

5.3: Simple Quantum Systems

Spin $S = 1/2$

The simplest quantum system is a two-level system and probably the best approximation to isolated two-level systems is found in magnetic resonance spectroscopy of dilute $S = 1/2$ spin systems. The Hamiltonian for an electron spin $S = 1/2$ in an external magnetic field along z is given by

$$\widehat{\mathcal{H}} = \gamma \hbar B_0 \widehat{S}_z, \quad (5.3.1)$$

where $\gamma = g\mu_B/\hbar$ is the gyromagnetic ratio and B_0 is the magnetic field expressed in units of 1 Tesla. The two states are designated by magnetic spin quantum number $m_S = \pm 1/2$ and have energies $\epsilon_{\pm} = \mp \gamma \hbar B_0/2$. The partition function is

$$Z = e^{\gamma \hbar B_0/2k_B T} + e^{-\gamma \hbar B_0/2k_B T}, \quad (5.3.2)$$

and the expectation value of \widehat{S}_z , which is proportional to longitudinal magnetization, by

$$\langle \widehat{S}_z \rangle = \sum m_S P(m_S) \quad (5.3.3)$$

$$= \frac{(-1/2) \cdot e^{\gamma \hbar B_0/2k_B T} + (1/2) e^{-\gamma \hbar B_0/2k_B T}}{Z} \quad (5.3.4)$$

$$= -\frac{1}{2} \tanh(\gamma \hbar B_0/2k_B T). \quad (5.3.5)$$

Usually one has $\gamma \hbar B_0 \ll 2k_B T$, which is called the high-temperature approximation. The series expansion of the hyperbolic tangent,

$$\tanh(x) = x - \frac{1}{3}x^3 + \frac{2}{15}x^5 + \dots, \quad (5.3.6)$$

can then be restricted to the leading term, which gives

$$\langle \widehat{S}_z \rangle = -\frac{\gamma \hbar B_0}{4k_B T}. \quad (5.3.7)$$

Harmonic Oscillator

A diatomic molecule has one vibrational mode along the bond direction x . If we assign masses m_A and m_B to the two atoms and a force constant f to the bond, we can write the Hamiltonian as

$$\widehat{\mathcal{H}} = \frac{1}{2} f \widehat{x}^2 + \frac{\widehat{p}^2}{2\mu}, \quad (5.3.8)$$

where the reduced mass μ is

$$\mu = \frac{m_A m_B}{m_A + m_B} \quad (5.3.9)$$

and where the first term on the right-hand side of Equation 5.3.8 corresponds to potential energy and the second term to kinetic energy.

Equation 5.3.8 can be cast in the form

$$\widehat{\mathcal{H}} = \frac{1}{2} \mu \omega^2 (R - R_E)^2 - \frac{\hbar^2}{2\mu} \frac{d^2}{dR^2}, \quad (5.3.10)$$

where we have substituted \widehat{x} by the deviation of the atom-atom distance R from the bond length R_E and introduced the angular oscillation frequency ω of a classical oscillator with

$$\omega = \sqrt{\frac{f}{\mu}}. \quad (5.3.11)$$

Equation 5.3.10 produces an infinite number of eigenstates with energies

$$\epsilon_v = \hbar\omega \left(v + \frac{1}{2} \right), \quad (5.3.12)$$

where $v = 0, 1, \dots, \infty$ is the *vibrational quantum number*. All energies are positive, even the one of the ground state with $v = 0$. This residual zero-point vibration can be considered as a consequence of Heisenberg's uncertainty principle, since for a non-oscillating diatomic molecule atom coordinates as well as momentum would be sharply defined, which would violate that principle. In the context of statistical thermodynamics the unfortunate consequence is that for an ensemble of N diatomic molecules for $T \rightarrow 0$ the vibrational contribution to the internal energy u approaches $u_0 = N\hbar\omega/2$ and thus the term u/T in the entropy expression (Equation ???) approaches infinity. We ignore this problem for the moment.

