

Problem 1. Momentum operator Show that the state $\psi_k(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}$ is an eigenstate of the momentum operator $\hat{\mathbf{p}} = -i\hbar\nabla$ and find the eigenvalue.

Solution. A state $|a\rangle$ is an eigenstate of an operator A if $A|a\rangle = a|a\rangle$, where a is a number and eigenvalue of $|a\rangle$ [1, p. 12]. Note that

$$\hat{\mathbf{p}}\psi_k(\mathbf{r}) = -i\hbar\nabla e^{i\mathbf{k}\cdot\mathbf{r}} = -i\hbar(i\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{r}} = \hbar\mathbf{k}e^{i\mathbf{k}\cdot\mathbf{r}} = \hbar\mathbf{k}\psi_k(\mathbf{r}),$$

so we have shown that $\psi_k(\mathbf{r})$ is an eigenvector of $\hat{\mathbf{p}}$ with eigenvalue $\hbar\mathbf{k}$. □

Problem 2. Density of states for free electrons

2(a) What is the fermi wavevector and fermi energy as a function of particle density for a free electron gas in one and two dimensions (define density appropriately)?

Solution. In three dimensions, the total number of occupied states inside the fermi sphere is given by Eq. (2.8) of the lecture notes,

$$N = 2 \frac{4\pi k_F^3/3}{(2\pi/L)^3}, \quad (1)$$

where k_F is the fermi wavevector, $L^3 = V$ is the volume, and 2 is the number of electron spin states. By inspection, then, the one- and two-dimensional equivalents to this equation are

$$N = 2 \frac{k_F}{2\pi/L} \quad (d=1), \quad N = 2 \frac{\pi k_F^2}{(2\pi/L)^2} \quad (d=2),$$

where k_F is the length of a one-dimensional fermi line and πk_F^2 is the area of a fermi circle of radius k_F . The one-dimensional volume is L , and the two-dimensional volume is L^2 . Solving for the wavevectors and writing them in terms of particle density $n = N/V$, we obtain

$$k_F = \pi n \quad (d=1), \quad k_F = \sqrt{2\pi n} \quad (d=2).$$

The fermi momentum is $p_F = \hbar k_F$ and the fermi energy is $E_F = p_F^2/2m$ [2, p. 36]. Both definitions hold regardless of dimension. So the fermi energy in one and two dimensions is

$$E_F = \frac{\pi^2 \hbar^2 n^2}{2m} \quad (d=1), \quad E_F = \frac{\pi \hbar^2 n}{m} \quad (d=2).$$

2(b) Calculate the density of states in energy for free electrons in one and two dimensions.

Solution. According to Eq. (2.10) of the lecture notes, the density of states $g(E)$ can be found by

$$g(E) dE = 2 \cdot \frac{\text{Volume of shell in } k \text{ space}}{\text{Volume of } k \text{ space per state}} = 2 \frac{4\pi k^2 dk}{(2\pi)^3/V},$$

where the final equality is for the three-dimensional case. For one and two dimensions, the equivalent expressions are

$$g(E) dE = 2 \frac{dk}{2\pi/L} \quad (d=1), \quad g(E) dE = 2 \frac{2\pi k dk}{(2\pi)^2/L^2} \quad (d=2).$$

Noting that

$$k = \sqrt{\frac{2mE}{\hbar^2}} \implies \frac{dk}{dE} = \sqrt{\frac{m}{2\hbar^2 E}},$$

which again is true regardless of dimension. So we find

$$\begin{aligned} (d=1) \quad g(E) &= \frac{L}{\pi} \frac{dk}{dE} = \frac{L}{\pi} \sqrt{\frac{m}{2\hbar^2 E}}, \\ (d=2) \quad g(E) &= \frac{L^2 k}{\pi} \frac{dk}{dE} = \frac{L^2}{\pi} \sqrt{\frac{2mE}{\hbar^2}} \sqrt{\frac{m}{2\hbar^2 E}} = \frac{L^2 m}{\pi \hbar^2}. \end{aligned}$$

Per unit volume, we have

$$g(E) = \frac{1}{\pi} \sqrt{\frac{m}{2\hbar^2 E}} \quad (d=1), \quad g(E) = \frac{L^2 m}{\pi \hbar^2} \quad (d=2).$$

2(c) Show how the 3D density of states can be rewritten as

$$\frac{3}{2} \frac{n}{E_F} \sqrt{\frac{E}{E_F}} \quad (2)$$

with $n = N/V$.

Solution. The 3D density of states per unit volume is given by Eq. (2.11) in the lecture notes,

$$g(E) = \frac{V}{\pi^2} \frac{m}{\hbar^2} \sqrt{\frac{2mE}{\hbar^2}}.$$

We will work backward to reach this form from Eq. (2).

