

Supplement to Chapter 4

REVIEW QUESTIONS

- 4.1 What is a statistical ensemble and how is it related to the probability density?
- 4.2 Describe the probability density for the uniform ensemble for a quantum system, defining any symbols you use.
- 4.3 For a quantum system, what is the meaning of $\Omega(E)$, the normalization constant for the uniform ensemble?
- 4.4 How is $\Omega(E)$ related to $C(E)$, the uniform ensemble normalization constant for the equivalent classical system?
- 4.5 How is $\Omega(E)$ related to the entropy of the system?
- 4.6 For a quantum system, what is the microcanonical probability distribution?
- 4.7 Describe the energy spectrum (the eigenvalues and their degeneracies) of a system of K quantized harmonic oscillators.
- 4.8 Calculate $\Omega'(E)$ for a system of K harmonic oscillators.
- 4.9 For a system of oscillators, how is the density of normal-modes function $D(\omega)$ defined?
- 4.10 Given $D(\omega)$, write a formula for the thermal energy of a lattice as a function of the temperature.
- 4.11 For $kT \gg \hbar\omega$, what is the average thermal energy of a normal mode of angular frequency ω ?
- 4.12 For $kT \ll \hbar\omega$, what is the average thermal energy of a normal mode of angular frequency ω ?
- 4.13 Why is it true that, at low T , only the long-wavelength vibrations of a lattice contribute to the specific heat?
- 4.14 Describe Einstein's approximation for the vibrational specific heat of a solid.
- 4.15 Describe the Debye approximation for the vibrational specific heat of a solid.
- 4.16 How are the Debye frequency and the Debye temperature defined?
- 4.17 Explain why the Debye theory gives accurate values for the vibrational specific heat of solids at temperatures much larger and much smaller than T_D .
- 4.18 Prove that the probability of finding a system that is in contact with a much larger thermal reservoir in energy eigenstate ψ_n is $\text{const.} \times \exp(-\beta E_n)$. You may assume a microcanonical ensemble for the combined system.
- 4.19 For a quantum mechanical system, how is the partition function Z defined? What parameters is it a function of?
- 4.20 How is the canonical potential related to the partition function?
- 4.21 How is the canonical potential related to the entropy of the system in practical units (Kelvins, etc.)?
- 4.22 What is the probability density in phase space for the classical canonical ensemble?
- 4.23 How is the canonical partition function defined for a classical system?

- 4.24** Using the dumbbell, or rigid rotor, model of a diatomic molecule, describe the full set of canonical coordinates and momenta needed to define the state of one molecule.
- 4.25** Write the Hamiltonian function for a rigid rotor molecule, explaining any nonobvious terms in it.
- 4.26** Calculate the internal (rotational) partition function of a rigid rotor molecule.
- 4.27** What extra term is added to the Hamiltonian of a diatomic molecule if it is placed in an electric field?
- 4.28** Explain the meaning of the terms in the formula $N\bar{\mu}_z = kT \partial \phi / \partial \mathcal{E}$.
- 4.29** Derive the formula that was given in the last question.
- 4.30** Describe the “orientational dipole moment” and the “induced dipole moment” contributions to the average dipole moment of a molecular gas.
- 4.31** How does the orientational contribution to the electric susceptibility of a diatomic gas depend on the temperature?
- 4.32** Explain, in words, what the Schottky anomaly is.
- 4.33** Derive the specific heat for a system of two-level atoms.
- 4.34** State the equipartition theorem.
- 4.35** Derive the equipartition theorem.

EXERCISES

Exercise 4.1 Consider a quantum system that has energy eigenstates ψ_1, ψ_2, \dots with energies E_1, E_2, \dots . Let P_1, P_2, \dots be any probability distribution with the interpretation that P_n is the probability of finding the system in the state ψ_n . We define a quantity, called the *Boltzmann–Gibbs entropy*, by

$$\tilde{S} = - \sum_n P_n \log P_n \tag{S4.1}$$

(a) Show that the maximum value of \tilde{S} , subject to the constraints

$$\sum_n P_n = 1 \quad \text{and} \quad \sum_n E_n P_n = E \tag{S4.2}$$

is given by the canonical probability distribution $P_n = e^{-\beta E_n} / Z$. (b) Show that, for the canonical distribution, the value of \tilde{S} is equal to the entropy in rational units, S^o .

Solution (a) To maximize \tilde{S} , subject to the two constraints, we use Lagrange’s method and set $\partial F / \partial P_n = 0$, where

$$F = - \sum_n P_n \log P_n - \alpha \sum_n P_n - \beta \sum_n P_n E_n \tag{S4.3}$$

This gives

$$\log P_n + 1 + \alpha + \beta E_n = 0 \tag{S4.4}$$

which has the solution

$$P_n = \text{const.} \times e^{-\beta E_n} \tag{S4.5}$$

In order to satisfy the first constraint, we must set the constant equal to Z^{-1} . (b) Letting $P_n = e^{-\beta E_n} / Z$, we see that $\log P_n = -\beta E_n - \log Z$ and

$$\tilde{S} = \sum_n P_n (\log Z + \beta E_n) = \log Z + \beta E \tag{S4.6}$$

But, by Eq. (4.45), $\log Z = S^o - \beta E$, which shows that $\tilde{S} = S^o$.

Exercise 4.2 Calculate the thermal energy of a system of K one-dimensional classical harmonic oscillators, using a canonical ensemble.

Solution For a single harmonic oscillator of angular frequency ω the Hamiltonian is

$$H = p^2 / 2m + m\omega^2 x^2 / 2 \tag{S4.7}$$

and the partition function is

$$\begin{aligned} Z &= \frac{1}{h} \int e^{-\beta p^2 / 2m} dp \int e^{-\beta m\omega^2 x^2 / 2} dx \\ &= (2\pi m / \beta)^{1/2} (2\pi / \beta m\omega^2)^{1/2} / h \\ &= 1 / \beta \hbar \omega \end{aligned} \tag{S4.8}$$

The canonical potential of a single oscillator is

$$\phi = \log z = -\log \beta - \log(\hbar\omega) \tag{S4.9}$$

and the thermal energy is

$$\varepsilon = -\frac{\partial\phi}{\partial\beta} = kT \quad (\text{S4.10})$$

Since the K oscillators are independent, the energy of the system is

$$E = K\varepsilon = KkT \quad (\text{S4.11})$$

The simplicity of this calculation illustrates the advantage of the canonical versus the microcanonical or uniform ensembles.

Exercise 4.3 A system is composed of K one-dimensional classical oscillators. Assume that the potential for the oscillators contains a small quartic “anharmonic term.” That is

$$V(x) = \frac{k_o}{2}x^2 + \alpha x^4 \quad (\text{S4.12})$$

where $\alpha\langle x^4 \rangle \ll kT$. To first order in the parameter α , derive the anharmonic correction to the Dulong–Petit law.

