

Statistical Physics

Section 6: The Many Body Problem

In this section we discuss the Many body Problem with reference to a particular context: vibrations of a crystalline solid.

6. 1. Many Particle Schrödinger equation

Consider a system of N distinguishable particles of mass m . (Ignore spin for the moment.) Schrödinger's equation is

$$\hat{H}\Psi(\underline{r}_1, \underline{r}_2, \dots, \underline{r}_N) = E\Psi \quad (1)$$

In general, the Hamiltonian operator is

$$\hat{H} = -\sum_{\alpha=1}^N \frac{\hbar^2 \nabla_{\alpha}^2}{2m} + U(\underline{r}_1, \underline{r}_2, \dots, \underline{r}_N) \quad (2)$$

where α labels the particles and U is the *interaction potential* which depends on the relative positions of all the particles e.g. we could have the Coulomb interaction between particles with charge e

$$U(\underline{r}_1, \underline{r}_2, \dots, \underline{r}_N) = \sum_{\alpha < \gamma = 1}^N \phi(|\underline{r}_{\alpha} - \underline{r}_{\gamma}|) \quad \text{where} \quad \phi = \frac{e^2}{|\underline{r}_{\alpha} - \underline{r}_{\gamma}|} \quad (3)$$

This is an example of a '2-body' interaction.

For the case where $U = 0$, the statistical mechanics of this system can be solved as we have seen in our previous work on weakly interacting systems. However in general when $U \neq 0$ we run up against...

The Bedrock Problem: We cannot solve the many body problem! (except in very special cases).

However, as we have seen, one case where we can solve (1) is when the potential energy term contains no interaction terms i.e. when

$$U(\underline{r}_1, \underline{r}_2, \dots, \underline{r}_N) = \sum_{\alpha} U_{\alpha}(\underline{r}_{\alpha}) . \quad (4)$$

Then we can write the Hamiltonian of (2) as

$$\hat{H} = \sum_{\alpha} \hat{H}_{\alpha} \quad (5)$$

and the many-body eigenfunctions are factorised

$$\Psi(\underline{r}_1, \underline{r}_2, \dots, \underline{r}_N) = \prod_{\alpha} \psi(\underline{r}_{\alpha}) \quad (6)$$

Aside In order to impose indistinguishability we should take suitable symmetrised combinations of these eigenfunctions to form the wavefunctions. Different symmetrised combinations correspond to fermions and bosons.

We refer to (5) as a *diagonal* form of the Hamiltonian since the particles are not coupled by any ‘off-diagonal’ terms such as $H_{\alpha\beta}$.

Crudely speaking, the whole of many body physics is concerned with making transformations and/or approximations which put the Hamiltonian (2) into a diagonal form.

6. 2. Specific heat of a crystalline solid

We consider N atoms situated near the sites of a regular lattice. We call the displacement vector of atom α from the lattice site \underline{r}^α .

Einstein Theory (see P3) Here we simply replace (2) by a non-interacting H

$$\hat{H} = - \sum_{\alpha=1}^N \frac{\hbar^2 \nabla_\alpha^2}{2m} + \sum_{\alpha=1}^N \frac{m\omega^2 |\underline{r}^\alpha|^2}{2} \quad (7)$$

where ω is a free parameter which we can fix by comparing to experimental data. The Hamiltonian is a sum of N 3d quantum harmonic oscillators and ω is the frequency of each oscillator. Thus the physical model is that each atom sits in its own harmonic potential well and oscillates independently of the others.

Figure 1: Left hand: model of crystal solid as atoms connect by harmonic springs (this is the harmonic approximation). Right hand: model of each atom as independent harmonic oscillator (Einstein Model)

Recall that a three dimensional harmonic oscillator is the same as 3 one dimensional harmonic oscillators. Therefore

$$E = \sum_{i=1}^{3N} \epsilon_i \quad \text{where} \quad \epsilon_i = \hbar\omega(n_i + 1/2). \quad (8)$$