Equation (1) can be written as follows:

$$N = 2 \frac{4\pi/3}{(2\pi)^3/V} \left(\frac{2mE_F}{\hbar^2} \right)^{3/2} \implies n = \frac{(2mE_F)^{3/2}}{3\pi^2 \hbar^3} \implies E_F^3 = \frac{(3\pi^2 \hbar^3 n)^2}{(2m)^3},$$

where we have used $k = \sqrt{2mE/\hbar^2}$. Feeding the last expression into Eq. (2), we obtain

$$g(E) = \frac{3}{2} n \sqrt{\frac{E}{E_F^3}} = \frac{3}{2} n \sqrt{E \frac{(2m)^3}{(3\pi^2 \hbar^3 n)^2}} = \frac{1}{\pi^2} \frac{m}{\hbar} \sqrt{\frac{2mE}{\hbar^2}}$$

as desired. □

Problem 3. Thermodynamic properties of a free electron metal

3(a) Derive the free electron formula for the fermi energy E_F , the fermi wavevector k_F , and the density of states at the fermi level $g(E_F)$.

Solution. A free electron has a wave function that is the solution of the time-independent Schrödinger equation. The solutions to this equation, subject to periodic boundary conditions, are plane waves: $\psi_{\mathbf{k}}(\mathbf{r}) \propto e^{i\mathbf{k} \cdot \mathbf{r}}$, where \mathbf{r} is the electron's position and \mathbf{k} its wavevector. The energy associated with such a state is $\epsilon_{\mathbf{k}} = \hbar^2 k^2 / 2m$, where $k = |\mathbf{k}|$. This follows because $\psi_{\mathbf{k}}(\mathbf{r})$ is an eigenstate of the momentum operator with eigenvalue $\hbar \mathbf{k}$, as was shown in problem 1 [2, pp. 32–34].

The allowed values of the components of \mathbf{k} are $k_i = 2\pi \varnothing / L$, where n_i are integers and $V = L^3$ is the volume of the metal. In the ground state at zero temperature, N free electrons fill the available one-electron energy levels of lowest energy. Two electrons of opposite spin can occupy each one-electron energy level. For large N , the filled levels occupy a sphere in k space; the shape is a sphere because it minimizes the energy of each state. The radius of this sphere is the magnitude of the wavevector corresponding to the state of highest energy, the fermi wavevector k_F . So the number of electrons that can occupy the fermi sphere is

$$N = \frac{4\pi k_F^3}{3} \frac{V}{(2\pi)^3},$$

where the first fraction is the volume of the Fermi sphere and the second is the quantization. Solving for k_F , we find the expression

$$k_F = (3\pi^2 n)^{1/3},$$

where $n = N/V$ is the density of electrons [2, pp. 34–36].

From this expression, we can easily write down the expression for the fermi energy:

$$E_F = \frac{\hbar^2 k_F^2}{2m} = \frac{\hbar^2 (3\pi^2 n)^{2/3}}{2m}. \quad (3)$$

The density of states $g(E)$ of a particular energy E represents the quantization of the spherical shell in k space whose radius corresponds to the energy. Since two electrons can occupy each state, this gives us

$$g(E) = 2(4\pi k^2) \left(\frac{L}{2\pi} \right)^3 = \frac{k^2 V}{\pi^2}.$$

3(b) Within the free electron model at zero temperature, show that the total energy for N electrons is $\bar{E} = 3NE_F/5$.

Solution. The general expression for the energy density is Eq. (2). The internal energy density $u = U/V$ is given by Eq. (2.14) in the lecture notes:

$$u = \int dE E g(E) f(E).$$

At zero temperature, the fermi distribution $f(E)$ is a step function [2, p. 45]. So this becomes

$$u = \int_0^{E_F} dE E \frac{3}{2} \frac{n}{E_F} \sqrt{\frac{E}{E_F}} = \frac{3}{2} \frac{n}{E_F^{3/2}} \int_0^{E_F} E^{3/2} = \frac{3}{2} \frac{n}{E_F^{3/2}} \frac{2}{5} E_F^{5/2} = \frac{3}{5} n E_F.$$

Multiplying both sides by V and noting that $\bar{E} = Vu$, we find

$$\bar{E} = \frac{3}{5} N E_F \quad (4)$$

as desired. □

3(c) Within the free electron model at zero temperature, calculate the pressure, p , using $p = -d\bar{E}/d\Omega$, where Ω is the volume.

