=\mathrm{Re}\{\exp(i\mathbf{k}\cdot\mathbf{r}-i\omega t+\varphi_0)\}$$

and

$$\exp(i\mathbf{k}\cdot\mathbf{r})\approx 1$$

in the long-wavelength limit. In this case, it is sufficient to consider $H_1(t)$ to be of the general form

$$\mathrm{H}_1(t)=-\mathcal{V}F(\omega)e^{-i\omega t} \tag{13.4.1}$$

where $\mathcal{V}$ is a Hermitian operator.

> Although we could use sin and cos to express the perturbation, the form in Equation 13.4.1 is a particularly convenient one, and since we will be seeking probabilities of transitions, the results we obtain will be real in the end.

Again, the question we seek to answer is given this form for the perturbation, what is the probability that the material system will be excited from an initial eigenstate $|E_i\rangle$ with energy E_i to a final state $|E_f\rangle$ with energy E_f? However, since the perturbation is periodic in time, what we really seek to know is if the perturbation is applied over a long time interval, what is the probability per unit time or rate at which transitions will occur. Thus, in order to make the calculation somewhat easier, let us consider a time interval T and choose $t_0=-T/2$ and $t=T/2$. At first order, the transition rate $R^{(1)}_{fi}(T)$ is just the total probability $P^{(1)}_{fi}(T)$ divided by the interval length T:

$$\begin{align} R^{(1)}_{fi}(T) &= \frac{P^{(1)}_{fi}(T)}{T} \tag{13.4.2} \\ &= \frac{1}{T\hbar^2}|F(\omega)|^2\left|\int_{-T/2}^{T/2}e^{i(\omega_{fi}-\omega)t}dt\right|^2|\langle E_f|\mathcal{V}|E_i\rangle|^2 \tag{13.4.3} \end{align}$$

For finite T, the integral can be carried out explicitly yielding

$$\int_{-T/2}^{T/2}e^{i(\omega_{fi}-\omega)t}dt=\frac{\sin(\omega_{fi}-\omega)T/2}{(\omega_{fi}-\omega)/2} \tag{13.4.4}$$

Thus, the transition rate can be expressed as

$$R^{(1)}_{fi}(T)=\frac{1}{\hbar^2}T|F(\omega)|^2|\langle E_f|\mathcal{V}|E_i\rangle|^2\frac{\sin^2(\omega_{fi}-\omega)T/2}{[(\omega_{fi}-\omega)T/2]^2} \tag{13.4.5}$$

In the limit of T very large, this expression becomes highly peaked only if $\omega_{fi}=\omega$. Otherwise, as $T\rightarrow\infty$, the expression vanishes. The condition $\omega_{fi}=\omega$ is equivalent to the condition $E_f=E_i+\hbar\omega$, which is a statement of energy conservation. Since $\hbar\omega$ is the energy quantum of the electromagnetic field, the transition can only occur if the energy of the field is exactly "tuned" for the the transition, and this "tuning" depends on the frequency of the field. In this way, the frequency of the field can be used as a probe of the allowed transitions, which then serves to probe the eigenvalue structure of H_0.

Now, let us consider the $T\rightarrow\infty$ more carefully. We shall denote the rate in this limit simply as R_{fi}. In this limit, the integral becomes

$$\lim_{T\to\infty}\int_{-T/2}^{T/2} e^{-i(\omega_{fi}-\omega)t}dt = \int_{-\infty}^{\infty} e^{i(\omega_{fi}-\omega)t}dt \tag{13.4.6}$$

$$= 2\pi\delta(\omega_{fi}-\omega) \tag{13.4.7}$$

$$= (2\pi\hbar\delta(E_f - E_i - \hbar\omega) \tag{13.4.8}$$

Therefore, the expression for the rate in this limit can be written as

$$R_{fi}(\omega) = \lim_{T\to\infty}\frac{P_{fi}^{(1)}(T)}{T} = \lim_{T\to\infty}\frac{1}{T\hbar^2}\left|\int_{-T/2}^{T/2} e^{i(\omega_{fi}-\omega)t}dt\right|^2 |F(\omega)|^2 |\langle E_f|\mathcal{V}|E_i\rangle|^2 \tag{13.4.9}$$

$$= \lim_{T\to\infty}\frac{1}{T\hbar^2}\left[\int_{-T/2}^{T/2} e^{-i(\omega_{fi}-\omega)t}dt\right]\left[\int_{-T/2}^{T/2} e^{i(\omega_{fi}-\omega)t}dt\right] |F(\omega)|^2 |\langle E_f|\mathcal{V}|E_i\rangle|^2 \tag{13.4.10}$$

where we have dropped the "(1)" superscript (it is understood that the result is derived from first-order perturbation theory), and indicate explicitly the dependence on the frequency ω. When one the first integral is replaced by the δ-function, the remaining integral becomes simply T, which cancels the T in the denominator. Thus, the expression for the rate is finally

$$R_{fi}(\omega) = \frac{2\pi}{\hbar}|F(\omega)|^2 |\langle E_f|\mathcal{V}|E_i\rangle|^2 \delta(E_f - E_i - \hbar\omega) \tag{13.4.11}$$

which is known as **Fermi's Golden Rule**. It states that, to first-order in perturbation theory, the transition rate depends only the square of the matrix element of the operator $\mathcal{V}$ between initial and final states and includes, via the δ-function, an energy-conservation condition. We will make use of the Fermi Golden Rule expression to analyze the application of an external monochromatic field to an ensemble of systems in order to derive expressions for the observed frequency spectra.