Solution Since the oscillators are noninteracting, the canonical potential of the system is K times the canonical potential of a single oscillator. The partition function of a single oscillator is

$$\begin{aligned} Z &= \frac{1}{h} \int_{-\infty}^{\infty} e^{-p^2/2mkT} dp \int_{-\infty}^{\infty} e^{-V(x)/kT} dx \\ &= \frac{\sqrt{2\pi mkT}}{h} \int_{-\infty}^{\infty} e^{-k_o x^2/2kT} e^{-\alpha x^4/kT} dx \\ &\approx \frac{\sqrt{2\pi mkT}}{h} \int_{-\infty}^{\infty} e^{-k_o x^2/2kT} (1 - \alpha x^4/kT) dx \end{aligned} \quad (\text{S4.13})$$

But

$$\int_{-\infty}^{\infty} e^{-k_o x^2/2kT} dx = \sqrt{2\pi kT/k_o} \quad (\text{S4.14})$$

and

$$\int_{-\infty}^{\infty} e^{-k_o x^2/2kT} x^4 dx = \frac{3}{4} \sqrt{\pi} (2kT/k_o)^{5/2} \quad (\text{S4.15})$$

and therefore

$$Z \approx \frac{kT}{\hbar\omega} (1 - 3\alpha kT/k_o^2) \quad (\text{S4.16})$$

where $\omega = \sqrt{k_o/m}$.

Using the expansion $\log(1-x) \approx -x$, we get, for the system of K oscillators,

$$\begin{aligned} \phi &= K[\log kT - \log(\hbar\omega) - 3\alpha kT/k_o^2] \\ &= -K[\log \beta + \log(\hbar\omega) + 3\alpha/k_o^2\beta] \end{aligned} \quad (\text{S4.17})$$

The thermal energy per oscillator is given by

$$\begin{aligned} \frac{E}{K} &= -\frac{\partial(\phi/K)}{\partial\beta} = \frac{1}{\beta} - \frac{3\alpha}{k_o^2\beta^2} \\ &= kT - \frac{3\alpha}{k_o^2} (kT)^2 \end{aligned} \quad (\text{S4.18})$$

The anharmonic correction tends to reduce the energy per oscillator in comparison to a perfectly harmonic oscillator, as T is increased.

Exercise 4.4 What is the thermal energy, at temperature T , of a particle of mass m in the one-dimensional potential $V(x) = \varepsilon_o|x/a|^n$? Note that the harmonic oscillator corresponds to $n = 2$. ε_o and a are parameters with the units of energy and length, respectively.

Solution The partition function is

$$\begin{aligned} Z &= \frac{1}{h} \int_{-\infty}^{\infty} e^{-\beta p^2/2m} dp \int_{-\infty}^{\infty} e^{-\beta V(x)} dx \\ &= 2 \frac{\sqrt{2\pi m/\beta}}{h} \int_0^{\infty} e^{-\beta \varepsilon_o (x/a)^n} dx \end{aligned} \tag{S4.19}$$

The integral over x can be done by the transformation of variables $z = \beta \varepsilon_o (x/a)^n$. This gives $x = a(z/\beta \varepsilon_o)^{1/n}$ and $dx = (1/n) a z^{(1-n)/n} / (\beta \varepsilon_o)^{1/n} dz$.

$$\begin{aligned} \int_0^{\infty} e^{-\beta \varepsilon_o (x/a)^n} dx &= \frac{a}{n(\beta \varepsilon_o)^{1/n}} \int_0^{\infty} e^{-z} z^{(1-n)/n} dz \\ &= \frac{a}{n(\beta \varepsilon_o)^{1/n}} \Gamma(1/n) \end{aligned} \tag{S4.20}$$

Therefore

$$Z = \text{const.} \times \beta^{-(1/2+1/n)} \tag{S4.21}$$

$$\phi = -(\frac{1}{2} + 1/n) \log \beta + \text{const.} \tag{S4.22}$$

and

$$E = -\frac{\partial \phi}{\partial \beta} = (1/2 + 1/n)kT \tag{S4.23}$$

What is surprising is that the thermal energy is exactly proportional to kT for any n . Only the proportionality constant is affected by the value of n . This means that, for any one-dimensional pure power potential, the particle has a constant specific heat.

Exercise 4.5 A quantum harmonic oscillator has energy levels $E_n = \hbar\omega(n + \frac{1}{2})$. What is the probability of finding the oscillator in its n th quantum state at temperature T ?

Solution The oscillator can be viewed as a small system coupled to a thermal reservoir at temperature T . The probability of finding the system in a quantum state of energy E_n is given by the canonical probability density

$$P_n = C e^{-\beta E_n} \tag{S4.24}$$

Since $E_n = \hbar\omega(n + \frac{1}{2})$, the normalization constant is

$$\begin{aligned} C^{-1} &= \sum_{n=0}^{\infty} e^{-\hbar\omega/2kT} e^{-n\hbar\omega/kT} \\ &= e^{-\hbar\omega/2kT} \sum_{n=0}^{\infty} x^n \quad (x \equiv e^{-\hbar\omega/kT}) \\ &= \frac{e^{-\hbar\omega/2kT}}{1 - e^{-\hbar\omega/kT}} \end{aligned} \tag{S4.25}$$

and therefore

$$P_n = (1 - e^{-\hbar\omega/kT}) e^{-n\hbar\omega/kT} \tag{S4.26}$$

Exercise 4.6 The Hamiltonian function of a two-dimensional dipolar molecule of mass m , moment of inertia I , and dipole moment μ , in an electric field \mathcal{E} , is (see Fig. S4.1)

$$H = \frac{1}{2m}(p_x^2 + p_y^2) + p_\theta^2/2I - \mu\mathcal{E} \cos \theta \tag{S4.27}$$

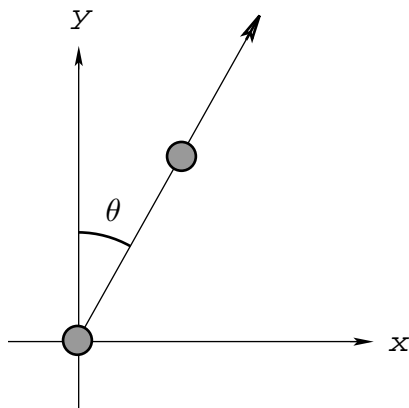


Fig. S4.1 The angle θ gives the orientation of a two-dimensional dipolar molecule.

(a) Calculate the canonical potential of a system of N classical dipolar molecules confined to an area A . Hint: The modified Bessel function $I_0(z)$ is defined by

$$I_0(z) = \frac{1}{\pi} \int_0^\pi e^{-z \cos \theta} d\theta \quad (\text{S4.28})$$

(b) Use the power series expansion

$$I_0(z) = \sum_{k=0}^{\infty} (z/2)^{2k} / (k!)^2 \quad (\text{S4.29})$$

and the asymptotic approximation for large z

$$I_0(z) \sim e^z / \sqrt{2\pi z} \quad (\text{S4.30})$$

to obtain low- and high-temperature approximations for the specific heat.