Solution. Substituting Eq. (3) into Eq. (4) yields

$$\bar{E} = \frac{3}{5} N \frac{\hbar^2 (3\pi^2 n)^{2/3}}{2m} = \frac{3}{5} \frac{\hbar^2 (3\pi^2)^{2/3} N^{5/3}}{2m \Omega^{2/3}}.$$

Then

$$p = -\frac{d\bar{E}}{d\Omega} = -\frac{3}{5} \frac{\hbar^2 (3\pi^2)^{2/3} N^{5/3}}{2m} \frac{d}{d\Omega} \left(\frac{1}{\Omega^{2/3}} \right) = \frac{2}{5} \frac{\hbar^2 (3\pi^2)^{2/3} N^{5/3}}{2m\Omega^{5/3}} = \frac{2}{5} \frac{N}{\Omega} \frac{\hbar^2 (3\pi^2 N)^{2/3}}{2m\Omega^{2/3}} = \frac{2}{5} n E_F. \quad (5)$$

3(d) Within the free electron model at zero temperature, calculate the bulk modulus $B = -\Omega dp/d\Omega$.

Solution. Using Eq. (5),

$$\frac{dp}{d\Omega} = \frac{2}{5} \frac{\hbar^2 (3\pi^2)^{2/3} N^{5/3}}{2m} \frac{d}{d\Omega} \left(\frac{1}{\Omega^{5/3}} \right) = -\frac{2}{3} \frac{\hbar^2 (3\pi^2)^{2/3} N^{5/3}}{2m\Omega^{8/3}},$$

and so

$$B = -\Omega \frac{dp}{d\Omega} = \frac{2}{3} \frac{\hbar^2 (3\pi^2)^{2/3} N^{5/3}}{2m\Omega^{5/3}} = \frac{2}{3} n E_F.$$

3(e) Potassium is monovalent and has an atomic concentration of $1.402 \times 10^{28} \text{ m}^{-3}$. Compare the bulk modulus calculated in 3(d) with the experimental value of $3.7 \times 10^9 \text{ Pa}$.

Solution. Applying $B = -\Omega dp/d\Omega$ and Eq. (3), we find

$$B = \frac{2}{3} \frac{\hbar^2 (3\pi^2)^{2/3} n^{5/3}}{2m_e} = \frac{2}{3} \frac{(1.055 \times 10^{-34} \text{ J s})^2 (3\pi^2)^{2/3} (1.402 \times 10^{28} \text{ m}^{-3})^{5/3}}{2(9.109 \times 10^{-31} \text{ kg})} = 3.2 \times 10^9 \text{ Pa},$$

where m_e is the electron mass [3]. This result is within 15% of the experimental value.

3(f) Estimate $g(E_F)$ for magnesium, which has a valence of 2 and an atomic concentration of $4.3 \times 10^{28} \text{ m}^{-3}$. Use this value to estimate the asymptotic low temperature specific heat, compared to the experimental value of $c_v/T = 1.3 \text{ mJ mol}^{-1} \text{ K}^{-2}$.

Solution. Using Eqs. (2) and (3),

$$g(E_F) = \frac{3}{2} \frac{n}{E_F} \sqrt{\frac{E_F}{E_F}} = \frac{3}{2} \frac{2m_e n^{1/3}}{\hbar^2 (3\pi^2)^{2/3}} = \frac{3}{2} \frac{2(9.109 \times 10^{-31} \text{ kg}) [2(4.3 \times 10^{28} \text{ m}^{-3})]^{1/3}}{(1.055 \times 10^{-34} \text{ J s})^2 (3\pi^2)^{2/3}} = 1.132 \times 10^{47} \text{ J}^{-1} \text{ m}^{-3},$$

where n is twice the given concentration since magnesium has a valence of 2.

According to Eq. (2.20) of the lecture notes, the asymptotic low temperature specific heat can be written

$$c_v = \frac{\pi^2}{3} k_B^2 T g(E_F),$$

so

$$\frac{c_v}{T} = \frac{\pi^2}{3} (1.381 \times 10^{-23} \text{ J K}^{-1})^2 (1.132 \times 10^{47} \text{ J}^{-1} \text{ m}^{-3}) = 71.03 \text{ J K}^{-2} \text{ m}^{-3}.$$

With the Avogadro constant N_A [3], we can use the given number density to convert between volume and moles:

$$\frac{n}{N_A} = \frac{4.3 \times 10^{28} \text{ m}^{-3}}{6.022 \times 10^{23} \text{ mol}^{-1}} = 71.404 \times 10^3 \text{ mol m}^{-3}.$$

Then we have

$$\frac{c_v}{T} = \frac{71.03 \text{ J K}^{-2} \text{ m}^{-3}}{71.404 \times 10^3 \text{ mol m}^{-3}} = 0.99 \text{ mJ mol}^{-1} \text{ K}^{-2},$$

which is within 25% of the experimental value.

