

## 8.1: Equilibrium, Nonequilibrium and Local Equilibrium

Classical equilibrium statistical mechanics is described by the full  $N$ -body distribution,

$$f^0(\mathbf{x}_1, \dots, \mathbf{x}_N; \mathbf{p}_1, \dots, \mathbf{p}_N) = \begin{cases} Z_N^{-1} \cdot \frac{1}{N!} e^{-\beta \hat{H}_N(\mathbf{p}, \mathbf{x})} & OCE \\ \Xi^{-1} \cdot \frac{1}{N!} e^{\beta \mu N} e^{-\beta \hat{H}_N(\mathbf{p}, \mathbf{x})} & GCE \end{cases} \quad (8.1.1)$$

We assume a Hamiltonian of the form

$$\hat{H}_N = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m} + \sum_{i=1}^N v(\mathbf{x}_i) + \sum_{i < j}^N u(\mathbf{x}_i - \mathbf{x}_j), \quad (8.1.2)$$

typically with  $v = 0$ , only two-body interactions. The quantity

$$f^0(\mathbf{x}_1, \dots, \mathbf{x}_N; \mathbf{p}_1, \dots, \mathbf{p}_N) \frac{d^d x_1 d^d p_1}{h^d} \dots \frac{d^d x_N d^d p_N}{h^d} \quad (8.1.3)$$

is the probability, under equilibrium conditions, of finding  $N$  particles in the system, with particle #1 lying within  $d^3 x_1$  of  $\mathbf{x}_1$  and having momentum within  $d^d p_1$  of  $\mathbf{p}_1$ . The temperature  $T$  and chemical potential  $\mu$  are constants, independent of position. Note that  $f(\{\mathbf{x}_i\}, \{\mathbf{p}_i\})$  is dimensionless.

Nonequilibrium statistical mechanics seeks to describe thermodynamic systems which are out of equilibrium, meaning that the distribution function is not given by the Boltzmann distribution above. For a general nonequilibrium setting, it is hopeless to make progress – we'd have to integrate the equations of motion for all the constituent particles. However, typically we are concerned with situations where external forces or constraints are imposed over some macroscopic scale. Examples would include the imposition of a voltage drop across a metal, or a temperature differential across any thermodynamic sample. In such cases, scattering at microscopic length and time scales described by the *mean free path*  $\ell$  and the *collision time*  $\tau$  work to establish *local equilibrium* throughout the system. A local equilibrium is a state described by a space and time varying temperature  $T(\mathbf{r}, t)$  and chemical potential  $\mu(\mathbf{r}, t)$ . As we will see, the Boltzmann distribution with  $T = T(\mathbf{r}, t)$  and  $\mu = \mu(\mathbf{r}, t)$  will not be a solution to the evolution equation governing the distribution function. Rather, the distribution for systems slightly out of equilibrium will be of the form  $f = f^0 + \delta f$ , where  $f^0$  describes a state of local equilibrium.

We will mainly be interested in the one-body distribution

$$\begin{aligned} f(\mathbf{r}, \mathbf{p}; t) &= \sum_{i=1}^N \langle \delta(\mathbf{x}_i(t) - \mathbf{r}) \delta(\mathbf{p}_i(t) - \mathbf{p}) \rangle \\ &= N \int \prod_{i=2}^N d^d x_i d^d p_i f(\mathbf{r}, \mathbf{x}_2, \dots, \mathbf{x}_N; \mathbf{p}, \mathbf{p}_2, \dots, \mathbf{p}_N; t). \end{aligned}$$

In this chapter, we will drop the  $1/\hbar$  normalization for phase space integration. Thus,  $f(\mathbf{r}, \mathbf{p}, t)$  has dimensions of  $h^{-d}$ , and  $f(\mathbf{r}, \mathbf{p}, t) d^3 r d^3 p$  is the average number of particles found within  $d^3 r$  of  $\mathbf{r}$  and  $d^3 p$  of  $\mathbf{p}$  at time  $t$ .