Then

$$Z_c = [Z(1)]^{3N}$$

where

$$Z(1) = \sum_{n=0}^{\infty} \exp -\beta\hbar\omega(n + 1/2) = \frac{\exp -\frac{x}{2}}{1 - \exp -x} \quad \text{where} \quad x = \beta\hbar\omega$$

where we have used the geometric series (see tutorial 3.3). We now proceed to calculate the energy:

$$\begin{aligned}
\bar{E} &= -\frac{\partial \ln Z_c}{\partial \beta} \\
&= -3N\hbar\omega \frac{\partial}{\partial x} \left[-\ln(1 - \exp -x) - \frac{x}{2} \right] \\
&= 3N\hbar\omega \left[\frac{\exp -x}{1 - \exp -x} + \frac{1}{2} \right] \\
&= \text{constant} + 3N\hbar\omega \frac{1}{\exp x - 1}
\end{aligned} \tag{9}$$

The heat capacity is given by

$$C_V = \left(\frac{\partial \bar{E}}{\partial T} \right)_V = \left(\frac{\partial x}{\partial T} \right)_\omega \left(\frac{\partial \bar{E}}{\partial x} \right)_\omega$$

Note that here the ‘constant volume’ constraint on the partial derivative is the same as the ‘constant ω ’ constraint. This is because the only way volume (or any other variable except temperature) can enter into the model is through the parameter ω .

We find

$$\begin{aligned}
C_V &= -3N \frac{(\hbar\omega)^2}{kT^2} \frac{d}{dx} \left[\frac{1}{\exp x - 1} \right] \\
&= 3Nk \frac{x^2 \exp x}{(\exp x - 1)^2}
\end{aligned} \tag{10}$$

The Einstein model does not do badly for such a simple approximation but it breaks down at low temperatures ($x = \hbar\omega/kT \gg 1$) where the predicted heat capacity

$$\frac{C_V}{3NK} \simeq (\hbar\omega/kT)^2 \exp(-\hbar\omega/kT)$$

is not borne out experimentally—instead a T^3 behaviour is observed.

The reason is that at low temperatures co-operative effects become important and one has to consider collective oscillations of the atoms rather than the independent oscillations of the Einstein theory which is only a reasonable approximation at high temperatures.

6. 3. Harmonic Approximation, Phonons and Debye Theory

Recall we denote by $\underline{r}^{(\alpha)}$ the displacement of atom α from its equilibrium position and $x_i^{(\alpha)}$ as its i th Cartesian component. In general the potential energy U could be a very complicated function $U(\underline{r}^{(1)}, \underline{r}^{(2)}, \dots, \underline{r}^{(N)})$ of the displacements of the atoms.

Now assuming the displacements are small we can make a Taylor series expansion (in $3N$ variables $x_i^{(\alpha)}$)

$$U = U_0 + \sum_{\alpha,i} \left. \frac{\partial U}{\partial x_i^{(\alpha)}} \right|_0 x_i^{(\alpha)} + \frac{1}{2} \sum_{\alpha,i,\gamma,j} \left. \frac{\partial^2 U}{\partial x_i^{(\alpha)} \partial x_j^{(\gamma)}} \right|_0 x_i^{(\alpha)} x_j^{(\gamma)} + \dots$$

Since U must be a minimum at the equilibrium positions the second term (linear in the x s is zero) vanishes. Retaining only the final term on the rhs is known as ‘the harmonic approximation’. Abbreviating the second partial derivatives to $A_{i\alpha j\gamma}$ we may write the total Hamiltonian as

$$\hat{H} = - \sum_{\alpha=1}^{3N} \frac{\hbar^2 \nabla_{\alpha}^2}{2} + \frac{1}{2} \sum_{\alpha, i, \gamma, j} A_{i\alpha j\gamma} x_i^{(\alpha)} x_j^{(\gamma)} \quad (11)$$

Now in principle we can *diagonalise* this Hamiltonian by transforming to appropriate coordinates. This is because it is simply the Hamiltonian of a system of $3N$ coupled harmonic oscillators.

Recall from second year Mathematical Physics that systems of coupled oscillators have normal modes in which all the displacements oscillate with the same frequency. The motion of the system can then be expressed in terms of the a superposition of normal mode excitations and the energy can be expressed as the sum of the energy in each normal mode.

