Problem 1. Einstein Model of Solid

A solid consists of an array of atoms in a crystal structure shown below. In a simple model (used by Einstein at the advent of quantum mechanics) each atom is assumed to oscillate independently of every other atom¹. The model has one free parameter ω_0 and predicts the general properties of specific heats of solids.

In one dimension a "solid" of N atoms consists of N independent harmonic oscillators. The Hamiltonian of each oscillator is

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega_0^2 x^2$$
 (1)

where m is the mass of the atom. In two dimensions each atom can oscillate in the x direction and the y direction. Thus, the solid of N atoms consists of 2N independent quantum oscillators. The Hamiltonian (or energy) of each atom is a sum of two harmonic oscillators:

$$H = H_x + H_y \tag{2}$$

$$= \left(\frac{p_x^2}{2m} + \frac{1}{2}m\omega_0^2 x^2\right) + \left(\frac{p_y^2}{2m} + \frac{1}{2}m\omega_0^2 y^2\right)$$
(3)

Finally in three dimensions (shown below) the solid of N atoms consists of 3N independent oscillators as shown below, and each atom can oscillate in the x, y, or z directions. The Hamiltonian of each atom shown in Fig. 1 consists of three harmonic oscillators:

$$H = H_x + H_y + H_z \tag{4}$$

$$= \left(\frac{p_x^2}{2m} + \frac{1}{2}m\omega_0^2 x^2\right) + \left(\frac{p_y^2}{2m} + \frac{1}{2}m\omega_0^2 y^2\right) + \left(\frac{p_z^2}{2m} + \frac{1}{2}m\omega_0^2 z^2\right)$$
(5)

The total Hamiltonian is a sum of the Hamiltonians of each atom.

(a) By appealing to the equi-partition theorem for a classical harmonic oscillator, argue that the mean energy of the solid at temperature T is

$$E = 3NkT, (6)$$

if the solid is treated as 3N independent classical oscillators. Determine the specific heat C_V^{1ml} for one mole of substance in this case.

(b) When each the solid is treated as 3N quantum harmonic oscillators, the energy of the solid is $E = 3N \langle \epsilon \rangle$, where the $\langle \epsilon \rangle$ is the average energy of the a single harmonic oscillator. By reviewing the results of previous homework, write down the total energy of the solid at temperature T, and record the mean vibrational quantum number \bar{n} of a single oscillator.

¹In reality the motions of the atoms are coupled to each other, and the oscillation pattern of the solid, may be found by breaking it up into normal modes.



Figure 1:

(c) The figure below shows N = 400 harmonic oscillators in equilibrium sharing the total available energy. The numbers indicate the energy level n of each oscillator – if one oscillator gains a unit of energy, e.g. increasing from $3\hbar\omega_0$ to $4\hbar\omega_0$, the rest of the oscillators will have one less unit of energy to share. Estimate the temperature of the system.

V 0 2 0 0 1 1 0 0 1 0 0 0 2

(d) Show that the specific heat C_V for one mole of solid is²

$$C_V^{1\,\mathrm{ml}} = 3R \frac{(\beta\hbar\omega_0)^2 \exp(-\beta\hbar\omega_0)}{(1 - \exp(-\beta\hbar\omega_0))^2} \,. \tag{8}$$

Make a Taylor series expansion of $C_V^{1\,\text{ml}}$ at high temperature, including the just leading term. What is the specific heat in the ultimate high temperature limit? Your result should be consistent with part (a). Why?

- (e) I downloaded the specific heat of silver and made a graph of the Einstein prediction for $C_V^{1\,\text{ml}}$. The Einstein model has a free parameter $\hbar\omega_0$. The graph below shows the prediction for $\hbar\omega_0 = 2E_0, E_0, E_0/2$ with $E_0 = 0.013 \text{ eV}$. The graph I get for silver is shown below (top) as well as the C_V for other substances (bottom).
 - (i) Diamond is known to be a very hard substance. Loosely explain how this fact is reflected in the data on C_V presented in the figure below? *Hint*: What does the graph of C_V for different substances tell you about the relative strengths of the spring constants of the material?

$$T\frac{\partial}{\partial T} = -\beta \frac{\partial}{\partial \beta} \tag{7}$$

²When computing C_V , it may be helpful to recognize that





Figure 2: Specific heats of solids: (a) The Einstein Model with $\hbar\omega_0$ treated as a parameter compared to the specific heat of silver. The graph approaches 3R at high temperature. (b) The specific heat C_V in units of R of various solids versus temperature. The specific heat approaches 3R at high temperature