Solution (a) The partition function of a gas with internal degrees of freedom is a product of the translational partition function and the internal partition function.

$$Z = Z(\text{trans})Z(\text{int}) \quad (\text{S4.31})$$

where, for a two-dimensional gas,

$$\begin{aligned} Z(\text{trans}) &= \frac{A^N}{N!h^{2N}} \left(\int_{-\infty}^{\infty} e^{-\beta p^2/2m} dp \right)^{2N} \\ &= \frac{A^N (2\pi m/\beta)^N}{N!h^{2N}} \end{aligned} \quad (\text{S4.32})$$

and $Z(\text{int}) = z^N$, where

$$z = \frac{1}{h} \int_{-\infty}^{\infty} e^{-\beta p_\theta^2/2I} dp_\theta \int_{-\pi}^{\pi} e^{\beta \mu \mathcal{E} \cos \theta} d\theta \quad (\text{S4.33})$$

is the internal partition function for a single molecule. Using Eq. (S4.28), we obtain

$$z = \frac{\sqrt{2\pi I/\beta}}{h} 2\pi I_0(\beta \mu \mathcal{E}) \quad (\text{S4.34})$$

The canonical potential is

$$\phi = N \left[\log(A/N) - \frac{3}{2} \log \beta + \log I_0(\beta \mu \mathcal{E}) + C \right] \quad (\text{S4.35})$$

(b) As $T \rightarrow 0$, $\beta \rightarrow \infty$ and $I_o \approx e^{\beta\mu\mathcal{E}}/\sqrt{2\pi\beta\mu\mathcal{E}}$

$$\phi \approx N[\log(A/N) - 2 \log \beta + \mu\mathcal{E}\beta + \text{const.}] \quad (\text{S4.36})$$

Therefore

$$E = -\frac{\partial\phi}{\partial\beta} \approx \frac{2N}{\beta} - \mu\mathcal{E}N \quad (\text{S4.37})$$

and

$$C = \frac{\partial E}{\partial T} = 2Nk \quad (\text{S4.38})$$

(At low T , the dipoles in the electric field act as one-dimensional harmonic oscillators.) As $T \rightarrow \infty$, $\beta \rightarrow 0$, $I_o \approx 1 + \frac{1}{4}(\beta\mu\mathcal{E})^2$, and, using the identity $\log(1+x) \approx x$, one obtains the high-temperature approximations,

$$\phi \approx N[\log(A/N) - \frac{3}{2} \log \beta + \frac{1}{4}(\beta\mu\mathcal{E})^2 + C] \quad (\text{S4.39})$$

$$E \approx \frac{3}{2}NkT - N\frac{(\mu\mathcal{E})^2}{2kT}, \quad (\text{S4.40})$$

and

$$C \approx \frac{3}{2}Nk + \frac{1}{2}N(\mu\mathcal{E}/kT)^2 \quad (\text{S4.41})$$

(Notice that the dipole-field interaction becomes negligible when $kT \gg \mu\mathcal{E}$.)

Exercise 4.7 The probability of finding a three-dimensional dipolar molecule in a state described by the phase-space variables $(x, y, z, \theta, \phi, p_x, p_y, p_z, p_\theta, p_\phi) \equiv (x, p)$ is proportional to $e^{-\beta H(x, p)}$. Show that, if the electric field is not uniform, then the molecular gas is more dense where the field strength is higher.

Solution For a canonical ensemble, the single-particle phase space probability density is

$$P(x, p) = C e^{-\beta H(x, p)} \quad (\text{S4.42})$$

The Hamiltonian function is

$$H = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) + \frac{1}{2I}\left(p_\theta^2 + \frac{p_\phi^2}{\sin^2\theta}\right) - \mu\mathcal{E} \cos\theta \quad (\text{S4.43})$$

To get the spatial probability density we must integrate Eq. (S4.42) over all variables except x , y , and z . The integrals over p_x , p_y , p_z , and p_θ only give factors that are independent of x , y , and z and can therefore be lumped together with the normalization constant C . The integral of over p_ϕ is

$$\int_{-\infty}^{\infty} e^{-\beta p_\phi^2/2I \sin^2\theta} dp_\phi = \sqrt{2\pi I/\beta} \sin\theta \quad (\text{S4.44})$$

The square root factor can be combined with the normalization constant. This leaves only the integral over θ .

$$P(x, y, z) = \text{const.} \times \int_0^\pi e^{\beta\mu\mathcal{E} \cos\theta} \sin\theta d\theta \quad (\text{S4.45})$$

But

$$\begin{aligned} \int_0^\pi e^{a \cos\theta} \sin\theta d\theta &= \int_{-1}^1 e^{a \cos\theta} d(\cos\theta) \\ &= a^{-1}(e^a - e^{-a}) \\ &= 2 \sinh(a)/a \end{aligned} \quad (\text{S4.46})$$

Therefore

$$P(x, y, z) = \text{const.} \times \frac{\sinh[\beta\mu\mathcal{E}(x, y, z)]}{\mathcal{E}(x, y, z)} \quad (\text{S4.47})$$

Since $\sinh(x)/x$ is a monotonically increasing function of x , $P(x, y, z)$ is greatest where $\mathcal{E}(x, y, z)$ is greatest.

Exercise 4.8 In Problem 4.19 the reader is asked to evaluate the rotational partition function $Z(\text{rot})$ by using the approximation

$$\sum_{n=0}^{\infty} f(n) \approx \int_0^{\infty} f(x) dx \tag{S4.48}$$

where $f(n) = (2n + 1) \exp[-(\beta\hbar^2/2I)n(n + 1)]$. By considering the left-hand side of Eq. (S4.48) as an approximation to the integral on the right-hand side and by using an improved approximation to the integral, obtain an estimate of the error in the original approximation.

Solution We treat the integral from zero to infinity as a sum of integrals over unit intervals.

$$\int_0^{\infty} f(x) dx = \sum_{n=0}^{\infty} \int_n^{n+1} f(x) dx \tag{S4.49}$$

We now want to construct an approximation for an integral over a unit interval. Let us look at the first interval. Within the interval $0 \leq x \leq 1$ we approximate $f(x)$ by a polynomial $P(x)$ that satisfies the conditions that $P(0) = f(0)$, $P'(0) = f'(0)$, $P(1) = f(1)$, and $P'(1) = f'(1)$. In order to satisfy four conditions, we need four coefficients in the polynomial. We therefore choose a cubic polynomial.

$$P(x) = f(0) + f'(0)x + ax^2 + bx^3 \tag{S4.50}$$

It is a straightforward calculation to use the two conditions at $x = 1$ to determine the coefficients a and b . The results are that

$$a = 3f(0) - 2f'(0) - 3f(1) + f'(1) \tag{S4.51}$$

and

$$b = 2f(0) + f'(0) - 2f(1) + f'(1) \tag{S4.52}$$

Our approximation for the integral from 0 to 1 is

$$\begin{aligned} \int_0^1 f(x) dx &\approx \int_0^1 P(x) dx = f(0) + \frac{1}{2}f'(0) + \frac{1}{3}a + \frac{1}{4}b \\ &= \frac{f(0) + f(1)}{2} + \frac{f'(0) - f'(1)}{12} \end{aligned} \tag{S4.53}$$