Problem 4. Acoustic phonon dispersion in the monatomic chain By substituting Eq. (2.24) in Eq. (2.23) derive the dispersion relation Eq. (2.25) for the one-dimensional monatomic chain.

Solution. Equation (2.23) is

$$m \frac{\partial^2 u_n}{\partial t^2} = K(u_{n+1} - u_n) + K(u_{n-1} - u_n), \quad (6)$$

and Eq. (2.24) is

$$u_n(t) = u_0 \cos[qr_n - \omega(q)t]. \quad (7)$$

Using $r_n = na$ from p. 17 of the lecture notes, note that

$$\begin{aligned} \frac{2}{u_0}(u_{n+1} - u_n) &= 2 \{ \cos[q(n+1)a - \omega(q)t] - \cos[qna - \omega(q)t] \} \\ &= e^{iqna} e^{iqa} e^{-i\omega(q)t} + e^{-iqna} e^{-iqa} e^{i\omega(q)t} - e^{iqna} e^{-i\omega(q)t} - e^{-iqna} e^{i\omega(q)t} \\ &= e^{iqna} e^{-i\omega(q)t} (e^{iqa} - 1) + e^{-iqna} e^{i\omega(q)t} (e^{-iqa} - 1), \end{aligned}$$

and likewise

$$\frac{2}{u_0}(u_{n-1} - u_n) = \frac{e^{iqna} e^{-i\omega(q)t} (e^{-iqa} - 1) + e^{-iqna} e^{i\omega(q)t} (e^{iqa} - 1)}{2}.$$

Feeding these results into Eq. (6) yields

$$\begin{aligned} \frac{2m}{Ku_0} \frac{\partial^2 u_n}{\partial t^2} &= e^{iqna} e^{-i\omega(q)t} (e^{iqa} - 1) + e^{-iqna} e^{i\omega(q)t} (e^{-iqa} - 1) + e^{iqna} e^{-i\omega(q)t} (e^{-iqa} - 1) + e^{-iqna} e^{i\omega(q)t} (e^{iqa} - 1) \\ &= e^{iqna} e^{-i\omega(q)t} (e^{iqa} + e^{-iqa} - 2) + e^{-iqna} e^{i\omega(q)t} (e^{-iqa} + e^{iqa} - 2) \\ &= (e^{iqna} e^{-i\omega(q)t} + e^{-iqna} e^{i\omega(q)t}) (e^{iqa} + e^{-iqa} - 2) \\ &= 2 \cos[qna - \omega(q)t] [2 \cos(qa) - 2]. \end{aligned} \quad (8)$$

Differentiating Eq. (7), we find

$$\frac{\partial^2 u_n}{\partial t^2} = \frac{\partial}{\partial t} \left(\frac{\partial u_n}{\partial t} \right) = \frac{\partial}{\partial t} \{ u_0 \omega(q) \sin[qr_n - \omega(q)t] \} = -u_0 \omega^2(q) \cos[qr_n - \omega(q)t].$$

Making this substitution in Eq. (8) gives us

$$-\frac{m\omega^2(q)}{K} = 2[\cos(qa) - 1],$$

implying

$$m\omega^2(q) = 2K[1 - \cos(qa)] = 4K \sin^2\left(\frac{qa}{2}\right), \quad (9)$$

which is Eq. (2.25). □

Problem 5. Acoustic and optic phonons in the diatomic chain In the diatomic chain, we take the unit cell to be of length a , and take x_A and x_B to be the coordinates of the A and B atoms within the unit cell. Hence, in the n th cell,

$$r_{n,A} = na + x_A;$$

$$r_{n,B} = na + x_B$$

5(a) In the equations of motion Eq. (2.30), look for solutions of the form

$$u_{n,\alpha} = e_\alpha(q) \exp(i[qr_{n,\alpha} - \omega(q)t]) + e_\alpha^*(q) \exp(i[-qr_{n,\alpha} + \omega(q)t]) \quad (10)$$

where $\alpha = A$ or B , and e_α are complex numbers that give the amplitude and phase of the oscillation of the two atoms.

Separating out the terms that have the same time dependence, show that (for equal masses, $m_A = m_B = m$)

$$\begin{aligned} m\omega^2(q)e_A(q) &= D_{AA}(q)e_A(q) + D_{AB}(q)e_B(q), \\ m\omega^2(q)e_B(q) &= D_{BA}(q)e_A(q) + D_{BB}(q)e_B(q), \end{aligned}$$

where

$$\begin{aligned} D_{AA}(q) &= D_{BB}(q) = K + K', \\ -D_{AB}(q) &= K \exp(iq[r_{n,B} - r_{n,A}]) + K' \exp(iq[r_{n-1,B} - r_{n,A}]), \\ -D_{BA}(q) &= K \exp(iq[r_{n,A} - r_{n,B}]) + K' \exp(iq[r_{n+1,A} - r_{n,B}]). \end{aligned}$$

Check that $D_{AB} = D_{BA}^*$.