SECTION OVERVIEW

13.5: Quantum Linear Response Theory

Consider again the Hamiltonian for a system coupled to a time-dependent field

$$H = H_0 - BF_e(t)$$

We wish to solve the quantum Liouville equation

$$i\hbar \frac{\partial \rho}{\partial t} = [H, \rho]$$

in the linear regime where $F_e(t)$ is small.

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CHAPTER OVERVIEW

14: The Langevin and Generalized Langevin equations

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14.1: The Harmonic Bath Hamiltonian

In the theory of chemical reactions, it is often possible to isolate a small number or even a single degree of freedom in the system that can be used to characterize the reaction. This degree of freedom is coupled to other degrees of freedom (for example, reactions often take place in solution). Isomerization or dissociation of a diatomic molecule in solution is an excellent example of this type of system. The degree of freedom of paramount interest is the distance between the two atoms of the molecule - this is the degree of freedom whose detailed dynamics we would like to elucidate. The dynamics of the "bath" or environment to which is couples is less interesting, but still must be accounted for in some manner. A model that has maintained a certain level of both popularity and success is the so called "harmonic bath" model, in which the environment to which the special degree(s) of freedom couple is replaced by an effective set of harmonic oscillators. We will examine this model for the case of a single degree of freedom of interest, which we will designate q. For the case of the isomerizing or dissociating diatomic, q could be the coordinate $r - \langle r \rangle$, where r is the distance between the atoms. The particular definition of q ensures that $\langle q \rangle = 0$. The degree of freedom q is assumed to couple to the bath linearly, giving a Hamiltonian of the form

$$H = \frac{p^2}{2m} + \phi(q) + \sum_\alpha \left[\frac{p_\alpha^2}{2m_\alpha} + \frac{1}{2} m_\alpha \omega_\alpha^2 \left(x_\alpha + \frac{g_\alpha}{m_\alpha \omega_\alpha^2} q \right)^2 \right]$$

where the index α runs over all the bath degrees of freedom, ω_α are the harmonic bath frequencies, m_α are the harmonic bath masses, and g_α are the coupling constants between the bath and the coordinate q. p is a momentum conjugate to q, and m is the mass associated with this degree of freedom (e.g., the reduced mass μ in the case of a diatomic). The coordinate q is assumed to be subject to a potential $\phi(q)$ as well (e.g., an internal bond potential). The form of the coupling between the system (q) and the bath (x_α) is known as *bilinear*.

Below, using a completely classical treatment of this Hamiltonian, we will derive an equation for the detailed dynamics of q alone. This equation is known as the **generalized Langevin equation** (GLE).

14.2: The Random Force Term

Within the context of a harmonic bath, the term "random force" is something of a misnomer, since $R(t)$ is completely deterministic and not random at all!!! We will return to this point momentarily, however, let us examine particular features of $R(t)$ from its explicit expression from the harmonic bath dynamics. Note, first of all, that it does not depend on the dynamics of the system coordinate q (except for the appearance of $q(0)$). In this sense, it is independent or "orthogonal" to q within a phase space picture. From the explicit form of $R(t)$, it is straightforward to see that the correlation function

$$\langle \dot{q}(0) R(t) \rangle = 0$$

i.e., the correlation function of the system velocity $\dot{q}$ with the random force is 0. This can be seen by substituting in the expression for $R(t)$ and integrating over initial conditions with a canonical distribution weighting. For certain potentials $\phi(q)$ that are even in q (such as a harmonic oscillator), one can also show that

$$\langle q(0) R(t) \rangle = 0$$

Thus, $R(t)$ is completely uncorrelated from both q and $\dot{q}$, which is a property we might expect from a truly random process. In fact, $R(t)$ is determined by the detailed dynamics of the bath. However, we are not particularly interested or able to follow these detailed dynamics for a large number of bath degrees of freedom. Thus, we could just as well model $R(t)$ by a completely random process (satisfying certain desirable features that are characteristic of a more general bath), and, in fact, this is often done. One could, for example, postulate that $R(t)$ act over a maximum time t_{max} at discrete points in time $k\Delta t$, giving $N = t_{\rm max}/\Delta t$ values of $R_k = R(k\Delta t)$, and assume that R_k takes the form of a *gaussian random process*:

$$R_k = \sum_{j=1}^{N} \left[a_j e^{2\pi ijk/N} + b_j e^{-2\pi ijk/N} \right]$$

where the coefficients $\{a_j\}$ and $\{b_j\}$ are chosen at random from a gaussian distribution function. This might be expected to be suitable for a bath of high density, where strong collisions between the system and a bath particle are essentially nonexistent, but where the system only sees feels the relatively "soft" fluctuations of the less mobile bath. For a low density bath, one might try modeling $R(t)$ as a Poisson process of very strong collisions.

Whatever model is chosen for $R(t)$, if it is a truly random process that can only act at discrete points in time, then the GLE takes the form of a stochastic (based on random numbers) integro-differential equation. There is a whole body of mathematics devoted to the properties of such equations, where heavy use of an *calculus* is made.