Because the integral has the geometrical meaning of the area under the curve $f(x)$, it is clear that there is an equivalent formula that is valid for any unit interval.

$$\int_n^{n+1} f(x) dx \approx \frac{f(n) + f(n+1)}{2} + \frac{f'(n) - f'(n+1)}{12}$$

Using this in Eq. (S4.49) gives

$$\begin{aligned} \int_0^{\infty} f(x) dx &\approx \frac{1}{2}(f(0) + f(1)) + \frac{1}{12}(f'(0) - f'(1)) \\ &\quad + \frac{1}{2}(f(1) + f(2)) + \frac{1}{12}(f'(1) - f'(2)) \\ &\quad + \dots \\ &= \frac{1}{2}f(0) + \sum_{n=1}^{\infty} f(n) + \frac{1}{12}f'(0) \end{aligned} \tag{S4.54}$$

Rearranging this formula, to give the sum of $f(n)$ from 0 to ∞ , we get

$$\sum_{n=0}^{\infty} f(n) \approx \int_0^{\infty} f(x) dx + \frac{1}{2}f(0) - \frac{1}{12}f'(0) \tag{S4.55}$$

These are the first three terms in what is known as the *Euler summation formula*. Applying this to the function

$$f(x) = (2x + 1) \exp[-\alpha x(x + 1)]$$

with $\alpha = \beta \hbar^2 / 2I$, gives

$$\sum_{n=0}^{\infty} f(n) \approx \frac{1}{\alpha} + \frac{1}{2}(1) - \frac{1}{12}(2 - \alpha) \approx \frac{1}{\alpha} + \frac{1}{3} \quad (\text{S4.56})$$

Therefore, the integral approximation is accurate when $2IkT/\hbar^2 \gg \frac{1}{3}$, or

$$T \gg \hbar^2 / 6kI \quad (\text{S4.57})$$

As can be seen in Table 6.1, $\hbar^2 / 6kI$ is typically less than 1 K. The full Euler summation formula is

$$\sum_{n=0}^{\infty} f(n) = \int_0^{\infty} f(x) dx + \frac{1}{2}f(0) - \frac{B_2}{2!} \frac{df}{dx} \Big|_0 - \frac{B_4}{4!} \frac{d^3 f}{dx^3} \Big|_0 - \frac{B_6}{6!} \frac{d^5 f}{dx^5} \Big|_0 - \dots \quad (\text{S4.58})$$

where the B_n s are the Bernoulli numbers, which can be found in any mathematical handbook.

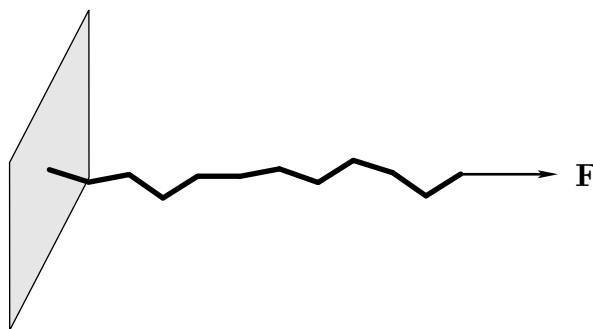


Fig. S4.2 A polymer chain, attached at one end.

Exercise 4.9 A polymer is a molecule composed of a long chain of identical molecular units, called monomers. Imagine a long polymer, made of N rodlike units, each of length l , attached end-to-end. Assume that the connections between the monomers are completely flexible so that the rods can make any angle with respect to one another. One end of the polymer is held fixed while a constant force F , in the x direction, is applied to the other end (Fig. S4.2). Except for an arbitrary constant, which can be ignored, the potential energy of any configuration of the polymer can be written as

$$U(\theta_1, \phi_1, \dots, \theta_N, \phi_N) = - \sum_{i=1}^N Fl \cos \theta_i \quad (\text{S4.59})$$

where θ_i and ϕ_i are polar angles defining the orientation, in three dimensions, of the i th monomer with respect to an axis parallel to the x axis. Assume that the configurational probability density,

$$P(\theta_1, \phi_1, \dots, \theta_N, \phi_N) = Z^{-1} \exp(-\beta U)$$

where

$$\int P(\theta_1, \phi_1, \dots, \theta_N, \phi_N) \prod_{i=1}^N \sin \theta_i d\theta_i d\phi_i = 1 \quad (\text{S4.60})$$

and $\beta = 1/kT$. (a) Calculate the configurational partition function Z . (b) Calculate $\langle U \rangle$ as a function of F and β . (c) Make the assumption, which is true for a classical system, that the average kinetic energy is proportional to T and use the thermodynamic relation

$$S = \int \frac{\partial E}{\partial T} \frac{dT}{T} = \int \frac{\partial E}{\partial \beta} \beta d\beta \quad (\text{S4.61})$$

where the integrals are indefinite integrals, to calculate the entropy.

Solution (a)

$$Z = \int \exp\left(\beta \sum F l \cos \theta_i\right) \sin \theta_1 d\theta_1 d\phi_1 \cdots \sin \theta_N d\theta_N d\phi_N = z^N \quad (\text{S4.62})$$

where

$$\begin{aligned} z &= 2\pi \int_0^\pi e^{\beta F l \cos \theta} \sin \theta d\theta \\ &= 2\pi \int_{-1}^1 e^{\beta F l \cos \theta} d(\cos \theta) \\ &= 4\pi \frac{\sinh(\beta F l)}{\beta F l} \end{aligned} \quad (\text{S4.63})$$

(b)

$$\begin{aligned} \langle U \rangle &= \left\langle -\sum F l \cos \theta_i \right\rangle \\ &= \frac{-\partial Z / \partial \beta}{Z} \\ &= -\frac{\partial \log Z}{\partial \beta} \\ &= -N \frac{\partial \log z}{\partial \beta} \\ &= -N \frac{\partial}{\partial \beta} (\log \sinh(\beta F l) - \log \beta + \text{const.}) \\ &= N[\beta^{-1} - F l \coth(\beta F l)] \end{aligned} \quad (\text{S4.64})$$

(c) Let $a \equiv F l$. Assuming that the kinetic energy is given by $K = N\gamma kT$, we can write the total thermal energy per monomer as

$$\frac{E}{N} = (\gamma + 1)/\beta - a \coth(a\beta) \quad (\text{S4.65})$$

Then

$$\frac{\partial(E/N)}{\partial \beta} = -(\gamma + 1)/\beta^2 + a^2 \text{csch}^2(a\beta) \quad (\text{S4.66})$$

and, by Eq. (S4.61),

$$\frac{S}{N} = -(\gamma + 1) \int \frac{d\beta}{\beta} + a^2 \int \text{csch}^2(a\beta) \beta d\beta \quad (\text{S4.67})$$