In the GCE, we sum the RHS above over  $N$ . Assuming  $v = 0$  so that there is no one-body potential to break translational symmetry, the equilibrium distribution is time-independent and space-independent:

$$f^0(\mathbf{r}, \mathbf{p}) = n (2\pi m k_B T)^{-3/2} e^{-\mathbf{p}^2 / 2m k_B T}, \quad (8.1.4)$$

where  $n = N/V$  or  $n = n(T, \mu)$  is the particle density in the OCE or GCE. From the one-body distribution we can compute things like the particle current,  $\mathbf{j}$ , and the energy current,  $\mathbf{j}_\varepsilon$ :

$$\begin{aligned} \mathbf{j}(\mathbf{r}, t) &= \int d^d p f(\mathbf{r}, \mathbf{p}; t) \frac{\mathbf{p}}{m} \\ \mathbf{j}_\varepsilon(\mathbf{r}, t) &= \int d^d p f(\mathbf{r}, \mathbf{p}; t) \varepsilon(\mathbf{p}) \frac{\mathbf{p}}{m}, \end{aligned}$$

where  $\varepsilon(\mathbf{p}) = \mathbf{p}^2 / 2m$ . Clearly these currents both vanish in equilibrium, when  $f = f^0$ , since  $f^0(\mathbf{r}, \mathbf{p})$  depends only on  $\mathbf{p}^2$  and not on the direction of  $\mathbf{p}$ . In a *steady state* nonequilibrium situation, the above quantities are time-independent.

Thermodynamics says that

$$dq = T ds = d\varepsilon - \mu dn, \quad (8.1.5)$$

where  $s$ ,  $\varepsilon$ , and  $n$  are entropy density, energy density, and particle density, respectively, and  $dq$  is the differential heat density. This relation may be case as one among the corresponding current densities:

$$\mathbf{j}_q = T\mathbf{j}_s = \mathbf{j}_\varepsilon - \mu\mathbf{j}. \quad (8.1.6)$$

Thus, in a system with no particle flow,  $\mathbf{j} = 0$  and the *heat current*  $\mathbf{j}_q$  is the same as the energy current  $\mathbf{j}_\varepsilon$ .

When the individual particles are not point particles, they possess angular momentum as well as linear momentum. Following Lifshitz and Pitaevskii, we abbreviate  $\Gamma = (\mathbf{p}, \mathbf{L})$  for these two variables for the case of diatomic molecules, and  $\Gamma = (\mathbf{p}, \mathbf{L}, \hat{\mathbf{n}} \cdot \mathbf{L})$  in the case of spherical top molecules, where  $\hat{\mathbf{n}}$  is the symmetry axis of the top. We then have, in  $d = 3$  dimensions,

$$d\Gamma = \begin{cases} d^3p & \text{point particles} \\ d^3p L dL d\Omega_L & \text{diatomic molecules} \\ d^3p L^2 dL d\Omega_L d\cos\vartheta & \text{symmetric tops,} \end{cases} \quad (8.1.7)$$

where  $\vartheta = \cos^{-1}(\hat{\mathbf{n}} \cdot \hat{\mathbf{L}})$ . We will call the set  $\Gamma$  the ‘kinematic variables’. The instantaneous number density at  $\mathbf{r}$  is then

$$n(\mathbf{r}, t) = \int d\Gamma f(\mathbf{r}, \Gamma; t). \quad (8.1.8)$$

One might ask why we do not also keep track of the angular orientation of the individual molecules. There are two reasons. First, the rotations of the molecules are generally extremely rapid, so we are justified in averaging over these motions. Second, the orientation of, say, a rotor does not enter into its energy. While the same can be said of the spatial position in the absence of external fields, (i) in the presence of external fields one must keep track of the position coordinate  $\mathbf{r}$  since there is physical transport of particles from one region of space to another, and (iii) the collision process, which as we shall see enters the dynamics of the distribution function, takes place in real space.

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