Solution. Equation (2.30) is

$$m_A \frac{\partial^2 u_{n,A}}{\partial t^2} = K(u_{n,B} - u_{n,A}) + K'(u_{n-1,B} - u_{n,A}), \quad m_B \frac{\partial^2 u_{n,B}}{\partial t^2} = K'(u_{n+1,A} - u_{n,B}) + K(u_{n,A} - u_{n,B}). \quad (11)$$

Note that

$$\begin{aligned} \frac{\partial^2 u_{n,\alpha}}{\partial t^2} &= \frac{\partial}{\partial t} \{ -i\omega(q)e_\alpha(q) \exp(i[qr_{n,\alpha} - \omega(q)t]) + i\omega(q)e_\alpha^*(q) \exp(i[-qr_{n,\alpha} + \omega(q)t]) \} \\ &= -\omega^2(q) \{ e_\alpha(q) \exp(i[qr_{n,\alpha} - \omega(q)t]) + e_\alpha^*(q) \exp(i[-qr_{n,\alpha} + \omega(q)t]) \} \\ &= -\omega^2(q)u_{n,\alpha}, \end{aligned}$$

so the first of Eq. (10) can be written

$$\begin{aligned} [K + K' - m_A\omega^2(q)]u_{n,A} &= Ku_{n,B} + K'u_{n-1,B}, \\ &= Ke_B(q)e^{iqr_{n,B}}e^{-i\omega(q)t} + Ke_B^*(q)e^{-iqr_{n,B}}e^{i\omega(q)t} + K'e_B(q)e^{iqr_{n-1,B}}e^{-i\omega(q)t} \\ &\quad + K'e_B^*(q)e^{-iqr_{n-1,B}}e^{i\omega(q)t} \\ &= Ke_B(q)e^{iq[na+x_B]}e^{-i\omega(q)t} + K'e_B(q)e^{iq[(n-1)a+x_B]}e^{-i\omega(q)t} + Ke_B^*(q)e^{-iq[na+x_B]}e^{i\omega(q)t} \\ &\quad + K'e_B^*(q)e^{-iq[(n-1)a+x_B]}e^{i\omega(q)t} \\ &= (K + e^{-iqa}K')e_B(q)e^{iq(na+x_B)}e^{-i\omega(q)t} + (K + e^{-iqa}K')e_B^*(q)e^{-iq(na+x_B)}e^{i\omega(q)t} \\ &= (K + e^{-iqa}K')u_{n,B}. \end{aligned}$$

Generalizing this, we have

$$[K + K' - m_A\omega^2(q)]u_{n,A} = (K + e^{-iqa}K')u_{n,B}, \quad [K + K' - m_B\omega^2(q)]u_{n,B} = (K + e^{iqa}K')u_{n,A}.$$

Collecting terms of like time dependence yields

$$[K + K' - m\omega^2(q)]e_A(q)e^{iqr_{n,A}} = (K + e^{-iqa}K')e_B(q)e^{iqr_{n,B}}, \quad (12)$$

$$[K + K' - m\omega^2(q)]e_B(q)e^{iqr_{n,B}} = (K + e^{iqa}K')e_A(q)e^{iqr_{n,A}}, \quad (13)$$

for $e^{-i\omega t}$, and

$$\begin{aligned}[K + K' - m\omega^2(q)]e_A^*(q)e^{-iqr_{n,A}} &= (K + e^{-iqa}K')e_B^*(q)e^{-iqr_{n,B}}, \\ [K + K' - m\omega^2(q)]e_B^*(q)e^{-iqr_{n,B}} &= (K + e^{-iqa}K')e_A^*(q)e^{-iqr_{n,A}}.\end{aligned}$$

for $e^{i\omega t}$.