Einstein Solid
(a) There are 3N escillators. The Hamiltonian
of the oscillator is

$$H = p^{2} + 1 m w_{0}^{2} \times^{2}$$
So for N = I mol
NA kg = R and So

$$M = p^{2} + 1 m w_{0}^{2} \times^{2}$$
So for N = I mol
NA kg = R and So

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$$M = I m (1 + \bar{m}) \implies 1 = 1 m (1 + \bar{m})$$
So for $\beta = m = 1 m (1 + \bar{m})$

$$KT = hw = m$$

Now we can estimate the \bar{n} by counting up the numbers in the figure and dividing by 400 (the number of atoms). Doing this we find $\bar{n} = 1$. So $\beta \hbar \omega = \ln((1+1)/1) = \ln(2)$ and $kT = \hbar \omega / \ln(2)$.

d) We know that

$$C_{V} = \begin{pmatrix} \partial E \\ \partial T \end{pmatrix} \quad \text{with} \quad E = 3N \quad Ew}{e^{\beta Ew} - 1}$$
We use that for any quantity X

$$\frac{\partial X}{\partial T} = \frac{\partial X}{\partial \beta} \frac{2\beta}{\partial T} = \frac{\partial X}{\partial \beta} \frac{2}{\partial T} \begin{pmatrix} 1 \\ kT \end{pmatrix}$$

$$\frac{\partial X}{\partial T} = \frac{\partial X}{\partial \beta} \frac{2\beta}{\partial T} = \frac{\partial X}{\partial \beta} \frac{2}{\partial T} \begin{pmatrix} kT \end{pmatrix}$$

$$\frac{\partial X}{\partial T} = -k\beta^{2} \frac{2}{\beta X}$$

$$\frac{\partial X}{\partial T} = \frac{2\beta}{\beta \beta}$$
So

$$C_{V} = -k\beta^{2} \frac{2}{\beta \beta} \begin{pmatrix} kw \\ e^{\beta kw} - 1 \end{pmatrix}$$
Differentiating

$$C_{V} = 3Nk\beta^{2} (kw)^{2} e^{\beta kw} (e^{\beta kw} - 1)^{2}$$
For I mal N = NA NB kg = R

$$C_{V}^{Im1} = 3R (\beta kw)^{2} e^{\beta kw} - 1)^{2}$$

In the high temperature limit the mean #
of quanta in the oscillator gets larger and larger.
In this limit the dynamics should be classical.
(see previous homework)
Expanding for
$$\beta \pm w \ll 1$$
 (high temperature), we
approximate:
 $e\beta \pm w \approx 1 \pm \beta \pm w$
And
 $C_v^{(m)} \approx 3R (\beta \pm w)^2 (1)$
 $(1 \pm \beta \pm w - 1)^2$
 $C_v^{(m)} \approx 3R$
 $(\beta \pm w)^2 (1)^2$
 $(1 \pm \beta \pm w)^2$
 $(1 \pm \beta \pm w)^$

Problem 2. An engine cycle

One mole of an ideal monoatomic gas operates in an engine cycle shown below. Here the givens are the temperatures, $T_a = 400 K$ and $T_c = 250 K$, and the pressure, $P_c = 1$ bar. These values are recorded in the table below.



Using the ideal gas law PV = nRT, it is straightforward to show that the volumes at a and c are $V_a = V_c = 20.8 \text{ L}$, and that the pressure at a is $P_a = 1.6 \text{ bar}$, as recorded in the table below.

(a) Find the volume and temperature at b, completing the table shown below.

state	pressure	volume	temperature
a	1.6 bar	$20.8\mathrm{L}$	400 K
b	$1.0\mathrm{bar}$?	?
с	1.0 bar	20.8 L	$250\mathrm{K}$

- (b) Find the work done by the gas per cycle.
- (c) Find the efficiency of the engine.

Solution

(a) We have

$$p_a V_a^{\gamma} = p_b V_b^{\gamma}$$
 with $\gamma = C_p / C_v = 5/3$ for a MAIG (9)

We used the ideal gas relation $C_p^{1\text{ml}} = C_V^{1\text{ml}} + R$. Solving

$$V_b = V_a \left(\frac{p_a}{p_b}\right)^{1/\gamma} = 1.0 \,\mathrm{L} \,\left(\frac{1.6 \,b}{1.0 \,\mathrm{b}}\right)^{1/\gamma} = 27.6 \,\mathrm{L}$$
(10)

