

Problem 1. Working with the speed distribution

Consider the Maxwell speed distribution

- (a) In three dimensions, evaluate the most probable speed v_* , i.e the speed where $P(v)$ is maximized. You should find $v_* = (2kT/m)^{1/2}$.
- (b) Repeat (a) in two dimensions. You should find $v_* = (kT/m)^{1/2}$.
- (c) (Optional) Determine the probability to have speed in a specific range, $v_* < v < 2v_*$. Follow the following steps:
 - (i) Write down the appropriate integral.
 - (ii) Change variables to a dimensionless speed $u = v/\sqrt{k_B T/m}$, i.e. u is the speed in units of $\sqrt{k_B T/m}$, and express the probability as an integral over u .
 - (iii) Write a short program (in any language) to evaluate the dimensionless integral, by (for example) dividing up the interval into 200 bins, and evaluate the integral with Riemann sums. You should find

$$\mathcal{P} \simeq 0.53 \tag{1}$$

Problem 2. 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

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

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:

$$H = H_x + H_y \quad (3)$$

$$= \left(\frac{p_x^2}{2m} + \frac{1}{2}m\omega_0^2x^2 \right) + \left(\frac{p_y^2}{2m} + \frac{1}{2}m\omega_0^2y^2 \right) \quad (4)$$

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:

$$H = H_x + H_y + H_z \quad (5)$$

$$= \left(\frac{p_x^2}{2m} + \frac{1}{2}m\omega_0^2x^2 \right) + \left(\frac{p_y^2}{2m} + \frac{1}{2}m\omega_0^2y^2 \right) + \left(\frac{p_z^2}{2m} + \frac{1}{2}m\omega_0^2z^2 \right) \quad (6)$$

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

$$E = 3NkT, \quad (7)$$

if the solid is treated as $3N$ independent classical oscillators. Determine the specific heat C_V^{lm} 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.

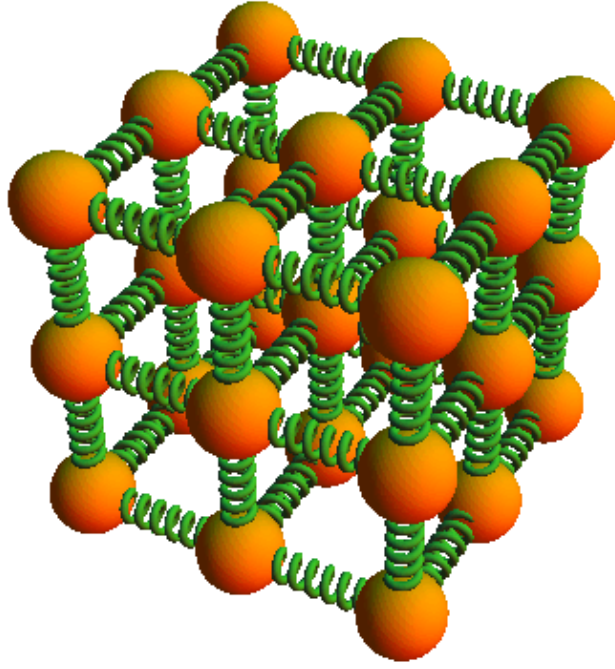


Figure 1:

- (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.

1	0	1	0	2	1	0	0	2	1	3	1	1	0	0	0	0	1	0
1	2	2	2	0	0	0	0	0	1	1	0	0	3	5	1	0	0	0
0	0	1	1	0	2	0	0	6	1	1	0	1	1	1	0	2	0	0
0	3	3	0	0	2	0	0	3	0	1	3	0	2	0	0	0	3	0
2	0	0	1	0	6	0	4	1	0	0	0	2	1	0	0	1	1	1
1	0	6	0	4	0	1	2	1	0	0	0	1	0	0	0	0	3	4
0	0	0	1	2	4	0	0	1	0	0	2	0	1	2	1	1	2	0
1	3	0	0	2	0	1	0	1	0	0	3	0	4	0	2	1	0	6
1	1	1	0	0	0	0	1	0	3	1	2	0	0	0	0	1	0	0
0	0	0	0	0	2	0	3	1	0	0	0	0	0	3	0	0	2	2
9	1	0	1	1	0	2	1	0	1	0	0	0	3	7	3	0	2	3
2	2	0	0	0	0	0	1	0	1	7	1	3	1	0	1	3	0	1
0	5	3	0	1	2	4	8	1	0	4	0	3	0	1	0	0	0	4
0	0	0	0	1	0	0	0	0	1	0	1	0	0	2	3	0	2	0
0	1	1	0	0	2	0	4	0	1	0	4	0	1	1	1	1	8	5
0	0	0	0	1	0	0	0	2	0	1	0	1	1	2	0	0	1	1
3	0	0	0	4	0	0	1	0	1	2	0	0	1	2	0	2	0	1
0	0	1	2	1	0	0	0	0	0	1	0	0	2	0	1	1	0	0
1	0	1	0	0	0	1	0	3	1	0	0	0	0	2	9	0	0	5
0	0	1	2	3	0	1	2	0	2	4	0	0	1	2	0	0	0	1