Moreover we can, in principle, make a transformation to *normal co-ordinates* $q_r = \sum_{i\alpha} \lambda_{ri\alpha} x_i^{(\alpha)}$ where here $\lambda_{ri\alpha}$ are the components of the transformation matrix. Note that the normal coordinates are collective co-ordinates involving all the $x_i^{(\alpha)}$ and describe complicated **co-operative oscillations**. Since there are $3N$ co-ordinates $x_i^{(\alpha)}$, there are $3N$ normal modes.

We do not wish to get into the details of the transformation to normal coordinates but just note the important result that after transforming to the normal co-ordinates q_r labelled by r ($r = 1 \dots 3N$) the Hamiltonian (11) becomes

$$\hat{H} = - \sum_{r=1}^{3N} \frac{\hbar^2}{2m} \frac{\partial^2}{\partial q_r^2} + \sum_{r=1}^{3N} \frac{m\omega_r^2 |q_r|^2}{2m} \quad (12)$$

which is of diagonal form i.e. the normal mode coordinates diagonalise the Hamiltonian

The normal modes are quantum oscillators, and the quanta of energy are known as **phonons**. Phonons really do exist and are much-studied experimentally e.g. by scattering neutrons or x-rays off the solid.

Thus

$$E = \sum_{r=1}^{3N} \hbar\omega_r (n_r + 1/2) \quad n_r = \text{number of phonons in mode } r \quad (13)$$

We now proceed to compute the canonical partition function

$$Z_c = \prod_{r=1}^{3N} Z_r \quad \text{where} \quad Z_r = \frac{\exp -x_r/2}{1 - \exp -x_r} \quad \text{with} \quad x_r = \beta\hbar\omega_r$$

The energy follows as

$$\begin{aligned} \bar{E} &= - \frac{\partial \ln Z_c}{\partial \beta} \\ &= \text{constant} + \sum_r \hbar\omega_r \frac{1}{\exp \beta\hbar\omega_r - 1} \end{aligned} \quad (14)$$

We can ignore the first term as it is just a constant. The second can be compared to the energy of an ideal Bose gas at $\mu = 0$. The phonons behave with Bose statistics and $\frac{1}{\exp \beta\hbar\omega_r - 1}$ is the mean number of phonons in mode r . Thus we have a gas of phonons

(the chemical potential $\mu = 0$ since the number of phonons is not a conserved quantity). Using a density of modes we can write the energy as

$$\bar{E} = \int \hbar\omega \frac{1}{\exp \beta\hbar\omega - 1} g(\omega) d\omega \quad (15)$$

To calculate \bar{E} we need the spectrum of frequencies ω_r i.e. the ‘phonon spectrum’ or *density of modes*

$$g(\omega)d\omega = \text{the number of modes with frequency between } \omega \text{ and } \omega + d\omega.$$

In second year one calculated normal modes and normal coordinates for systems of $N = 2$ or 3 particles in one dimension. Continuing this programme for large N in 3d, to obtain the full normal mode spectrum is generally very difficult! Thus approximations are required.

Debye Theory

The Debye theory is to posit a form for the density of modes

$$g(\omega) = AV\omega^2 \quad (16)$$

This can be motivated by a calculation of the low frequency modes that correspond to sound waves. For these modes the wavelength λ is much larger than the lattice spacing a : $\lambda \gg a$. The idea is then to treat the crystalline solid as an elastic medium and write down a classical wave equation which, for standing waves, reads

$$\nabla^2\phi + k^2\phi = 0 .$$

here $\phi(\underline{r})$ is the displacement field i.e. the displacement from equilibrium of an atom at position \underline{r} ; k is the magnitude of the 3d wavevector \underline{k} , the wavelength is given by $\lambda = 2\pi/k$ and $k = \omega/c$ where c is the speed of sound in the solid.

Thus the calculation of the density of modes is basically the same as was done in Physics 3 for EM radiation. A slight complication in the present case is that the speed of sound is different for *longitudinal* waves (where the atomic displacements are parallel to the wave propagation direction) than for *transverse* waves (where the displacements are orthogonal to the propagation direction). For transverse waves there are two orthogonal polarisations. See Baierlein for details. Here we content ourselves with simply assuming (16).