The temperature follows

$$P_b V_b = RT_b$$
 $T_b = \frac{P_b V_b}{R} = \frac{1.0 \text{ b} \cdot 27.6 \text{ L}}{8.32 J/^{\circ} \text{K}} = 331 \text{ }^{\circ} \text{K}$ (11)

We used that $1 \text{ b} \cdot \text{L} = 100 \text{ J}.$

(b) For the leg $a \to b$ the work by the system is denoted W_{ba} ; The heat input to the system is $Q_{ba} = 0$; the change in energy is $\Delta U_{ba} = U_b - U_a$. For a gas with constant specific heat

$$U = C_V T \tag{12}$$

For a monoatomic gas, the specific heat is $C_V = \frac{3}{2}Nk$, or for one mole:

$$C_V^{\rm 1ml} = \frac{3}{2}R\,. \tag{13}$$

Thus, by the first law

$$\Delta U_{ba} = Q_{ba} - W_{ba} \Rightarrow U_{ba} = -W_{ba} \tag{14}$$

and so

$$-W_{ba} = \Delta U_{ba} = C_V (T_b - T_a) = -855 \,\mathrm{J} \tag{15}$$

We used $C_V^{\text{1ml}} = 3/2R$.

For the $c \to b$ leg, we proceed similarly using

$$W = \int_{c}^{b} p dV.$$
(16)

Thus

$$\Delta U_{cb} = C_V (T_c - T_b) = -1016 \,\mathrm{J} \tag{17}$$

$$W_{cb} = p(V_c - V_b) = -678 \,\mathrm{J} \tag{18}$$

We also have from the first law that the heat inputted is

$$Q_{cb} = \Delta U_{cb} + W_{cb} = -1694 \,\mathrm{J}\,. \tag{19}$$

Finally for the last leg $c \to a$ we have $W_{ac} = 0$, and thus since by the first law $dU = dQ - dW_{out}$.

$$\Delta U_{ac} = Q_{ac} \tag{20}$$

Using

$$\Delta U_{ac} = C_V (T_a - T_c) = 1872 \,\mathrm{J} \tag{21}$$

we find $Q_{ac} = 1872 \,\mathrm{J}$

Now the efficiency is easily worked out

$$\eta = \frac{W_{\text{net}}}{Q_{\text{in}}} = \frac{W_{ba} + W_{cb}}{Q_{ac}} = \frac{855 - 678}{1872} \simeq 0.095$$
(22)

Problem 3. Isothermal Atmosphere

Consider a gas at temperature T near the earth's surface. The potential energy due to gravity is

$$U = mgz \tag{23}$$

where z is height above the earth's surface, z = 0. Our goal is to use partition functions to evaluate the probality that a particle will have height z above the earth's surface

For simplicity assume that the x, y coordinates are in a large "box" of area L^2 , but the heigh z runs from zero (the earth's surface) to infinity (outer space), i.e.

$$0 < x, y < L \qquad 0 < z < \infty \tag{24}$$

The spatial coordinates are $\boldsymbol{r} = (x, y, z)$ and the momentum coordinates are $\boldsymbol{p} = (p_x, p_y, p_z)$

(a) Write down the Hamiltonian of a particle and compute the (single particle) partition function of the classical particle. You shold find

$$Z_1 = \frac{L^2 \ell (2\pi m k T)^{3/2}}{h^3} \tag{25}$$

where $\ell \equiv kT/mg$. Express Z_1 using the thermal de Broglie wavelength. What are the units of Z_1 ?

(b) Determine the probability distribution

$$\mathrm{d}\mathscr{P}_{\boldsymbol{r},\boldsymbol{p}} = P(\boldsymbol{r},\boldsymbol{p})\mathrm{d}^{3}\boldsymbol{r}\mathrm{d}^{3}\boldsymbol{p}$$
(26)

and show that it factorizes into probability of position $P(\mathbf{r})$ times a probability of momentum $P(\mathbf{p})$.

- (c) By differentiating the partition function (or better $\ln Z$) find: (i) the mean energy $\langle \epsilon \rangle$, and (ii) the variance in the energy $\langle (\delta \epsilon)^2 \rangle$.
- (d) Compute the mean height $\langle z \rangle$ in two ways:
 - (i) Compute the probability distribution for height z, $d\mathscr{P}_z$ by integrating over (or "maginalizing over") the unobserved coordinates. Sketch this distribution and use it to find the mean height $\langle z \rangle$.
 - (ii) Use the equipartition to find the mean kinetic energy and combine this with your result $\langle \epsilon \rangle$ to determine the mean potential energy, $\langle U \rangle$. Are your results from (i) and (ii) consistent with each other?
- (e) Make a reasonable estimate for this height in kilometers, by estimating the the typical mass of an air molecule, and a typical temperature.