The partition function of the harmonic oscillator is an infinite series,

$$Z = \sum_{v=0}^{\infty} e^{-\hbar\omega(v+1/2)/k_B T} \quad (5.3.13)$$

$$= e^{-\hbar\omega/2k_B T} \sum_{v=0}^{\infty} e^{-\hbar\omega v/k_B T} \quad (5.3.14)$$

$$= e^{-\hbar\omega/2k_B T} \sum_{v=0}^{\infty} \left(e^{-\hbar\omega/k_B T} \right)^v \quad (5.3.15)$$

$$= e^{-\hbar\omega/2k_B T} \sum_{n=0}^{\infty} x^n. \quad (5.3.16)$$

where we have substituted $x = e^{-\hbar\omega/k_B T}$ and $n = v$ to obtain the last line. Since for finite temperatures $0 < e^{-\hbar\omega/k_B T} < 1$, the infinite series $\sum_{n=0}^{\infty} x^n$ converges to $1/(1-x)$. Hence,

$$Z = \frac{e^{-\hbar\omega/2k_B T}}{1 - e^{-\hbar\omega/k_B T}}. \quad (5.3.17)$$

We can again discuss the behavior for $T \rightarrow 0$. In the denominator, the argument of the exponential function approaches $-\infty$, so that the denominator approaches unity. In the numerator the argument of the exponential function also approaches $-\infty$, so that the partition function approaches zero and Helmholtz free energy $f = -k_B T \ln Z$ can only be computed as a limiting value. The term $k_B \ln Z$ in the entropy Equation ??? approaches $-\infty$.

This problem can be healed by shifting the energy scale by $\Delta E = -\hbar\omega/2$. We then have¹⁸

$$Z = \frac{1}{1 - e^{-\hbar\omega/k_B T}}. \quad (5.3.18)$$

With this shift, the partition function and the population of the ground state $v=0$ both approach 1 when the temperature approaches zero. For the term u/T in the entropy expression we still need to consider a limiting value, but it can be shown that $\lim_{T \rightarrow 0} u/T = 0$. Since $k_B \ln Z = 0$ for $Z = 1$, entropy of an ensemble of harmonic oscillators vanishes at the zero point in agreement with Nernst's theorem. Helmholtz free energy $f = -k_B T \ln Z$ approaches zero.

For computing a Boltzmann distribution we can shift all energy levels by the same offset ΔE without influencing the P_i , as such a shift leads to a multiplication by the same factor of the numerator and of all terms contributing to the partition function. Such a shift can remove an infinity of the partition function.

This partition function can also be expressed with a *characteristic vibrational temperature*

$$\Theta_{\text{vib}} = \frac{\hbar\omega}{k_B}. \quad (5.3.19)$$

This temperature is usually higher than room temperature. We have

$$Z_{\text{vib}} = \frac{1}{1 - e^{-\Theta_{\text{vib}}/T}}. \quad (5.3.20)$$

Thus, $Z \approx 1$ at room temperature, which implies that only the vibrational ground state is significantly populated. Vibration does not significantly contribute to entropy at room temperature.

Einstein and Debye Models of a Crystal

The considerations on the harmonic oscillator can be extended to a simple model for vibrations in a crystal. If we assume that all atoms except one are fixed at their average locations, the potential at the unique atom is parabolic. This assumption made by Einstein may at first sight violate his own dictum that "Everything should be made as simple as possible, but not simpler.". We shall come back to this point below. For the moment we consider Einstein's approach as a very simple *mean field approach*. Instead of the one-dimensional harmonic oscillator treated in Section [section:harmonic_oscillator], we now have a three-dimensional harmonic oscillator. For sufficiently high point symmetry at the unique atom, we can assume an isotropic force constant f . Each atom is then described by three independent harmonic oscillators along three orthogonal directions. The harmonic oscillators of different atoms are also independent by construction. Because we want to compute an absolute internal energy we revert to the partition function of the harmonic oscillator without energy shift given in Equation 5.3.17. The partition function for a crystal with N atoms, considering that the atoms in a crystal lattice are distinguishable and that thus Equation ??? applies, is then given by

$$Z = \left(\frac{e^{-\hbar\omega/2k_B T}}{1 - e^{-\hbar\omega/k_B T}} \right)^{3N} . \quad (5.3.21)$$