The first integral gives $-(\gamma + 1) \log \beta$. The second can be calculated by the identity

$$\begin{aligned} \int \text{csch}^2(a\beta) \beta d\beta &= -\frac{\partial}{\partial a} \int \coth(a\beta) d\beta \\ &= -\frac{\partial}{\partial a} [\log \sinh(a\beta)/a] \\ &= -\frac{\beta \coth(a\beta)}{a} + \frac{\log \sinh(a\beta)}{a^2} \end{aligned} \quad (\text{S4.68})$$

giving

$$\frac{S}{N} = -(\gamma + 1) \log \beta + \log \sinh(a\beta) - a\beta \coth(a\beta) + C \quad (\text{S4.69})$$

Exercise 4.10 A system is composed of a large number N of one-dimensional quantum harmonic oscillators whose angular frequencies are distributed over the range $\omega_a \leq \omega \leq \omega_b$ with a frequency distribution function $D(\omega) = A/\omega$. (a) Calculate the specific heat per oscillator at temperature T . (b) Evaluate the result in the limits of high and low T .

Solution (a) We will use a canonical ensemble. The partition function of a single oscillator of angular frequency ω , is

$$\begin{aligned} z_\omega &= \sum_{n=0}^{\infty} \exp\left(-\beta\hbar\omega\left(n + \frac{1}{2}\right)\right) \\ &= e^{-\beta\hbar\omega/2} \sum_{n=0}^{\infty} \left(e^{-\beta\hbar\omega}\right)^n \\ &= e^{-\beta\hbar\omega/2} / (1 - e^{-\beta\hbar\omega}) \\ &= \frac{1}{2} \sinh(\beta\hbar\omega/2) \end{aligned} \quad (\text{S4.70})$$

The canonical potential of the oscillator is

$$\phi_\omega = -\log[2 \sinh(\beta\hbar\omega/2)] \quad (\text{S4.71})$$

The average thermal energy of the oscillator is

$$E_\omega = -\frac{\partial\phi}{\partial\beta} = \frac{\hbar\omega}{2} \coth(\beta\hbar\omega/2) \quad (\text{S4.72})$$

The energy of the system of N oscillators is given in terms of the frequency distribution function by

$$\begin{aligned} E &= \int_{\omega_a}^{\omega_b} D(\omega) E_\omega d\omega \\ &= A \frac{\hbar}{2} \int_{\omega_a}^{\omega_b} \coth(\beta\hbar\omega/2) d\omega \\ &= (A/\beta) \log\left(\frac{\sinh(\beta\hbar\omega_b/2)}{\sinh(\beta\hbar\omega_a/2)}\right) \\ &= AkT \log\left(\frac{\sinh(\hbar\omega_b/2kT)}{\sinh(\hbar\omega_a/2kT)}\right) \end{aligned} \quad (\text{S4.73})$$

The constant A can be written in terms of N by using the normalization condition

$$N = \int_{\omega_a}^{\omega_b} D(\omega) d\omega = A \int_{\omega_a}^{\omega_b} \frac{d\omega}{\omega} = A \log(\omega_b/\omega_a) \quad (\text{S4.74})$$

Therefore, the thermal energy per oscillator $\varepsilon = E/N$ is

$$\varepsilon = \frac{kT}{\log(\omega_b/\omega_a)} \log\left(\frac{\sinh(\hbar\omega_b/2kT)}{\sinh(\hbar\omega_a/2kT)}\right) \quad (\text{S4.75})$$

The specific heat per oscillator is $\partial\varepsilon/\partial T$.

$$\begin{aligned} C &= \frac{k}{\log(\omega_b/\omega_a)} \log\left[\frac{\sinh(\hbar\omega_b/2kT)}{\sinh(\hbar\omega_a/2kT)}\right] \\ &\quad + \frac{\hbar\omega_a \coth(\hbar\omega_a/2kT)}{2T \log(\omega_b/\omega_a)} - \frac{\hbar\omega_b \coth(\hbar\omega_b/2kT)}{2T \log(\omega_b/\omega_b)} \end{aligned} \quad (\text{S4.76})$$

(b) If $2kT \gg \hbar\omega$, then $\sinh(\hbar\omega/2kT) \approx \hbar\omega/2kT$ and $\coth(\hbar\omega/2kT) \approx 2kT/\hbar\omega$. Therefore, in the high temperature limit, the first term in Eq. (S4.76) approaches k while the second and third terms cancel one another.

$$C \approx k \quad (\text{S4.77})$$

This is the expected Dulong–Petit result. In the low-temperature limit $\hbar\omega/2kT$ becomes very large. But for large values of x ,

$$\log(e^x - e^{-x}) = \log[e^x(1 - e^{-2x})] \approx x - e^{-2x} \quad (\text{S4.78})$$

and

$$\coth x = \frac{1 + e^{-2x}}{1 - e^{-2x}} \approx 1 + 2e^{-2x} \quad (\text{S4.79})$$

These approximations give

$$\begin{aligned} C \approx & \frac{k}{\log(\omega_b/\omega_a)} \left(\frac{\hbar(\omega_b - \omega_a)}{2kT} + e^{-\hbar\omega_a/kT} - e^{-\hbar\omega_b/kT} \right) \\ & + \frac{\hbar}{2T \log(\omega_b/\omega_a)} \left(\omega_a + 2\omega_a e^{-\hbar\omega_a/kT} - \omega_b - 2\omega_b e^{-\hbar\omega_b/kT} \right) \end{aligned} \quad (\text{S4.80})$$

Using the facts that $\hbar\omega/kT \gg 1$ and $e^{-\hbar\omega_a/kT} \gg e^{-\hbar\omega_b/kT}$, we get

$$C \approx \frac{\hbar\omega_a e^{-\hbar\omega_a/kT}}{T \log(\omega_b/\omega_a)} \quad (\text{S4.81})$$

This is an example of the general rule that if a system of oscillators has a lowest frequency that is larger than zero, then the specific heat always has a factor of $\exp(-\hbar\omega_{\min}/kT)$ at very low temperatures.

Exercise 4.11 In Eq. (4.32), the vibrational energy of a solid is expressed in terms of the Debye integral

$$I(\lambda) = \int_0^\lambda \frac{x^2 dx}{e^x - 1} \quad (\text{S4.82})$$

Work out approximations to this integral, giving at least two terms, for the two extremes $\lambda \gg 1$ and $\lambda \ll 1$.