14.3: The Dynamic Friction Kernel

The convolution integral term

$$\int_0^t d\tau\ \dot{q}(\tau)\zeta(t-\tau)$$

is called the **memory integral** because it depends, in general, on the entire history of the evolution of q. Physically it expresses the fact that the bath requires a finite time to respond to any fluctuation in the motion of the system (q). This, in turn, affects how the bath acts back on the system. Thus, the force that the bath exerts on the system presently depends on what the system coordinate q did in the past. However, we have seen previously the regression of fluctuations (their decay to 0) over time. Thus, we expect that what the system did very far in the past will no longer the force it feels presently, i.e., that the lower limit of the memory integral (which is rigorously 0) could be replaced by $t-t_{\text{mem}}$, where t_{mem} is the maximum time over which memory of what the system coordinate did in the past is important. This can be interpreted as a indicating a certain decay time for the friction kernel $\zeta(t)$. In fact, $\zeta(t)$ often does decay to 0 in a relatively short time. Often this decay takes the form of a rapid initial decay followed by a slow final decay, as shown in the figure below:

Consider the extreme case that the bath is capable of responding infinitely quickly to changes in the system coordinate q. This would be the case, for example, if there were a large mass disparity between the system and the bath ($m \gg m_\alpha$). Then, the bath retains *no* memory of what the system did in the past, and we could take $\zeta(t)$ to be a δ-function in time:

$$\zeta(t) = 2\zeta_0\delta(t)$$

Then

$$\int_0^t d\tau\ \dot{q}(\tau)\zeta(t-\tau) = \int_0^t d\tau\dot{q}(t-\tau)\zeta(\tau) = 2\zeta_0\int_0^t d\tau\ \delta(\tau)\dot{q}(t-\tau) = \zeta_0\dot{q}(t)$$

and the GLE becomes

$$m\ddot{q} = -\frac{\partial\phi}{\partial q} - \zeta_0\dot{q} + R(t)$$

This simpler equation of motion is known as the **Langevin equation** and it is clearly a special case of the more generalized equation of motion. It is often invoked to describe Brownian motion where clearly such a mass disparity is present. The constant ζ_0 is known as the static friction and is given by

$$\zeta_0 = \int_0^\infty dt\ \zeta(t)$$

In fact, this is a general relation for determining the static friction constant.

The other extreme is a very sluggish bath that responds slowly to changes in the system coordinate. In this case, we may take $\zeta(t)$ to be a constant $\zeta \equiv \zeta(0)$, at least, for times short compared to the response time of the bath. Then, the memory integral becomes

$$\int_0^t d\tau\ \dot{q}(\tau)\zeta(t-\tau) \approx \zeta(q(t)-q(0))$$

and the GLE becomes

$$m\ddot{q} = -\frac{\partial}{\partial q}\left(\phi(q) + \frac{1}{2}\zeta(q-q_0)^2\right) + R(t)$$

where the friction term now manifests itself as an extra harmonic term added to the potential. Such a term has the effect of trapping the system in certain regions of configuration space, an effect known as **dynamic caging**. An example of this is a dilute mixture of small, light particles in a bath of heavy, large particles. The light particles can get trapped in regions of space where many bath particles are in a sort of spatial 'cage." Only the rare fluctuations in the bath that open up larger holes in configuration space allow the light particles to escape the cage, occasionally, after which, they often get trapped again in a new cage for a similar time interval.

14.4: Relation between the Dynamic Friction Kernel and the Random Force

From the definitions of $R(t)$ and $\zeta(t)$, it is straightforward to show that there is a relation between them of the form

$$\langle R(0)R(t)\rangle = kT\zeta(t)$$

This relation is known as the *second fluctuation dissipation theorem*. The fact that it involves a simple autocorrelation function of the random force is particular to the harmonic bath model. We will see later that a more general form of this relation exists, valid for a general bath. This relation must be kept in mind when introducing models for $R(t)$ and \zeta(t). In effect, it acts as a constraint on the possible ways in which one can model the random force and friction kernel.

14.5: Derivation of the GLE

The GLE can be derived from the harmonic bath Hamiltonian by simply solving Hamilton's equations of motion, which take the form

$$\dot{q} = \frac{P}{m}$$

$$\dot{p} = -\frac{\partial \phi}{\partial q} - \sum_{\alpha} g_{\alpha} x_{\alpha} - \sum_{\alpha} \frac{g_{\alpha}^2}{m_{\alpha}\omega_{\alpha}^2} q$$

$$\dot{x}_{\alpha} = \frac{P_{\alpha}}{m_{\alpha}}$$

$$\dot{p}_{\alpha} = -m_{\alpha}\omega_{\alpha}^2 x_{\alpha} - g_{\alpha} q$$

This set of equations can also be written as second order differential equation:

$m\ddot{q}$	=	$-\frac{\partial \phi}{\partial q} - \sum_{\alpha} g_{\alpha} x_{\alpha} - \sum_{\alpha} \frac{g_{\alpha}^2}{m_{\alpha}\omega_{\alpha}^2} q$
$m_{\alpha}\ddot{x}_{\alpha}$	=	$-m_{\alpha}\omega_{\alpha}^2 x_{\alpha} - g_{\alpha} q$

In order to derive an equation for q, we solve explicitly for the dynamics of the bath variables and then substitute into the equation for q. The equation for x_{α} is a second order inhomogeneous differential equation, which can be solved by Laplace transforms. We simply take the Laplace transform of both sides. Denote the Laplace transforms of q and x_{α} as

$\tilde{q}(s)$	=	$\int_0^{\infty} dt\ e^{-st} q(t)$
$\tilde{x}_{\alpha}$	=	$\int_0^{\infty} dt\ e^{-st} x_{\alpha}(t)$

and recognizing that

$$\int_0^{\infty} dt\ e^{-st} \ddot{x}_{\alpha}(t) = s^2 \tilde{x}_{\alpha}(s) - s x_{\alpha}(0) - \dot{x}_{\alpha}(0)$$

we obtain the following equation for $\tilde{x}_{\alpha}(s)$:

$$(s^2 + \omega_{\alpha}^2)\tilde{x}_{\alpha}(s) = s x_{\alpha}(0) + \dot{x}_{\alpha}(0) - \frac{g_{\alpha}}{m_{\alpha}} \tilde{q}(s)$$

or

$$\tilde{x}_{\alpha}(s) = \frac{s}{s^2 + \omega_{\alpha}^2} x_{\alpha}(0) + \frac{1}{s^2 + \omega_{\alpha}^2} \dot{x}_{\alpha}(0) - \frac{g_{\alpha}}{m_{\alpha}} \frac{\tilde{q}(s)}{s^2 + \omega_{\alpha}^2}$$