Please do not substitute, $k_B = 1.38 \times 10^{-23} \text{J/}^{\circ} \text{K}^{-1}$, and try not to look up numbers. Rather puts the numbers in physical terms, and remember them. A list of useful constants that you need for this course is maintained on the web site.

- (f) (Optional) If the gas density at z = 0 is n_0 , what is the density n(z) at height z?
- (g) (Optional) A mechanical analysis of the forces in the the gas says that

$$\frac{dp(z)}{dz} = -mgn(z) \tag{27}$$

where p(z) is the pressure in the gas at height z. Explain briefly the physical meaning of Eq. (27), and then show that part (e) is consistent with Eq. (27) and the ideal gas law, $pV = n_{\rm ml}RT$ provided the temperature is constant.

Solution

(a) The Hamiltonian is the kinetic plus potential energy as a function of p and r

$$\mathcal{H}(\boldsymbol{r},\boldsymbol{p}) = \frac{p^2}{2m} + mgz \tag{28}$$

with $p^2 = p_x^2 + p_y^2 + p_z^2$ the squared magnitude of the momentum. The partition function

$$Z_1 = \int \frac{\mathrm{d}^3 \boldsymbol{r} \mathrm{d}^3 \boldsymbol{p}}{h^3} e^{-p^2/2mkT} e^{-mgz/kT} \,. \tag{29}$$

The integration over the x, y spatial coordinates gives L^2 . The momentum integrations is the same as for the velocity distributions discussed in class

$$\int dp_x dp_y dp_z \, e^{-(p_x + p_y^2 + p_z^2)/2mkT} = \left[\int dp_x e^{-p_x^2/2mkT}\right]^3 = (2\pi mkT)^{3/2} \,. \tag{30}$$

The integral over z is the new bit:

$$\int_0^\infty dz \, e^{-mgz/kT} = \frac{kT}{mg} \equiv \ell \tag{31}$$

In total we have

$$Z_1 = \frac{1}{h^3} L^2 \left(\frac{kT}{mg}\right) \left(2\pi m kT\right)^{3/2} \tag{32}$$

(b) We have

$$\mathrm{d}\mathscr{P}_{\boldsymbol{r},\boldsymbol{p}} = \frac{1}{Z_1} e^{-\mathcal{H}(\boldsymbol{r},\boldsymbol{p})/kT} \frac{\mathrm{d}^3 \boldsymbol{r} \,\mathrm{d}^3 \boldsymbol{p}}{h^3} \,. \tag{33}$$

So the normalization constant is Z_1h^3 , leading to

$$\mathrm{d}\mathscr{P}_{\boldsymbol{r},\boldsymbol{p}} = \left(\frac{e^{-p^2/2mkT}\mathrm{d}^3 p}{(2\pi mkT)^{3/2}}\right) \left(\frac{mg}{kT}e^{-mgz/kT}\mathrm{d}z\right) \left(\frac{\mathrm{d}x\,\mathrm{d}y}{L^2}\right) \,. \tag{34}$$

In writing this expression we have put the factors that make up Z underneath the differentials that they stemmed from, e.g.

$$\int dz e^{-mgz/kT} = \ell \qquad d\mathscr{P} \propto \frac{1}{\ell} e^{-mgz/kT} dz \,. \tag{35}$$

We see that the probability factorizes – it is a probability of momentum p; times a probability of height z; times a probability of transverse coordinates x, y (which is just a constant $1/L^2$).

(c) We need to compute

$$\langle \epsilon \rangle = -\frac{\partial \ln Z}{\partial \beta} \tag{36}$$

$$\left\langle \delta \epsilon^2 \right\rangle = \frac{\partial \ln^2 Z}{\partial \beta^2} = -\frac{\partial \left\langle \epsilon \right\rangle}{\partial \beta} \tag{37}$$

We only need the dependence on $\ln Z$ on β . We see that $Z \propto \beta^{-5/2}$:

$$\ln Z = \ln(\beta^{-5/2}) + \text{const} \tag{38}$$

We do not need to be explicit about the constant as we are planning to differentiate the result. This simplification is extremely common. So,

$$\langle \epsilon \rangle = -\frac{\partial \ln Z}{\partial \beta} = \frac{5}{2} \frac{1}{\beta} = \frac{5}{2} kT \tag{39}$$

$$\left\langle \delta \epsilon^2 \right\rangle = \frac{\partial \ln^2 Z}{\partial \beta^2} = -\frac{\partial \left\langle \epsilon \right\rangle}{\partial \beta} = \frac{5}{2} \frac{1}{\beta^2} = \frac{5}{2} (kT)^2 \tag{40}$$