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

$$C_V^{1\text{ml}} = 3R \frac{(\beta \hbar \omega_0)^2 \exp(-\beta \hbar \omega_0)}{(1 - \exp(-\beta \hbar \omega_0))^2}. \quad (9)$$

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) Download a text file with the experimental data on the specific heat of silver³, [see here](#). Make a graph of the data, and the Einstein prediction for $C_V^{1\text{ml}}$ for $\hbar \omega_0 = 4E_0, 2E_0, E_0, E_0/2, E_0/4$ with $E_0 = 0.013 \text{ eV}$. E_0 was a free parameter in the Einstein model. The graph I get for silver is shown below as well as the C_V for other substances:
- (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?

²It is generally when computing C_V to recognize that

$$T \frac{\partial}{\partial T} = -\beta \frac{\partial}{\partial \beta} \quad (8)$$

³The file contains two columns, the first is the temperature in Kelvin, the second is the specific heat in units of $J/(\text{mol } K)$

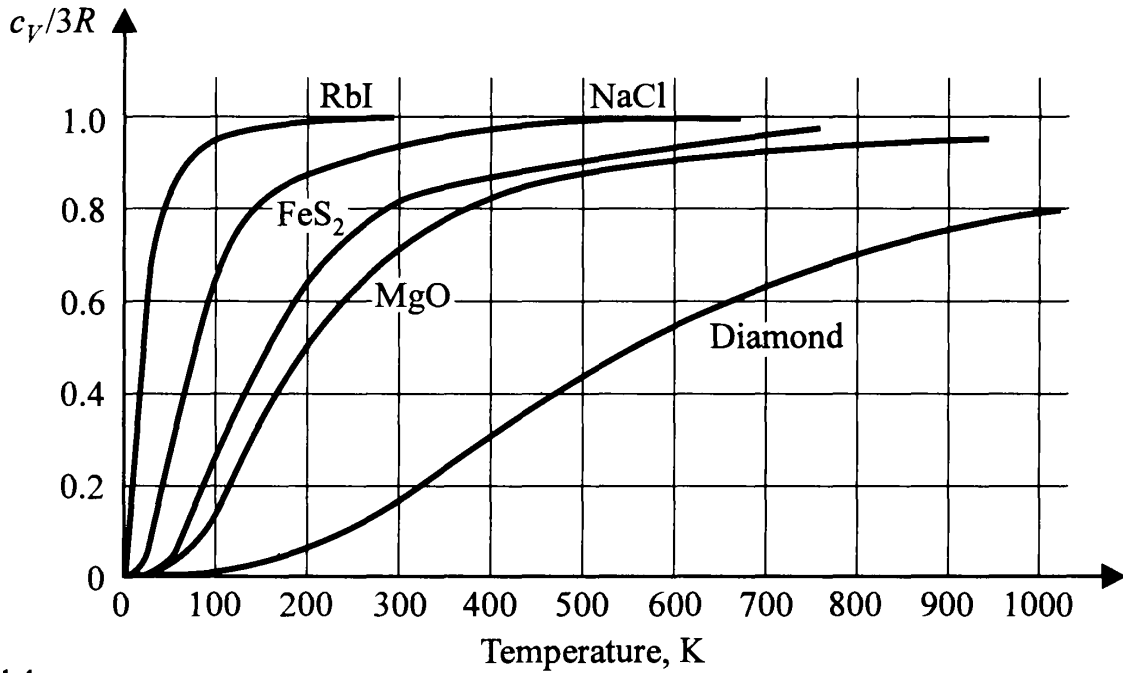
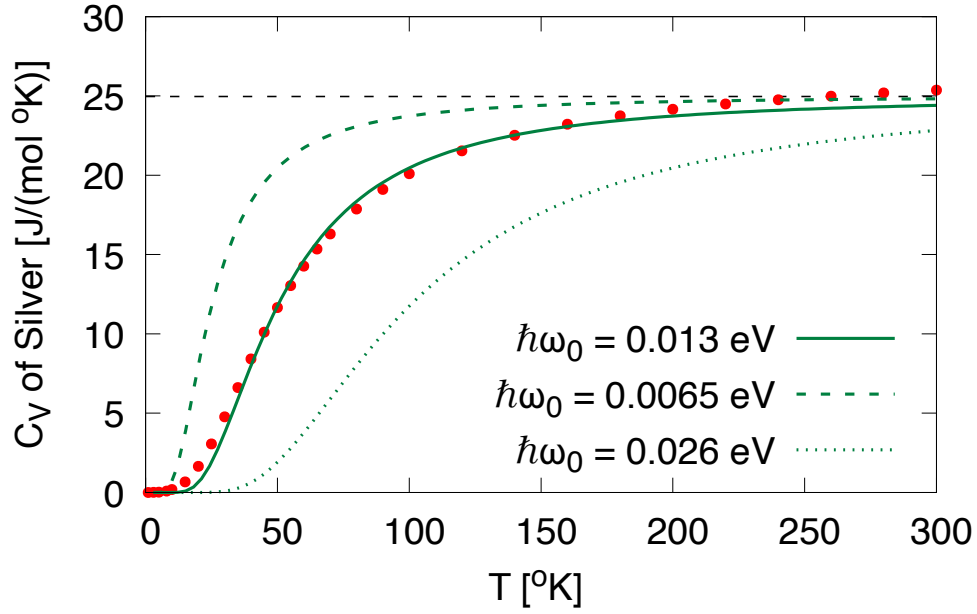