$x_{\alpha}(t)$can be obtained by inverse Laplace transformation, which is equivalent to a contour integral in the complex s-plane around a contour that encloses all the poles of the integrand. This contour is known as the *Bromwich* contour. To see how this works, consider the first term in the above expression. The inverse Laplace transform is

$$\frac{1}{2\pi i} \oint ds\ \frac{s e^{st}}{s^2 + \omega_{\alpha}^2} = \frac{1}{2\pi i} \oint ds\ \frac{s e^{st}}{(s + i\omega_{\alpha})(s - i\omega_{\alpha})}$$

The integrand has two poles on the imaginary s-axis at $\pm i\omega_{\alpha}$. Integration over the contour that encloses these poles picks up both residues from these poles. Since the poles are simple poles, then, from the residue theorem:

$$\frac{1}{2\pi i} \oint ds\ \frac{s e^{st}}{(s + i\omega_{\alpha})(s - i\omega_{\alpha})} = \frac{1}{2\pi i} \left[2\pi i \left(\frac{i\omega_{\alpha} e^{i\omega_{\alpha} t}}{2i\omega_{\alpha}} + \frac{-i\omega_{\alpha} e^{i\omega_{\alpha} t}}{-2i\omega_{\alpha}} \right) \right] = \cos \omega_{\alpha} t$$

By the same method, the second term will give $(\sin \omega_{\alpha} t)/\omega_{\alpha}$. The last term is the inverse Laplace transform of a product of $q(S)\tilde{q}(s)$ and $1/(s^2 + \omega_{\alpha}^2)$. From the convolution theorem of Laplace transforms, the Laplace transform of a convolution gives the product of Laplace transforms:

$$\int_0^{\infty} dt\; e^{-st} \int_0^t d\tau\; f(\tau) g(t-\tau) = \tilde{f}(s) \tilde{g}(s)$$

Thus, the last term will be the convolution of $q(t)$ with $(\sin \omega_\alpha t)/\omega_\alpha$. Putting these results together, gives, as the solution for $x_\alpha(t)$:

$$x_\alpha(t) = x_\alpha(0) \cos \omega_\alpha t + \frac{\dot{x}_\alpha(0)}{\omega_\alpha} \sin \omega_\alpha t - \frac{g_\alpha}{m_\alpha \omega_\alpha} \int_0^t d\tau q(\tau) \sin \omega_\alpha (t-\tau)$$

The convolution term can be expressed in terms of $\dot{q}$ rather than q by integrating it by parts:

$$\frac{g_\alpha}{m_\alpha \omega_\alpha} \int_0^t d\tau\; q(\tau) \sin \omega_\alpha (t-\tau) = \frac{g_\alpha}{m_\alpha \omega_\alpha^2} \left[q(t) - q(0) \cos \omega_\alpha t \right] - \frac{g_\alpha}{m_\alpha \omega_\alpha^2} \int_0^t d\tau\; \dot{q}(\tau) \cos \omega_\alpha (t-\tau)$$

The reasons for preferring this form will be made clear shortly. The bath variables can now be seen to evolve according to

$$x_\alpha(t) = x_\alpha(0) \cos \omega_\alpha t + \frac{\dot{x}(0)}{\omega_\alpha} \sin \omega_\alpha t + \frac{g_\alpha}{m_\alpha \omega_\alpha^2} \int_0^t d\tau\; \dot{q}(\tau) \cos \omega_\alpha (t-\tau) - \frac{g_\alpha}{m_{alpha} \omega_\alpha^2} \left[q(t) - q(0) \cos \omega_\alpha t \right]$$

Substituting this into the equation of motion for q, we find

$$m\ddot{q} = -\frac{\partial \phi}{\partial q} - \sum_\alpha g_\alpha \left[x_\alpha(0) \cos \omega_\alpha t + \frac{P_\alpha(0)}{m_\alpha \omega_\alpha} \sin \omega_\alpha t + \frac{g_\alpha}{m_\alpha \omega_\alpha^2} q(0) \cos \omega_\alpha t \right] - \sum_\alpha \frac{g_\alpha^2}{m_\alpha \omega_\alpha^2} \int_0^t d\tau \dot{q}(\tau) \cos \omega_\alpha (t-\tau)$$

$$+\sum_\alpha \frac{g_\alpha^2}{m_\alpha \omega_\alpha^2} q(t) - \sum_\alpha \frac{g_\alpha^2}{m_\alpha \omega_\alpha^2} q(t)$$

We now introduce the following notation for the sums over bath modes appearing in this equation:

1.

Define a dynamic *friction kernel*

$$\zeta(t) = \sum_\alpha \frac{g_\alpha}{m_\alpha \omega_\alpha^2} \cos \omega_\alpha t$$

2.