Rearranging Eqs. (12) and (13), we have

$$\begin{aligned}m\omega^2(q)e_A(q) &= (K + K')e_A(q) - (K + e^{-iqa}K')e^{iq(r_{n,B}-r_{n,A})}e_B(q) \\ &= (K + K')e_A(q) - (e^{iq(r_{n,B}-r_{n,A})}K + e^{iq(r_{n-1,B}-r_{n,A})}K')e_B(q), \\ m\omega^2(q)e_B(q) &= -(K + e^{iqa}K')e^{iq(r_{n,A}-r_{n,B})}e_A(q) - (K + K')e_B(q) \\ &= -(e^{iq(r_{n,A}-r_{n,B})}K + e^{iq(r_{n+1,A}-r_{n,B})}K')e_A(q) - (K + K')e_B(q),\end{aligned}$$

which gives us

$$\begin{aligned}D_{AA}(q) &= D_{BB}(q) = K + K', \\ D_{AB}(q) &= -e^{iq(r_{n,B}-r_{n,A})}K - e^{iq(r_{n-1,B}-r_{n,A})}K', \\ D_{BA}(q) &= -e^{iq(r_{n,A}-r_{n,B})}K - e^{iq(r_{n+1,A}-r_{n,B})}K',\end{aligned}$$

as we wanted to show. \square

Finally, note that

$$\begin{aligned}D_{BA}^* &= [-e^{iq(r_{n,A}-r_{n,B})}K - e^{iq(r_{n+1,A}-r_{n,B})}K']^* = -e^{iq(r_{n,B}-r_{n,A})}K - e^{iq(r_{n,B}-r_{n+1,A})}K' \\ &= -e^{iq(r_{n,B}-r_{n,A})}K - e^{iq(r_{n,B}-r_{n,A})}e^{-iqa}K' = -e^{iq(r_{n,B}-r_{n,A})}K - e^{iq(r_{n-1,B}-r_{n,A})}K' \\ &= D_{AB}\end{aligned}$$

as desired. \square

5(b) The 2×2 matrix equation can have a nontrivial solution if the determinant vanishes:

$$\begin{vmatrix} D_{AA}(q) - m\omega^2(q) & D_{AB}(q) \\ D_{BA}(q) & D_{BB}(q) - m\omega^2(q) \end{vmatrix} = 0.$$

Hence show that the frequencies of the modes are given by

$$m\omega^2(q) = K + K' \pm \sqrt{(K + K')^2 - 4KK' \sin^2\left(\frac{qa}{2}\right)}.$$

Solution. The determinant is

$$0 = [D_{AA}(q) - m\omega^2(q)][D_{BB}(q) - m\omega^2(q)] - D_{AB}(q)D_{BA}(q) = [D_{AA}(q) - m\omega^2(q)]^2 - D_{AB}(q)D_{BA}(q),$$

which implies

$$\begin{aligned}m\omega^2(q) &= D_{AA}(q) \pm \sqrt{D_{AB}(q)D_{BA}(q)} \\ &= K + K' \pm \sqrt{(e^{iq(r_{n,B}-r_{n,A})}K + e^{iq(r_{n-1,B}-r_{n,A})}K')(e^{iq(r_{n,A}-r_{n,B})}K + e^{iq(r_{n+1,A}-r_{n,B})}K')} \\ &= K + K' \pm \sqrt{(K + e^{-iqa}K')e^{iq(r_{n,B}-r_{n,A})}(K + e^{iqa}K')e^{iq(r_{n,A}-r_{n,B})}}\end{aligned}$$

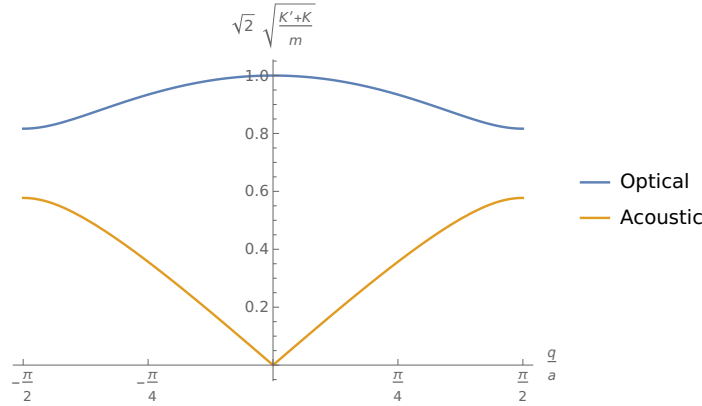


Figure 1: Dispersion curves for $K/K' = 2$. The optical branch (blue) corresponds to the upper sign in Eq. (16), and the acoustic branch (gold) to the lower sign.

$$\begin{aligned}
 &= K + K' \pm \sqrt{(K + e^{-iqa}K')(K + e^{iqa}K')} = K + K' \pm \sqrt{K^2 + (e^{iqa} + e^{-iqa})KK' + K'^2} \\
 &= K + K' \pm \sqrt{K^2 + 2\cos(qa)KK' + K'^2} \tag{14}
 \end{aligned}$$

$$\begin{aligned}
 &= K + K' \pm \sqrt{K^2 + \left[2 - 4\sin^2\left(\frac{qa}{2}\right)\right]KK' + K'^2} \\
 &= K + K' \pm \sqrt{K^2 + 2KK' + K'^2 - 4\sin^2\left(\frac{qa}{2}\right)KK'} \\
 &= K + K' \pm \sqrt{(K + K')^2 - 4KK'\sin^2\left(\frac{qa}{2}\right)}, \tag{15}
 \end{aligned}$$

where we have used the double-angle formula $\cos(2x) = 1 - 2\sin^2(x)$ [4]. \square

5(c) Sketch the dispersion relations when $K/K' = 2$.