Solution For $\lambda \gg 1$, it is useful to decompose the integral as

$$I(\lambda) = \int_0^\infty \frac{x^3 dx}{e^x - 1} - \int_\lambda^\infty \frac{x^3 dx}{e^x - 1} \quad (\text{S4.83})$$

The first integral is given in the Mathematical Appendix. It is equal to $\pi^4/15$. In the second integral, since $x \geq \lambda$, $e^x \gg 1$ and the -1 in the denominator can be neglected. This leads to an integral that can be done.

$$\begin{aligned} I(\lambda) & \approx \frac{\pi^4}{15} - \int_\lambda^\infty e^{-x} x^3 dx \\ & = \frac{\pi^4}{15} - (1 + \lambda + \frac{1}{2}\lambda^2 + \frac{1}{6}\lambda^3)e^{-\lambda} \end{aligned} \quad (\text{S4.84})$$

For $\lambda \ll 1$, one can use the expansion of the exponential function in the denominator of the integrand.

$$e^x - 1 \approx x + \frac{1}{2}x^2 \quad (\text{S4.85})$$

Then $x^3/(e^x - 1) \approx x^2(1 + x/2)^{-1} \approx x^2 - x^3/2$ and

$$I(\lambda) \approx \int_0^\lambda (x^2 - x^3/2) dx = \frac{1}{3}\lambda^3 - \frac{1}{8}\lambda^4 \quad (\text{S4.86})$$

Exercise 4.12 Consider a system of N classical particles in a potential field $U(\mathbf{r})$. Using the canonical ensemble, show that the equilibrium particle density is of the Maxwell–Boltzmann form

$$n(\mathbf{r}) = n_0 e^{-U(\mathbf{r})/kT} \quad (\text{S4.87})$$

Solution The Hamiltonian function for the N -particle system is

$$H = \sum_{i=1}^N p_i^2/2m + \sum_{i=1}^N U(\mathbf{r}_i) \quad (\text{S4.88})$$

The probability density for finding the system in state $(\mathbf{r}_1, \mathbf{p}_1, \dots, \mathbf{r}_N, \mathbf{p}_N)$ is, according to Eq. (4.52),

$$P(\mathbf{r}_1, \mathbf{p}_1, \dots, \mathbf{r}_N, \mathbf{p}_N) = I^{-1} e^{-\beta H} \quad (\text{S4.89})$$

The normalization integral I factors into N identical terms

$$\begin{aligned} I &= \int e^{-\beta H} d^3r_1 d^3p_1 \cdots d^3r_N d^3p_N \\ &= \left(\int e^{-\beta U(\mathbf{r})} d^3r \int e^{-\beta p^2/2m} d^3p \right)^N \\ &= (2\pi m/\beta)^{3N/2} \left(\int e^{-\beta U} d^3r \right)^N \end{aligned} \quad (\text{S4.90})$$

The probability of finding particle number 1 at location \mathbf{r} , regardless of its momentum and regardless of the positions and momenta of all the other particles, is calculated by setting \mathbf{r}_1 equal to \mathbf{r} and integrating $P(\mathbf{r}, \mathbf{p}_1, \dots, \mathbf{r}_N, \mathbf{p}_N)$ over all the irrelevant variables. The integrations simply cancel equivalent terms in the normalization constant, leaving

$$P_1(\mathbf{r}) = \frac{e^{-\beta U(\mathbf{r})}}{\int e^{-\beta U} d^3r} \quad (\text{S4.91})$$

The probability of finding particle number 1 inside d^3r is $P_1(\mathbf{r}) d^3r$. Since all particles have the same distribution, the average number of particles inside the volume element d^3r is $NP_1(\mathbf{r}) d^3r$. But that defines the particle density function. Thus

$$n(\mathbf{r}) = \frac{Ne^{-\beta U(\mathbf{r})}}{\int e^{-\beta U} d^3r} \quad (\text{S4.92})$$

which is of the Maxwell–Boltzmann form.

Exercise 4.13 Calculate the specific heat of a quantized square drumhead (a square elastic membrane with zero boundary conditions on the edges).

Solution The wave function for a drumhead, $u(x, y, t)$, represents the displacement, in the z direction at time t , of that point on the drumhead with coordinates (x, y) . If μ is the mass per unit area and σ is the surface tension (the pulling force per unit length within the membrane), then $u(x, y, t)$ satisfies the wave equation

$$\mu \frac{\partial^2 u}{\partial t^2} - \sigma \left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} \right) = 0 \quad (\text{S4.93})$$

For an $L \times L$ drumhead, the boundary conditions are

$$u(0, y, t) = u(L, y, t) = u(x, 0, t) = u(x, L, t) = 0 \quad (\text{S4.94})$$

The normal-mode solutions are of the form

$$u(x, y, t) = A_{mn}(t) \sin(m\pi x/L) \sin(n\pi y/L) \quad (\text{S4.95})$$

Putting this into Eq. (S4.93), we see that A_{mn} satisfies a harmonic oscillator equation

$$\frac{d^2 A_{mn}}{dt^2} + \omega_{mn}^2 A_{mn} = 0 \quad (\text{S4.96})$$

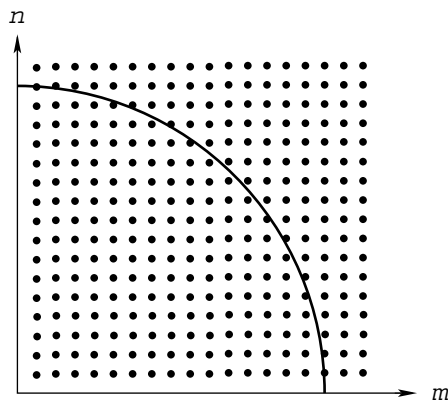


Fig. S4.3 Each pair of integers gives one normal mode of the square drumhead.

where

$$\omega_{mn}^2 = (\sigma\pi^2/\mu L^2)(m^2 + n^2) \quad (\text{S4.97})$$

The integers m and n must be positive. Let $N(\omega)$ be the number of normal modes with angular frequencies less than ω . Then $N(\omega)$ is the number of pairs of positive integers with $\sqrt{m^2 + n^2} < \sqrt{\mu/\sigma} L\omega/\pi \equiv R$. For large L we can approximate this by the area shown in Fig. S4.3.

$$N(\omega) = \frac{\pi}{4} R^2 = \frac{\mu L^2}{4\pi\sigma} \omega^2 \quad (\text{S4.98})$$

This gives the normal mode frequency distribution function

$$D(\omega) = \frac{dN(\omega)}{d\omega} = \frac{\mu L^2}{2\pi\sigma} \omega \quad (\text{S4.99})$$

According to Eq. (4.25), the thermal energy of the system at temperature T is

$$E = \frac{\mu L^2}{2\pi\sigma} \int_0^\infty \frac{\hbar\omega^2 d\omega}{e^{\hbar\omega/kT} - 1} \quad (\text{S4.100})$$

Changing to the integration variable $x = \hbar\omega/kT$ and using the Table of Integrals, we get

$$\begin{aligned} E &= \frac{\mu L^2 (kT)^3}{2\pi\sigma\hbar^2} \int_0^\infty \frac{x^2 dx}{e^x - 1} \\ &= \frac{\mu L^2 (kT)^3}{\pi\sigma\hbar^2} \zeta(3) \end{aligned} \quad (\text{S4.101})$$

The specific heat per unit area of membrane is

$$\frac{C}{L^2} = \frac{3\mu k^3 \zeta(3)}{\pi\sigma\hbar^2} T^2 \quad (\text{S4.102})$$

This specific heat goes to infinity as T increases, which is unrealistic. The source of the problem is that we have used the wave equation to generate an infinite number of normal modes. In fact, the wave equation is only valid for normal modes with wavelengths much larger than microscopic dimensions.