Define a *random force*

$$R(t) = -\sum_\alpha g_\alpha \left[\left(x_\alpha(0) + \frac{g_\alpha}{m_\alpha \omega_\alpha^2} q(0) \right) \cos \omega_\alpha t + \frac{P_\alpha(0)}{m_\alpha \omega_\alpha} \sin \omega_\alpha t \right]$$

Using these definitions, the equation of motion for q reads

$$m\ddot{q} = -\frac{\partial \phi}{\partial q} - \int_0^t d\tau\; \dot{q}(\tau) \zeta(t-\tau) + R(t) \tag{1}$$

Eq. (1) is known as the *generalized Langevin equation*. Note that it takes the form of a one-dimensional particle subject to a potential $\phi(q)$, driven by a forcing function $R(t)$ and with a nonlocal (in time) damping term $-\int_0^t d\tau\; \dot{q}(\tau) \zeta(t-\tau)$, which depends, in general, on the entire history of the evolution of q. The GLE is often taken as a phenomenological equation of motion for a coordinate q coupled to a general bath. In this spirit, it is worth taking a moment to discuss the physical meaning of the terms appearing in the equation.

14.6: Mori-Zwanzig Theory- A more general derivation of the GLE

A derivation of the GLE valid for a general bath can be worked out. The details of the derivation are given in the book by Berne and Pecora called *Dynamic Light Scattering*. The system coordinate q and its conjugate momentum p are introduced as a column vector:

$$\mathbf{A} = \begin{pmatrix} q \\ p \end{pmatrix}$$

and, in addition, one introduces statistical *projection operators* P and Q that project onto subspaces in phase space parallel and orthogonal to A. These operators take the form

$$P = \langle \ldots \mathbf{A}^{\mathrm{T}} \rangle \langle \mathbf{A}\mathbf{A}^{\mathrm{T}} \rangle^{-1}$$

$$Q = I - P$$

These operators are Hermitian and satisfy the property of idempotency:

$$P^2 = P$$

$$Q^2 = Q$$

Also, note that

$$P\mathbf{A} = \mathbf{A}$$

$$Q\mathbf{A} = 0$$

The time evolution of $\mathbf{A}$ is given by application of the classical propagator:

$$\mathbf{A}(t) = e^{iLt}\mathbf{A}(0)$$

Note that the evolution of $\mathbf{A}$ is unitary, i.e., it preserves the norm of $\mathbf{A}$:

$$|\mathbf{A}(t)|^2 = |\mathbf{A}(0)|^2$$

Differentiating both sides of the time evolution equation for $\mathbf{A}$ gives:

$$\frac{dA}{dt} = e^{iLt} iL\mathbf{A}(0)$$

Then, an identity operator is inserted in the above expression in the form $I = P + Q$:

$$\frac{dA}{dt} = e^{iLt}(P+Q)iL\mathbf{A}(0) = e^{iLt}PiL\mathbf{A}(0) + e^{iLt}QiL\mathbf{A}(0)$$

The first term in this expression defines a frequency matrix acting on $\mathbf{A}$:

$e^{iLt}PiL\mathbf{A}(0)$	$=$	$e^{iLt}\langle iL\mathbf{A}\mathbf{A}^{\mathrm{T}}\rangle\langle \mathbf{A}\mathbf{A}^{\mathrm{T}}\rangle^{-1}\mathbf{A}$
	$=$	$\langle iL\mathbf{A}\mathbf{A}^{\mathrm{T}}\rangle\langle \mathbf{A}\mathbf{A}^{\mathrm{T}}\rangle^{-1}e^{iLt}\mathbf{A}$
	$=$	$\langle iL\mathbf{A}\mathbf{A}^{\mathrm{T}}\rangle\langle \mathbf{A}\mathbf{A}^{\mathrm{T}}\rangle^{-1}\mathbf{A}(t)$
	$\equiv$	$i\mathbf{\Omega}\mathbf{A}(t)$

where

$$\mathbf{\Omega} = \langle L\mathbf{A}\mathbf{A}^{\mathrm{T}}\rangle\langle \mathbf{A}\mathbf{A}^{\mathrm{T}}\rangle^{-1}$$

In order to evaluate the second term, another identity operator is inserted directly into the propagator:

$$e^{iLt} = e^{i(P+Q)Lt}$$

Consider the difference between the two propagators:

$$e^{iLt} - e^{iQLt}$$

If this difference is Laplace transformed, it becomes

$$(s - iL)^{-1} - (s - iQL)^{-1}$$

which can be simplified via the general operator identity:

$$\mathrm{A}^{-1} - \mathrm{B}^{-1} = \mathrm{A}^{-1}(\mathrm{B} - \mathrm{A})\mathrm{B}^{-1}$$

Letting

$$A = (s - iL)$$

$$B = (s - iQL)$$

we have

$(s - iL)^{-1} - (s - iQL)^{-1}$	$=$	$(s - iL)^{-1}(s - iQL - s + iL)(s - iQL)^{-1}$
	$=$	$(s - iL)^{-1} iPL(s - iQL)^{-1}$

or

$$(s - iL)^{-1} = (s - iQL)^{-1} + (s - iL)^{-1}(s - iQL - s + iL)(s - iQL)^{-1}$$

Now, inverse Laplace transforming both sides gives

$$e^{iLt} = e^{iQLt} + \int_0^t d\tau \; e^{iL(t-\tau)} \, iPLe^{iQL\tau}$$

Thus, multiplying fromthe right by $QiL\mathbf{A}$ gives

$$e^{iLt} QiL\mathbf{A} = e^{iQLt} QiL\mathbf{A} + \int_0^t d\tau \; e^{iL(t-\tau)} \, iPLe^{iQL\tau} QiL\mathbf{A}$$

Define a vector

$$\mathbf{F}(t) = e^{iQLt} QiL\mathbf{A}(0)$$

so that

$$e^{iLt} QiL\mathbf{A} = \mathbf{F}(t) + \int_0^t d\tau \; \langle iL\mathbf{F}(\tau)\mathbf{A}^T\rangle \langle \mathbf{A}\mathbf{A}^{\mathrm{T}}\rangle^{-1} \mathbf{A}(t - \tau)$$