Internal energy can be computed by Equation ???,

$$u_{\text{vib}} = k_B T^2 \left[\frac{\partial}{\partial T} \ln \left\{ \left(\frac{e^{-\hbar\omega/2k_B T}}{1 - e^{-\hbar\omega/k_B T}} \right)^{3N} \right\} \right]_V \quad (5.3.22)$$

$$= 3k_B N T^2 \left[\frac{\partial}{\partial T} \left\{ -\frac{\hbar\omega}{2k_B T} - \ln(1 - e^{-\hbar\omega/k_B T}) \right\} \right]_V \quad (5.3.23)$$

$$= 3k_B N T^2 \left[\frac{\hbar\omega}{2k_B T^2} + \frac{\hbar\omega/k_B T^2 \cdot e^{-\hbar\omega/k_B T}}{1 - e^{-\hbar\omega/k_B T}} \right] \quad (5.3.24)$$

$$= \frac{3}{2} N \hbar\omega + \frac{3N \hbar\omega}{e^{\hbar\omega/k_B T} - 1} . \quad (5.3.25)$$

With the characteristic vibrational temperature Θ_{vib} introduced in Equation 5.3.19 and by setting $N = N_{\text{Av}}$ to obtain a molar quantity, we find

$$U_{\text{vib}} = \frac{3}{2} R \Theta_{\text{vib}} + \frac{3R \Theta_{\text{vib}}}{e^{\Theta_{\text{vib}}/T} - 1} . \quad (5.3.26)$$

The molar heat capacity of an Einstein solid is the derivative of U_{vib} with respect to T . We note that we do not need to specify constant volume or constant pressure, since this simple model depends on neither of these quantities. We find

$$C_{\text{vib}} = 3R \frac{(\Theta_{\text{vib}}/T)^2 e^{\Theta_{\text{vib}}/T}}{(e^{\Theta_{\text{vib}}/T} - 1)^2} . \quad (5.3.27)$$

According to the rule of Dulong and Petit we should obtain the value $3R$ for $T \rightarrow \infty$. Since the expression becomes indeterminate ($0/0$), we need to compute a limiting value, which is possible with the approach of de l'Hospital where we separately differentiate the numerator and denominator. The derivation is lengthy but it indeed yields the limiting value $3R$:

$$\lim_{T \rightarrow \infty} C_{\text{vib}} = \lim_{T \rightarrow \infty} 3R \frac{(\Theta_{\text{vib}}/T)^2 e^{\Theta_{\text{vib}}/T}}{(e^{\Theta_{\text{vib}}/T} - 1)^2} \quad (5.3.28)$$

$$= 3R \lim_{T \rightarrow \infty} \frac{2(\Theta_{\text{vib}}/T)(-\Theta_{\text{vib}}/T^2)}{2(1 - e^{-\Theta_{\text{vib}}/T})(e^{\Theta_{\text{vib}}/T})(-\Theta_{\text{vib}}/T^2)} \quad (5.3.29)$$

$$= 3R \lim_{T \rightarrow \infty} \frac{(\Theta_{\text{vib}}/T)}{(1 - e^{-\Theta_{\text{vib}}/T})} \quad (5.3.30)$$

$$= 3R \lim_{T \rightarrow \infty} \frac{(-\Theta_{\text{vib}}/T^2)}{-e^{-\Theta_{\text{vib}}/T}(-\Theta_{\text{vib}}/T^2)} \quad (5.3.31)$$

$$= 3R. \quad (5.3.32)$$

In Equation 5.3.28 in the numerator and in going from Equation 5.3.29 to 5.3.30 we have set $e^{\Theta_{\text{vib}}/T}$ to 1, as we may for $T \rightarrow \infty$. As the expression was still indeterminate, we have computed the derivatives of numerator and denominator once again in going from Equation 5.3.30 to 5.3.31 and finally we have once more set $e^{-\Theta_{\text{vib}}/T}$ to 1 in going from Equation 5.3.31 to \refeq{x04}. We see that Einstein's very simple model agrees with the rule of [Dulong and Petit](#).