Figure 2: Specific heats of solids: (a) The Einstein Model with $\hbar\omega_0$ treated as a parameter compared to the specific heat of silver. The graph approaches $3R$ at high temperature. (b) The specific heat C_V in units of R of various solids versus temperature. The specific heat approaches $3R$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

Problem 3. Entropy changes of a MAIG

Find the change in entropy of n_{ml} moles of an ideal monoatomic ideal gas in the following processes:

- (a) the temperature changes from T_1 to T_2 at constant pressure;
- (b) the pressure changes from P_1 to P_2 at constant volume.

Consider the expression for the number of states in a mono-atomic ideal gas

$$\Omega = C(N)V^N E^{3N/2}, \quad (10)$$

and the corresponding entropy

$$S = Nk_B \log(V) + \frac{3}{2}Nk_B \log(E) + \text{const}. \quad (11)$$

Recall that in an adiabatic expansion of a monoatomic ideal gas no heat enters or exits the system and the entropy remains constant as the volume increases.

- (c) (i) Using Eq. (11) show that $\Delta S = 0$ for an adiabatic increase in volume from V_1 to V_2 . (*Hint:* How does the temperature change during an adiabatic expansion of a mono-atomic ideal gas?)
- (ii) Describe how the particles are redistributed in phase space so that the entropy and total phase space volume remains constant during the expansion.

Ans: (a) $\frac{5}{2}n_{\text{ml}}R \ln(T_2/T_1)$; (b) $\frac{3}{2}n_{\text{ml}}R \ln(P_2/P_1)$.

Problem 4. Entropy change in the mixing of hot and cold gasses

N_1, T_1 He	N_2, T_2 Ar
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Consider two mono-atomic ideal gasses, Helium and Argon, separated by a divider which partitions a container of volume V into two equal parts. There are N_1 Helium atoms on the left of the divider, and N_2 Argon atoms on the right of the divider. The Helium atoms are initially at a temperature of T_1 , while the Argon atoms are initially at a temperature of T_2 . After the dividing wall is removed, the two gasses mix and ultimately equilibrate.

- (a) Determine the final temperature of the system.
- (b) Determine the change in entropy of the system resulting from the mixing process in two ways:
 - (i) Directly count the number of states at the beginning and end.
 - (ii) Calculate the change in entropy by identifying an equilibrium path connecting the state at the beginning and the state at the end and using thermodynamics. Explain how the example illustrates the formula

$$\Delta S = \int \frac{dQ_{\text{rev}}}{T} > \frac{Q}{T} \quad (12)$$

Problem 5. Isothermal Atmosphere

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

$$U = mgz \quad (13)$$

where $z = 0$ is the earth's surface. Our goal is to use partition functions to evaluate the probability that the 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 z coordinate runs from zero (the earth's surface) to infinity (outer space), i.e.

$$0 < x, y < L \quad 0 < z < \infty \quad (14)$$

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

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

$$Z_1 = \frac{L^2 \ell (2\pi m k T)^{3/2}}{h^3} \quad (15)$$

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

$$d\mathcal{P}_{\mathbf{r}, \mathbf{p}} = P(\mathbf{r}, \mathbf{p}) d^3\mathbf{r} d^3\mathbf{p} \quad (16)$$

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 , $d\mathcal{P}_z$ by integrating 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 typical mass of an air molecule, and a typical temperature.

Please try not to look up numbers. Rather put 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) If the gas density at $z = 0$ is n_0 , what is the density $n(z)$ at height z ?
- (g) A mechanical analysis of the forces in the the gas says that

$$\frac{dp(z)}{dz} = -mgn(z) \tag{17}$$

where $p(z)$ is the pressure in the gas at height z . Explain briefly the physical meaning of Eq. (17), and then show that part (e) is consistent with Eq. (17) and the ideal gas law, $pV = n_{\text{ml}}RT$ provided the temperature is constant.