Because $\mathbf{F}(t)$ is completely orthogonal to $\mathbf{A}(t)$, it is straightforward to show that

$$Q\mathbf{F}(t) = \mathbf{F}(t)$$

Then,

$\langle iL\mathbf{F}(\tau)\mathbf{A}^{\mathrm{T}}\rangle \langle \mathbf{A}\mathbf{A}^{\mathrm{T}}\rangle^{-1}\mathbf{A}$	$=$	$\langle iLQ\mathbf{F}(\tau)\mathbf{A}^{\mathrm{T}}\rangle \langle \mathbf{A}\mathbf{A}^{\mathrm{T}}\rangle^{-1}\mathbf{A}$
	$=$	$-\langle Q\mathbf{F}(\tau)(iL\mathbf{A})^{\mathrm{T}}\rangle \langle \mathbf{A}\mathbf{A}^{\mathrm{T}}\rangle^{-1}\mathbf{A}$
	$=$	$-\langle Q^2\mathbf{F}(\tau)(iL\mathbf{A})^{\mathrm{T}}\rangle \langle \mathbf{A}\mathbf{A}^{\mathrm{T}}\rangle^{-1}\mathbf{A}$

	$=$	$-\langle Q\mathbf{F}(\tau)(QiL\mathbf{A})^{\mathrm{T}}\rangle\langle\mathbf{A}\mathbf{A}^{\mathrm{T}}\rangle^{-1}\mathbf{A}$
	$=$	$-\langle\mathbf{F}(\tau)\mathbf{F}^{\mathrm{T}}(0)\rangle\langle\mathbf{A}\mathbf{A}^{\mathrm{T}}\rangle^{-1}\mathbf{A}$

Thus,

$$e^{iLt}QiL\mathbf{A} = \mathbf{F}(t) - \int_0^t d\tau\ \langle\mathbf{F}(\tau)\mathbf{F}^T(0)\rangle\langle\mathbf{A}\mathbf{A}^{\mathrm{T}}\rangle^{-1}\mathbf{A}(t-\tau)$$

Finally, we define a memory kernel matrix:

$$\mathbf{K}(t) = \langle\mathbf{F}(\tau)\mathbf{F}^{\mathrm{T}}(0)\rangle\langle\mathbf{A}\mathbf{A}^{\mathrm{T}}\rangle^{-1}$$

Then, combining all results, we find, for $\frac{dbfA}{dt}$:

$$\frac{d\mathbf{A}}{dt} = i\boldsymbol{\Omega}(t)\mathbf{A} - \int_0^t d\tau\ \mathbf{K}(\tau)\mathbf{A}(t-\tau) + \mathbf{F}(t)$$

which equivalent to a generalized Langevin equation for a particle subject to a harmonic potential, but coupled to a general bath. For most systems, the quantities appearing in this form of the generalized Langevin equation are

$i\boldsymbol{\Omega}$	$=$	$\mathbf{K}(t)$
$\mathbf{F}(t)$	$=$	$\mathbf{K}(t)$
$\begin{pmatrix} 0 \\ R(t) \end{pmatrix}$	$=$	$\phi(q) = \frac{m\omega^2q^2}{2}$

It is easy to derive these expressions for the case of the harmonic bath Hamiltonian when

$$\langle R(0)R(t)\rangle = \langle R(0)e^{iLt}R(0)\rangle = kT\zeta(t)$$

For the case of a harmonic bath Hamiltonian, we had shown that the friction kernel was related to the random force by the fluctuation dissipation theorem:

$$exp(iQLt)$$

For a general bath, the relation is not as simple, owing to the fact that $\mathbf{F}(t)$ is evolved using a modified propagator $\langle R(0)e^{iQLt}R(0)\rangle = kT\zeta(t)$. Thus, the more general form of the fluctuation dissipation theorem is

$$\langle R(0)e^{iQLt}R(0)\rangle \approx \langle R(0)e^{iL_{\mathrm{cons}}t}R(0)\rangle$$

so that the dynamics of $R(t)$ is prescribed by the propagator $\langle R(0)e^{iQLt}R(0)\rangle = kT\zeta(t)$. This more general relation illustrates the difficulty of defining a friction kernel for a general bath. However, for the special case of a stiff harmonic diatomic molecule interacting with a bath for which all the modes are soft compared to the frequency of the diatomic, a very useful approximation results. One can show that

$$iL_{cons}$$

where $C_{vv}(t) = \frac{\langle\dot{q}(0)\dot{q}(t)\rangle}{\langle\dot{q}^2\rangle}$ is the Liouville operator for a system in which the diatomic is held rigidly fixed at some particular bond length (i.e., a constrained dynamics). Since the friction kernel is not sensitive to the details of the internal potential of the diatomic, this approximation can also be used for diatomics with stiff, *anharmonic* potentials. This approximation is referred to as the *rigid bond approximation* (see Berne, *et al*, *J. Chem. Phys.* **93**, 5084 (1990)).