Note

The model of the Einstein solid differs from a model of N_{Av} one-dimensional harmonic oscillators according to Section [section:harmonic_oscillator] only by a power of 3 in the partition function, which, after computing the logarithm, becomes a factor of 3 in the temperature-dependent term of U_{vib} and thus in C_{vib} . Hence, in the high-temperature limit the vibrational contribution to the molar heat capacity of a gas consisting of diatomic molecules is equal to R . It follows that, in this limit, each molecule contributes an energy $k_{\text{B}}T$ to the internal energy, i.e. each of the two degrees of freedom (potential and kinetic energy of the vibration) that are quadratic in the coordinates contributes a term $k_{\text{B}}T/2$. This agrees with the equipartition theorem. Likewise, the Einstein solid agrees with this theorem.

From experiments it is known that molar heat capacity approaches zero when temperature approaches zero. Again the limiting value can be computed by the approach of de l'Hospital, where this time we can neglect the 1 in $e^{\Theta_{\text{vib}}/T} - 1$, as $e^{\Theta_{\text{vib}}/T}$ tends to infinity for $T \rightarrow 0$. In the last step we obtain

$$\lim_{T \rightarrow 0} C_{\text{vib}} = 6R \lim_{T \rightarrow 0} \frac{1}{e^{\Theta_{\text{vib}}/T}} = 0. \quad (5.3.33)$$

Thus, the Einstein solid also agrees with the limiting behavior of heat capacity at very low temperatures.

Nevertheless the model is 'too simple', and Einstein was well aware of that. Vibrations of the individual atoms are not independent, but rather collective. The lattice vibrations, called phonons, have a spectrum whose computation is outside the scope of the Einstein model. A model that can describe this spectrum has been developed by Debye based on the density of states of frequencies ν . This density of states in turn has been derived by Rayleigh and Jeans based on the idea that the phonons are a system of standing waves in the solid. It is given by

$$D(\nu) = \frac{4\pi\nu^2}{c^3} V. \quad (5.3.34)$$

Debye replaced c by a mean velocity of wave propagation in the solid, considered one longitudinal and two transverse waves and only the $3N$ states with the lowest frequencies, as the solid has only $3N$ vibrational degrees of freedom. These considerations lead to a maximum phonon frequency ν_{max} and, after resubstitution of the mean velocity, to a frequency spectrum that is still proportional to ν^2 and scales with ν_{max}^{-3} . Instead of the characteristic vibration temperature, it is now convenient to define the **Debye temperature**

$$\Theta_{\text{D}} = \frac{h\nu_{\text{max}}}{k_{\text{B}}}. \quad (5.3.35)$$

In this model the molar heat capacity of the solid becomes

$$C_{\text{vib}} = 9R \left(\frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx \quad (5.3.36)$$

The integral can be evaluated numerically after series expansion and finally Debye's T^3 law,

$$\lim_{T \rightarrow 0} C_{\text{vib}} = 233.8R \frac{T^3}{\Theta_D^3}, \quad (5.3.37)$$

results. This law does not only correctly describe that the heat capacity vanishes at absolute zero, it also correctly reproduces the scaling law, i.e., the T^3 dependence that is found experimentally. The high-temperature limit can also be obtained by series expansion and is again Dulong-Petit's value of $3R$.

The Debye model is still an approximation. Phonon spectra of crystalline solids are not featureless. They are approximated, but not fully reproduced, by a ν^2 dependence. The deviations from the Debye model depend on the specific crystal structure.

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