(d) We have

$$\mathrm{d}\mathscr{P}_{\boldsymbol{r},\boldsymbol{p}} = \left(\frac{e^{-p^2/2m}\mathrm{d}^3 p}{(2\pi m k T)^{3/2}}\right) \left(\frac{mg}{kT} e^{-mgz/kT}\mathrm{d}z\right) \left(\frac{\mathrm{d}x\mathrm{d}y}{L^2}\right) \tag{41}$$

$$=P(p_x, p_y, p_z)d^3p \times P(z)dz \times P(x, y)dxdy$$
(42)

By construction (look carefully at part (a)) each of the terms is separately normalized and the probability factorizes. Integrating over p_x, p_y, p_z , and over x, y gives unity for each integral yielding

$$d\mathscr{P}_{z} = \int_{\text{over } x, y, p_{x}, p_{y}, p_{z}} d\mathscr{P}_{\boldsymbol{r}, \boldsymbol{p}} = \frac{mg}{kT} e^{-mgz/kT} = \frac{1}{\ell} e^{-\ell} dz$$
(43)

with $\ell = kT/mg$. Then we can calculate

$$\langle z \rangle = \int_0^\infty P(z) dz = \int_0^\infty \frac{1}{\ell} e^{-z/\ell} dz \times z$$
(44)

Changing variables to $u \equiv z/\ell$ we find

$$\langle z \rangle = \ell \int_0^\infty e^{-u} \mathrm{d}u \, u \equiv \ell \, \Gamma(2) = \ell$$

$$\tag{45}$$

An alternative way to proceed us to use that the mean kinetic energy is

$$\langle K \rangle = \left\langle \frac{p_x^2 + p_y^2 + p_z^2}{2m} \right\rangle = 3 \times \frac{1}{2}kT \tag{46}$$

i.e. the average of every quadratic form in the classical Hamiltonian (or energy as a function of as a function of position and momentum) is $\frac{1}{2}kT$. There are three quadratic forms in the kinetic energy. Then since the average energy is the sum of the average kinetic and average potential energy

$$\langle \epsilon \rangle = \langle K + mgz \rangle = \frac{5}{2}kT$$
 (47)

we find

$$\langle mgz \rangle = kT$$
 (48)

Thus as found above:

$$\langle z \rangle = \frac{kT}{mg}.\tag{49}$$

(e) First we interpret the height ℓ . The typical energy $\sim kT$. A particle with this kinetic energy on the earth's surface will fly to a height

$$\ell = \frac{kT}{mg} \,. \tag{50}$$

So, ℓ sets the scale for the height.

Now lets evaluate this for diatomic nitrogen (Air is 70% N_2). The molar mass of N_2 is 28 grams = 0.028 kg. Taking $R = 8.32 \text{ J/}^{\circ} \text{K}$ and $T = 300 \text{ }^{\circ} \text{K}$ we find

$$\ell = \frac{N_A kT}{N_A mg} = \frac{RT}{(0.028 \,\mathrm{kg})(9.8m/s^2)} \simeq 9.1 \,\mathrm{km} \tag{51}$$

(f) Clearly

$$\frac{n(z)}{n(0)} = \frac{P(z)}{P(0)}$$
(52)

 So

$$n(z) = n(0)e^{-mgz/kT}$$
(53)

where n(z) is the number of molecules per volume

(g) Take a slab of air of area \mathcal{A} and draw a free body diagram (see figure). Since the forces must balance we must have

$$-\mathcal{A} p(z+dz) + \mathcal{A} p(z) - mg \left(\mathcal{A} dz\right) n(z) = 0.$$
(54)

Here the first term is the pressure force pushing down on the slab; the second term is the pressure force pushing up on the slab; the third term is the weight of the slab (its volume is $dV = \mathcal{A} dz$ and there are n(z) particles of mass m per volume).



Thus

$$\frac{dp}{dz} = -mgn(z) \tag{55}$$

This equation used no statistical mechanics – it is only mechanics.

Now we use statistical mechanics to verify overall consistency. The pressure is given by the ideal gas law:

$$p(z) = \frac{NkT}{V} = n(z)kT = n(0)e^{-mgz/kT}kT.$$
(56)

Differentiating we have

$$\frac{dp}{dz} = -n(0)e^{-mgz/kT} mg = -n(z)mg.$$
(57)

Thus the pressure and density are consistent with the mechanics relation given in Eq. (55)