Now recall that there should be $3N$ normal modes in total. To respect this we introduce a ‘cut-off’ frequency ω_{\max} . Thus

$$\int_0^{\omega_{\max}} AV\omega^2 d\omega = \frac{AV\omega_{\max}^3}{3} = 3N , \quad (17)$$

from which we find

$$\omega_{\max} = \left(\frac{9\rho}{A}\right)^{1/3} . \quad (18)$$

Thus there is just one free parameter which we can take to be ω_{\max} .

This maximum frequency defines a characteristic temperature, usually written as Θ_D (although in lectures I used T^*), through

$$k_B\Theta_D = \hbar\omega_{\max} \quad (19)$$

Thus we can take the free parameter as Θ_D .

We now proceed to calculate the energy through

$$\begin{aligned}\bar{E} &= \int_0^\infty \hbar\omega g(\omega) \overline{n(\omega)} d\omega \\ &= AV\hbar \int_0^{\omega_{\max}} \frac{\omega^3}{\exp(\beta\hbar\omega) - 1} d\omega\end{aligned}$$

First consider the high T limit $T \gg \Theta_D (= \hbar\omega_{\max}/k_B)$ which implies $\hbar\omega/k_B T \ll 1$. We expand $\exp(\beta\hbar\omega) \simeq 1 + \beta\hbar\omega$ to obtain

$$\bar{E} \simeq AV\hbar \int_0^{\omega_{\max}} \frac{\omega^3}{\beta\hbar\omega} d\omega = 3Nk_B T \quad (20)$$

where we have used (17). (20) is just the equipartition result—as we expect, high temperature recovers a classical limit and h disappears from physical results.

Now consider the low T limit $T \ll \Theta_D$. In this case we change variables to $x = \beta\hbar\omega$ to get the dependence on physical parameters out of the integral and leave the dimensionless integral as a constant:

$$\bar{E} = \frac{AV\hbar}{(\beta\hbar)^4} \int_0^{\Theta_D/T} \frac{x^3}{\exp(x) - 1} dx$$

Now for $T \ll \Theta_D$ we can replace the upper limit of the integral by infinity and obtain an integral whose value happens to be $\pi^4/15$. The precise value is actually not important here, what is important is that it is a finite, non-zero constant.

Thus at low temperatures $\bar{E} \propto T^4$ and the heat capacity

$$C_V \propto T^3 \quad (21)$$

which is the key result of the Debye theory and improves greatly upon the Einstein model prediction. It is well borne experimentally for e.g. for copper or solid Argon (see Baierlein Fig. 6.9; Mandl Fig. 6.7). For comparison with experiment there is a single fitting parameter—the Debye temperature Θ_D .

Note that at low T only the low frequency modes will be excited and it is precisely these modes that are correctly described by the Debye theory as sound waves (i.e. by approximating the solid by an elastic medium). Thus the Debye theory is correct at both low and high T ! (But remains an approximation in between).

6. 4. The importance of the density of modes

Recall that the energy for both EM radiation (see Physics 3) and the vibrational energy of the crystalline solid can be written as

$$\bar{E} = \int_0^\infty \hbar\omega g(\omega) \overline{n(\omega)} d\omega$$

where $\overline{n(\omega)}$ is the B-E distribution. Thus the way that the details of the system/theory/model enter is through the density of modes $g(\omega)$.

This has several implications

- Seemingly disparate systems will be described by the same theory if they have the same form of $g(\omega)$ e.g. blackbody radiation and the Debye theory of crystalline solids both have $g(\omega) \propto \omega^2$
- One can build up better and better theories by making better and better approximations to the true density of modes (which is often very complicated)

e.g.

For the crystalline solid the Einstein model (which considers oscillators all of the same frequency) corresponds to a density of modes that is a delta function at a single frequency (the Einstein frequency).

The Debye theory is an improvement corresponding to a density of modes with a quadratic frequency dependence, cut off at ω_{\max} (the Debye frequency).