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14.7: Example- Vibrational dephasing and energy relaxation

Recall that the Fourier transform of a time correlation function can be related to some kind of frequency spectrum. For example, the Fourier transform of the velocity autocorrelation function of a particular degree of freedom q of interest

$$v = \dot{q}$$

where $I(\omega)$, gives the relevant frequencies contributing to the dynamics of q, but does not give amplitudes. This "frequency" spectrum $I(\omega) = \int_0^\infty \; dt \; e^{i\omega t} C_{\text{vv}}(t)$ is simply given by

$$C_{vv}(t)$$

That is, we take the Laplace transform of $s = -i\omega$ using T_2. Since $s = -i\omega$ carries information about the relevant frequencies of the system, the decay of $s = -i\omega$ in time is a measure of how strongly coupled the motion of q is to the rest of the bath, i.e., how much of an overlap there is between the relevant frequencies of the bath and those of q. The more of an overlap there is, the more mixing there will be between the system and the bath, and hence, the more rapidly the motion of the system will become vibrationally "out of phase" or decorrelated with itself. Thus, the decay time of $s = -i\omega$, which is denoted $C_{\varepsilon\varepsilon} = \frac{\langle \varepsilon(0)\varepsilon(t)\rangle}{\langle \varepsilon^2\rangle}$ is called the *vibrational dephasing time*.

Another measure of the strength of the coupling between the system and the bath is the time required for the system to dissipate energy into the bath when it is excited away from equilibrium. This time can be obtained by studying the decay of the energy autocorrelation function:

$$\varepsilon(t)$$

where $\varepsilon(t) = \frac{1}{2} m \dot{q}^2 + \phi(q) - kT$ is defined to be

$$T_1$$

The decay time of this correlation function is denoted $\phi(q) = \frac{1}{2} m\omega^2 q^2$.

The question then becomes: what are these characteristic decay times and how are they related? To answer this, we will take a phenomenological approach. We will assume the validity of the GLE for q:

$$m\ddot{q} = -\frac{\partial \phi}{\partial q} - \int_0^t \; d\tau \; \dot{q}(\tau)\zeta(t-\tau) + R(t)$$

and use it to calculate $\phi(q) = \frac{1}{2} m\omega^2 q^2$ and $C_{\varepsilon\varepsilon} = \frac{\langle \varepsilon(0)\varepsilon(t)\rangle}{\langle \varepsilon^2\rangle}$.

Suppose the potential $\phi(q)$ is harmonic and takes the form

$$\ddot{q} = -\omega^2 q - \int_0^t \; d\tau \; \dot{q}(t-\tau)\gamma(\tau) + f(t)$$

Substituting into the GLE and dividing through by m gives

$$\gamma(t) = \frac{\zeta(t)}{m} \qquad f(t) = \frac{R(t)}{m}$$

where

$$\dot{q}(0)$$

An equation of motion for $s = -i\omega$ can be obtained directly by multiplying both sides of the GLE by $\langle \dot{q}(0)\ddot{q}(t)\rangle = -\omega^2 \langle \dot{q}(0) q(t)\rangle - \int_0^t d\tau \langle \dot{q}(0)\dot{q}(t-\tau)\rangle\gamma(\tau) + \langle \dot{q}(0) f(t)\rangle$ and averaging over a canonical ensemble:

$$\langle \dot{q}(0) f(t)\rangle = \frac{1}{m}\langle \dot{q}(0) R(t)\rangle = 0$$

Recall that

$$\langle \dot{q}(0)\ddot{q}(t)\rangle = \frac{d}{dt}\langle \dot{q}(0)\dot{q}(t)\rangle = \frac{dC_{\text{vv}}}{dt}$$

and note that

$$\int_0^t d\tau\ \langle \dot{q}(0)\dot{q}(\tau)\rangle = \langle \dot{q}(0)q(t)\rangle - \langle \dot{q}(0)q(0)\rangle = \langle \dot{q}(0)q(t)\rangle$$

also

$$\langle \dot{q}(0)q(t)\rangle = \int_0^t d\tau\ C_{\text{vv}}(\tau)$$

Thus,

$$\frac{d}{dt}C_{\text{vv}}(t)$$

Combining these results gives an equation for $s = -i\omega$

$-\int_0^t\ d\tau\ \left(\omega^2 + \gamma(t-\tau)\right) C_{\text{vv}}(\tau)$	=	$-\int_0^t\ d\tau\ K(t-\tau)C_{\text{vv}}(\tau)$
$-\int_0^t\ d\tau\ \left(\omega^2 + \gamma(t-\tau)\right) C_{\text{vv}}(\tau)$	=	$K(t)$

which is known as the *memory function equation* and the kernel $s\tilde{C}_{vv}(s) - C_{\text{vv}}(0) = -\tilde{C}_{vv}(s)\tilde{K}(s)$ is known as the memory function or memory kernel. This type of integro-differential equation is called a *Volterra* equation and it can be solved by Laplace transforms.

Taking the Laplace transform of both sides gives

$$C_{\text{vv}}(0) = 1$$

However, it is clear that $\tilde{K}(s) = \frac{\omega^2}{s} + \tilde{\gamma}(s)$ and also

$$s\tilde{C}_{vv}(s) - 1$$

Thus, it follows that

$\left(\frac{\omega^2}{s} + \tilde{\gamma}(s)\right) \tilde{C}_{vv}(s)$	=	$\tilde{C}_{vv}(s)$
$\frac{s}{s^2 + s\tilde{\gamma}(s) + \omega^2}$	=	$s^2 + s\tilde{\gamma}(s) + \omega^2 = 0$

In order to perform the inverse Laplace transform, we need the poles of the integrand, which will be determined by the solutions of

$$\tilde{\gamma}(s)$$

which we could solve directly if we knew the explicit form of ω.