Solution. There are two dispersion curves since there are two solutions in Eq. (15). The expressions for the branches are

$$\omega(q) = \frac{1}{\sqrt{m}} \sqrt{K + K' \pm \sqrt{(K + K')^2 - 4KK'\sin^2\left(\frac{qa}{2}\right)}} \begin{cases} \text{optical,} \\ \text{acoustic,} \end{cases} \tag{16}$$

where the acoustic (optical) branch corresponds to the upper (lower) sign. Both branches are shown in Fig. 1, with the $K/K' = 2$ case on the left and the $K = K'$ case on the right.

5(d) Discuss what happens if $K = K'$.

Solution. If $K = K'$, then not only are the masses of the two atoms identical, but so are their restorative forces. Thus, the system is essentially reduced to a monatomic chain [2, p. 437]. Picking up from Eq. (14),

$$m\omega^2(q) = 2K \pm \sqrt{2K^2 + 2\cos(qa)K^2} = 2K \pm K\sqrt{4\cos^2\left(\frac{qa}{2}\right)} = 2K \left[1 - \cos\left(\frac{qa}{2}\right)\right] = 4K\sin^2\left(\frac{qa}{4}\right),$$

where we have used the double-angle formula $\cos(2x) = 2\cos^2(x) - 1$ [4]. This is Eq. (9) with $qa \rightarrow qa/2$. So in this limit, the diatomic chain is reduced to a monatomic chain with lattice constant $a/2$ [2, p. 437].

Problem 6. Lattice specific heat

6(a) From Eq. (2.44) derive the formula for the Debye specific heat Eq. (2.45).

Solution. Equation (2.44) is

$$U_D = \int_0^{\omega_D} d\omega \frac{V\omega^2}{2\pi^2 v^3} \frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1}$$

From Eq. (2.43), $C_V = (\partial U / \partial T)_V$. As on p. 23 of the lecture notes, we multiply the right side by three since there are three acoustic branches. So

$$C_V = 3 \left(\frac{\partial U_D}{\partial T} \right)_V = 3 \int_0^{\omega_D} d\omega \frac{V\omega^2}{2\pi^2 v^3} \hbar\omega \frac{\partial}{\partial T} \left(\frac{1}{e^{\hbar\omega/k_B T} - 1} \right). \quad (17)$$

Let $x = \hbar\omega/k_B T$. Then

$$\frac{\partial}{\partial T} \left(\frac{1}{e^{\hbar\omega/k_B T} - 1} \right) = \frac{\partial x}{\partial T} \frac{\partial}{\partial x} \left(\frac{1}{e^x - 1} \right) = \left(-\frac{\hbar\omega}{k_B T^2} \right) \left(-\frac{e^x}{(e^x - 1)^2} \right) = \frac{\hbar\omega}{k_B T^2} \frac{e^{\hbar\omega/k_B T}}{(e^{\hbar\omega/k_B T} - 1)^2}.$$

So Eq. (17) becomes

$$C_V = 3 \int_0^{\omega_D} d\omega \frac{V\hbar^2\omega^4}{2\pi^2 v^3 k_B T^2} \frac{e^{\hbar\omega/k_B T}}{(e^{\hbar\omega/k_B T} - 1)^2} = 3 \int_0^{\omega_D} d\omega \frac{V k_B^3 T^2}{2\pi^2 \hbar^2 v^3} \frac{x^4 e^x}{(e^x - 1)^2}.$$

We can write $x = \Theta_D/T$, where $\Theta_D = \hbar\omega_D/k_B$ as on p. 23 of the lecture notes. Then, changing our variable of integration,

$$\begin{aligned} C_V &= 3 \int_0^{\Theta_D/T} \frac{k_B T dx}{\hbar} \frac{V k_B^3 T^2}{2\pi^2 \hbar^2 v^3} \frac{x^4 e^x}{(e^x - 1)^2} = 3 \int_0^{\Theta_D/T} \frac{k_B T dx}{\hbar} \frac{V k_B^3 T^2}{2\pi^2 \hbar^2 v^3} \frac{x^4 e^x}{(e^x - 1)^2} = 3 \frac{V k_B^4 T^3}{2\pi^2 \hbar^3 v^3} \int_0^{\Theta_D/T} dx \frac{x^4 e^x}{(e^x - 1)^2} \\ &= 3 \frac{V \omega_D^3}{2\pi^2 v^3} k_B \frac{T^3}{\Theta_D^3} \int_0^{\Theta_D/T} dx \frac{x^4 e^x}{(e^x - 1)^2}. \end{aligned} \quad (18)$$