Exercise 4.14 A piston of mass M , in a frictionless vertical cylinder of area A , encloses an N -particle ideal gas. (a) Describing the state of the piston by a single coordinate z_o and momentum p_o (which is not realistic, since it actually has a microscopic structure), and using a canonical ensemble, calculate the probability distribution $P(z_o)$ for the piston height. Neglect the effect of the gravitational field on the ideal

gas particles. (b) Show that, for large N , it is a Gaussian function. (c) Show that the fluctuation in the gas volume is given by

$$\frac{\Delta V}{V} = \frac{1}{\sqrt{N}} \quad (\text{S4.103})$$

Solution (a) The Hamiltonian function for the system is

$$H = \frac{p_o^2}{2M} + Mgz_o + \sum_{i=1}^N p_i^2/2m \quad (\text{S4.104})$$

The x and y coordinates of the gas particles are restricted to the area A . Their z coordinates must be less than z_o . The canonical probability density function is

$$P(z_o, p_o, \mathbf{r}_1, \mathbf{p}_1, \dots, \mathbf{r}_N, \mathbf{p}_N) = I^{-1} e^{-\beta H} \quad (\text{S4.105})$$

The normalization integral is

$$\begin{aligned} I &= \int_o^\infty dz_o e^{-\beta Mgz_o} \int_o^{z_o} dz_1 \cdots dz_N \\ &\quad \times \int_A dx_1 dy_1 \cdots dx_N dy_N (2\pi M/\beta)^{1/2} (2\pi m/\beta)^{3N/2} \\ &= (2\pi M/\beta)^{1/2} (2\pi m/\beta)^{3N/2} A^N \int_o^\infty z_o^N e^{-\beta Mgz_o} dz_o \\ &= (2\pi M/\beta)^{1/2} (2\pi m/\beta)^{3N/2} A^N N! / (\beta M g)^{N+1} \end{aligned} \quad (\text{S4.106})$$

where we have made use of the integral formula for $N!$ given in the Mathematical Appendix.

The probability distribution for z_o is obtained by integrating over all other coordinates and over all momenta. Most of the integrals cancel factors in I , leaving

$$P(z_o) = \frac{(\beta W)^{N+1}}{N!} z_o^N e^{-\beta W z_o} \quad (\text{S4.107})$$

with $W = Mg$. (b) The most probable value of z_o , which we will call z^* , is given by $P'(z^*) = 0$. This gives

$$\frac{N}{z^*} - \beta W = 0 \quad (\text{S4.108})$$

or

$$z^* = \frac{NkT}{W} \quad (\text{S4.109})$$

$P(z_o)$ can be written as

$$P(z_o) = \frac{(\beta W)^{N+1}}{N!} e^{-g(z_o)} \quad (\text{S4.110})$$

with $g(z) = \beta W z - N \log z$. Expanding $g(z)$ to second order about z^* , we get (with $\zeta = z - z^*$)

$$g \approx \beta W z^* - N \log z^* + \frac{1}{2} N (\zeta/z^*)^2 \quad (\text{S4.111})$$

Therefore

$$P(z^* + \zeta) = \frac{(\beta W)^{N+1} (z^*)^N e^{-\beta W z^*}}{N!} e^{-N(\zeta/z^*)^2/2} \quad (\text{S4.112})$$

Using the fact that $\beta W z^* = N$ and Stirling's approximation in the form $N! \approx N^N e^{-N} (2\pi N)^{1/2}$, we can write this as

$$P(z^* + \zeta) = \frac{\sqrt{N/2\pi}}{z^*} e^{-N(\zeta/z^*)^2/2} \quad (\text{S4.113})$$

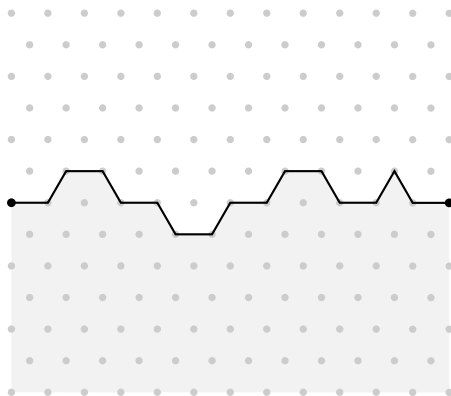


Fig. S4.4 The surface of a two-dimensional liquid.

(c) The mean-square fluctuation in the height of the piston is

$$(\Delta z_o)^2 = \frac{\sqrt{N/2\pi}}{z^*} \int_{-\infty}^{\infty} e^{-N(\zeta/z^*)^2/2} \zeta^2 d\zeta = \frac{(z^*)^2}{N} \quad (\text{S4.114})$$

But, because V is proportional to z^* ,

$$\frac{\Delta V}{V} = \frac{\Delta z_o}{z^*} = \frac{1}{\sqrt{N}} \quad (\text{S4.115})$$

Exercise 4.15 Shown in Fig. S4.4 is the surface of a two-dimensional “liquid.” In order to make the possible surface configurations discrete, we assume that the surface is confined to a triangular lattice. Assume that the surface is pinned at the two points shown and that the energy of the system is proportional to the surface length. The two pins are L lattice distances apart. Assume also that overhangs (places where the outward-pointing normal to the surface points downward, rather than upward) are forbidden. Use the microcanonical ensemble to calculate the length of the surface as a function of temperature.