However, if $\tilde{\gamma}(0)$ is sufficiently larger than $s = s_0 + s_1 + s_2 + \cdots$, then it is possible to develop a perturbation solution to this equation. Let us assume the solutions for s can be written as $(s_0 + s_1 + s_2 + \cdots)^2 + (s_0 + s_1 + s_2 + \cdots)\tilde{\gamma}(s_0 + s_1 + s_2 + \cdots) + \omega^2 = 0$

Substituting in this ansatz gives

$$\tilde{\gamma}$$

Since we are assuming $s_0^2 + \omega^2 = 0$ is small, then to lowest order, we have

$$s_0 = \pm i\omega$$

so that $2s_0s_1 + s_0\tilde{\gamma}(s_0) = 0$. The first order equation then becomes

$$s_1 = -\frac{\tilde{\gamma}(s_0)}{2} = -\frac{\tilde{\gamma}(\pm i\omega)}{2}$$

or

$$\tilde{\gamma}(\pm i\omega)$$

Note, however, that

$\int_0^\infty \; dt \; \gamma(t)e^{\pm i\omega t}$	=	$\int_0^\infty \; dt \; [\gamma(t)\cos\omega t \pm i\gamma(t)\sin\omega t]$
	=	$\gamma'(\omega) \pm i\gamma''(\omega)$
	=	$s \approx \pm i\left(\omega + \gamma''(\omega)\right) - \frac{\gamma'(\omega)}{2} \equiv \pm i\Omega - \frac{\gamma'(\omega)}{2}$

Thus, stopping the first order result, the poles of the integrand occur at

$$s_+$$

Define

$i\Omega - \frac{\gamma'(\omega)}{2}$	=	$s-$
$-i\Omega - \frac{\gamma'(\omega)}{2}$	=	$\tilde{C}_{vv}(s) \approx \frac{s}{(s-s_+)(s-s_-)}$

Then

$$C_{\rm vv}(t) = \frac{1}{2\pi i}\oint \frac{se^{st}\;ds}{(s-s_+)(s-s_-)}$$

and $s = -i\omega$ is then given by the contour integral

$$C_{\rm vv}(t) = \frac{s_+e^{s_+t}}{(s_+ - s_-)} + \frac{s_-e^{s_-t}}{(s_- - s_+)}$$

Taking the residue at each pole, we find

$$C_{\rm vv}(t) = e^{-\gamma'(\omega)t/2}\left[\cos\Omega t - \frac{\gamma'(\omega)}{2\Omega}\sin\Omega t\right]$$

which can be simplified to give

$$\Omega$$

Thus, we see that the GLE predicts $s = -i\omega$ oscillates with a frequency $\frac{1}{T_2} = \frac{\gamma'(\omega)}{2} = \frac{\zeta'(\omega)}{2m}$ and decays exponentially. From the exponential decay, we can directly read off the time $C_{\epsilon\epsilon} = \frac{\langle\epsilon(0)\epsilon(t)\rangle}{\langle\epsilon^2\rangle}$:

$$2m$$

That is, the value of the real part of the Fourier (Laplace) transform of the friction kernel evaluated at the renormalized frequency divided by $C_{\rm qq}(t) = \langle q(0)q(t)\rangle$ gives the vibrational dephasing time! By a similar scheme, one can easily show that the position autocorrelation function $C_{\rm qq}(t) = e^{-\gamma'(\omega)t/2}\left[\cos\Omega t + \frac{\gamma'(\omega)}{2\Omega}\sin\Omega t\right]$ decays with the same dephasing time. It's explicit form is

$$C_{\varepsilon\varepsilon}(t)$$

The energy autocorrelation function $C_{\rm qq}(t)$ can be expressed in terms of the more primitive correlation functions $C_{\varepsilon\varepsilon}(t) = \frac{1}{2}C^2_{\rm vv}(t) + \frac{1}{2}C^2_{qq}(t) + \frac{1}{\omega^2}\dot{C}^2_{qq}(t)$ and $s = -i\omega$. It is a straightforward, although extremely tedious, matter to show that the relation, valid for the harmonic potential of mean force, is

$$C_{\varepsilon\varepsilon}(t) = e^{-\gamma'(\omega)t} \times (\text{oscillatory functions of } t)$$

Substituting in the expressions for $c_{\varepsilon\varepsilon}(t) = \frac{1}{2}C^2_{vv}(t) + \frac{1}{2}C^2_{qq}(t) + \frac{1}{\omega^2}C^2_{qq}(t)$ and $s = -i\omega$ $C_{\rm vv}(t)$ gives

$$\frac{1}{T_1} = \gamma'(\omega) = \frac{\zeta'(\omega)}{m}$$

so that the decay time $\phi(q) = \frac{1}{2}m\omega^2q^2$ can be seen to be

$$\frac{1}{T_2} = \frac{1}{2T_1}$$

and therefore, the relation between $\phi(q) = \frac{1}{2}m\omega^2q^2$ and $C_{\varepsilon\varepsilon} = \frac{\langle\varepsilon(0)\varepsilon(t)\rangle}{\langle\varepsilon^2\rangle}$ can be seen immediately to be

$$\omega$$

The incredible fact is that this result is also true quantum mechanically. That is, by doing a simple, purely classical treatment of the problem, we obtained a result that turns out to be the correct *quantum mechanical* result!

Just how big are these times? If ω is very large compared to any typical frequency relevant to the bath, then the friction kernel evaluated at this frequency will be extremely small, giving rise to a long decay time. This result is expect, since, if $\tilde{\gamma}(0)$ is large compared to the bath, there are very few ways in which the system can dissipate energy into the bath. The situation changes dramatically, however, if a small amount of anharmonicity is added to the potential of mean force. The figure below illustrates the point for a harmonic diatomic molecule interacting with a Lennard-Jones bath. The top figure shows the velocity autocorrelation function for an oscillator whose frequency is approximately 3 times the characteristic frequency of the bath, while the bottom one shows the velocity autocorrelation function for the case that the frequency disparity is a factor of 6.

Figure 1:

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