From Eq. (2.38),

$$\omega_D^3 = \frac{6\pi^2 v^3 N}{V} \implies 3N = \frac{V \omega_D^3}{2\pi^2 v^3}.$$

With this, Eq. (18) becomes

$$C_V = 9N k_B \left(\frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} dx \frac{x^4 e^x}{(e^x - 1)^2}, \quad (19)$$

which is Eq. (2.45). □

6(b) Evaluate the integral at *high* temperature $T \gg \Theta_D$, and therefore determine the high temperature behavior of the specific heat.

Solution. When $\Theta_D \ll T$, $x \ll 1$ in the integrand of Eq. (19), and we can Taylor expand the integrand about $x = 0$ [2, p. 460]. The first term of the expansion, evaluated with Mathematica, is x^2 . Then the specific heat is

$$C_V \sim 9N k_B \left(\frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} dx x^2 = 9N k_B \left(\frac{T}{\Theta_D} \right)^3 \left[\frac{x^3}{3} \right]_{\Theta_D/T} = 3N k_B. \quad (20)$$

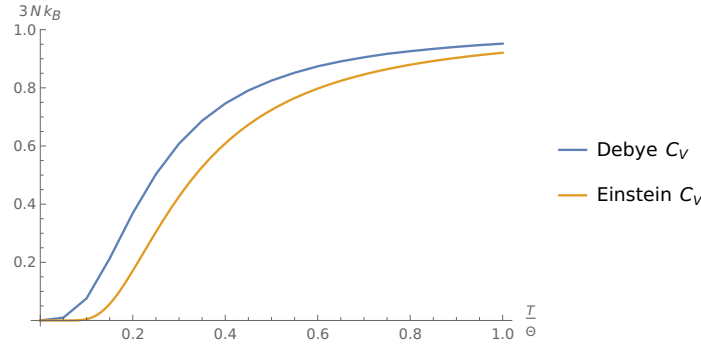


Figure 2: Comparison of the Debye (blue) and Einstein (gold) heat capacity models, where $\Theta = \Theta_D$ or Θ_E as appropriate.

6(c) Using the formula

$$\int_0^\infty dx \frac{x^4 e^x}{(e^x - 1)^2} = \frac{4\pi^4}{15},$$

determine the low temperature behavior of the Debye specific heat.

Solution. Substituting the given formula into Eq. (19) where $\Theta_D/T \gg 1$ for small T , we find

$$C_V \approx 9Nk_B \left(\frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} dx \frac{x^4 e^x}{(e^x - 1)^2} = 9Nk_B \left(\frac{T}{\Theta_D} \right)^3 \frac{4\pi^4}{15} = \frac{12\pi^4}{5} Nk_B \left(\frac{T}{\Theta_D} \right)^3.$$

6(d) Sketch the heat capacity formulae from the Debye and Einstein models and compare them.

Solution. From Eqs. (19) and (20), the Debye specific heat goes as $(T/\Theta_D)^3$ at low temperatures and as $3Nk_B$ at high temperatures. So the shape of the curve will be concave up for small T/Θ_D , and the curve will asymptote as T/Θ_D from the left.

As stated on p. 22 of the lecture notes, the specific heat for the Einstein model is given by Eq. (2.43),

$$C_V = 3Nk_B \left(\frac{\Theta_E}{T} \right)^2 \frac{e^{\Theta_E/T}}{(e^{\Theta_E/T} - 1)^2}$$

where $\Theta_E = \hbar\omega_0/k_B$, and goes as $3e^{-\Theta_E/T}$ at low temperatures and as $3Nk_B$ at high temperatures. So the qualitative shape of the curve will be the same as for the Debye model. However, the Debye curve will rise much more rapidly since it has an extra factor of $4\pi^4/5$. Hence, the Einstein heat capacity will always be less than the Debye heat capacity.

Figure 2 shows both heat capacity formulae. Here, the Einstein curve is evaluated exactly with Mathematica while the Debye curve is drawn using the numerical data from Ashcroft & Mermin [2, p. 461]. As expected, both curves have the same overall shape, and the Einstein curve is below the Debye one. The difference between the models is largest at low temperatures, where the Debye model is in better agreement with experimental data [5, p. 117].

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