Solution Let N_o be the number of horizontal surface elements, N_+ be the number of surface elements that rise from left to right, and N_- be the number of surface elements that fall from left to right. The length of the surface in lattice units is $N_o + N_+ + N_-$. If we take the zero-energy configuration as the flat, lowest-energy state, then the energy of any configuration can be written in terms of N_o, N_+ , and N_- as

$$E = \varepsilon(N_o + N_+ + N_- - L) \quad (\text{S4.116})$$

In order for the surface to reach the fixed point on the right, it is necessary that $N_+ = N_-$. Because the projection of the surface onto the line between the pins always has length L , it is also necessary that $N_o + (N_+ + N_-)/2 = L$. From these two equations we can easily write N_+ and N_- in terms of N_o .

$$N_+ = N_- = L - N_o \quad (\text{S4.117})$$

For a system with discrete states, $\Omega(E)$ is the number of states that have energy E . But, combining Eqs. (S4.100) and (S4.101), we can write E in terms of N_o .

$$E = \varepsilon(L - N_o) \quad (\text{S4.118})$$

Therefore, the value of E determines the value of N_o and hence the values of N_+ and N_- also. For given N_o, N_+ , and N_- we can get all possible surface configurations by permuting the three types of surface elements. The number of such configurations is $(N_o + N_+ + N_-)!/N_o!N_+!N_-!$. The spacing between neighboring energy values is ε . Therefore

$$\Omega'(E) = \frac{(N_o + N_+ + N_-)!}{N_o!N_+!N_-!} \frac{1}{\varepsilon} = \frac{(2L - N_o)!}{N_o!((L - N_o)!)^2} \frac{1}{\varepsilon} \quad (\text{S4.119})$$

S^o is the logarithm of Ω' . Using Stirling's formula and the fact that $L - N_o = E/\varepsilon$, we see that

$$\begin{aligned} S^o &= (2L - N_o) \log(2L - N_o) - N_o \log N_o \\ &\quad - 2(L - N_o) \log(L - N_o) - \log \varepsilon \\ &= \left(L + \frac{E}{\varepsilon}\right) \log\left(L + \frac{E}{\varepsilon}\right) - \left(L - \frac{E}{\varepsilon}\right) \log\left(L - \frac{E}{\varepsilon}\right) \\ &\quad - 2\frac{E}{\varepsilon} \log\left(\frac{E}{\varepsilon}\right) - \log \varepsilon \end{aligned} \quad (\text{S4.120})$$

The thermodynamic relation $\partial S^o / \partial E = 1/kT$ gives

$$\frac{1}{kT} = \frac{1}{\varepsilon} \left[\log\left(L + \frac{E}{\varepsilon}\right) + \log\left(L - \frac{E}{\varepsilon}\right) - 2 \log\left(\frac{E}{\varepsilon}\right) \right] \quad (\text{S4.121})$$

or

$$\frac{\varepsilon}{kT} = \log \left[\frac{L^2 \varepsilon^2 - E^2}{E^2} \right] \quad (\text{S4.122})$$

which gives

$$e^{\varepsilon/kT} = \frac{L^2 \varepsilon^2 - E^2}{E^2} \quad (\text{S4.123})$$

This equation can easily be solved for E .

$$E = \frac{L\varepsilon}{(e^{\varepsilon/kT} + 1)^{1/2}} \quad (\text{S4.124})$$

Since E is equal to ε times the length of the surface minus its minimum length, we see that the length of the surface at temperature T is

$$l(T) = L[1 + (e^{\varepsilon/kT} + 1)^{-1/2}] \quad (\text{S4.125})$$

For $kT \ll \varepsilon$ $l(T) \approx L$ and for $kT \gg \varepsilon$ $l(T) \approx L(1 + 1/\sqrt{2})$.

Exercise 4.16 For zero-mass particles, or for ordinary particles when $kT \gg mc^2$, one can approximate the relativistic relationship between energy and momentum by the simple extreme relativistic relation

$$E(p) = c|\mathbf{p}| \quad (\text{S4.126})$$

Calculate the pressure and energy of a classical extremely relativistic gas as functions of density and temperature and show that $pV = E/3$.

Solution The partition function for a system of N particles in a volume V is

$$Z = \frac{V^N}{h^{3N} N!} \left(4\pi \int_0^\infty e^{-\beta c p} p^2 dp \right)^N \quad (\text{S4.127})$$

But

$$\int_0^\infty e^{-\beta c p} p^2 dp = \frac{1}{(\beta c)^3} \int_0^\infty e^{-x} x^2 dx = \frac{2}{(\beta c)^3} \quad (\text{S4.128})$$

Therefore

$$Z = \frac{(8\pi)^N V^N}{(\beta c h)^{3N} N!} \quad (\text{S4.129})$$

and

$$\phi = N[\log(V/N) - 3 \log \beta + \text{const.}] \quad (\text{S4.130})$$

The pressure and energy are given by

$$\beta p = \frac{\partial \phi}{\partial V} = \frac{N}{V} \quad (\text{S4.131})$$

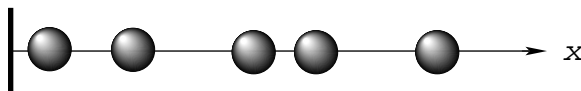


Fig. S4.5 Hard-core particles on a line.

and

$$E = -\frac{\partial\phi}{\partial\beta} = \frac{3N}{\beta} \quad (\text{S4.132})$$

or

$$pV = NkT \quad \text{and} \quad E = 3NkT \quad (\text{S4.133})$$

Exercise 4.17 The system shown in Fig. S4.5 consists of N impenetrable beads of diameter a on a frictionless wire. The rightmost bead is subjected to a constant force F toward the origin. (a) Calculate the partition function of the system as a function of N , β , and F . Note: Since the beads cannot pass through one another, they should be taken as distinguishable and the $N!$ should be omitted in the definition of Z . (b) Calculate the specific heat of the system and the average position of the rightmost particle as functions of T . (c) For a one-dimensional system, the pressure is simply the force being applied to the last particle (there is no “area” to divide by). Show that the pressure equation of state is $p = nkT/(1 - na)$, where the density, $n \equiv N/\langle x_N \rangle$.

Solution (a) We let x_n be the coordinate of the left side of the n th bead. The force on the N th particle is derivable from the potential $U = F(x_N - (N - 1)a)$ where the constant term in the potential has been chosen so that $U = 0$ when the system is in its lowest-energy state. That is, the state with $x_N = (N - 1)a$. Therefore, the Hamiltonian function is

$$H = \sum_{n=1}^N p_n^2/2m + F(x_N - (N - 1)a) \quad (\text{S4.134})$$

The coordinates are restricted by the N inequalities,

$$0 < x_1, \quad x_1 + a < x_2, \quad x_2 + a < x_3, \dots, \quad x_{N-1} + a < x_N \quad (\text{S4.135})$$

Therefore, the partition function is

$$\begin{aligned} Z &= \left(\frac{1}{h} \int_{-\infty}^{\infty} e^{-\beta p^2/2m} dp \right)^N \int_{-\infty}^{\infty} dx_1 \\ &\times \int_{x_1+a}^{\infty} dx_2 \cdots \int_{x_{N-1}+a}^{\infty} dx_N e^{-\beta F(x_N - (N-1)a)} \end{aligned} \quad (\text{S4.136})$$

We define a coordinate transformation from the coordinates (x_1, x_2, \dots, x_N) to new coordinates (u_1, u_2, \dots, u_N) by the equations $u_1 = x_1$, $u_2 = x_2 - (x_1 + a)$, $u_3 = x_3 - (x_2 + a)$, \dots , $u_N = x_N - (x_{N-1} + a)$. We notice that

$$u_1 + u_2 + \dots + u_N = x_N - (N - 1)a \quad (\text{S4.137})$$

Written in terms of the new coordinates

$$\begin{aligned} Z &= (2\pi m/\beta h^2)^{N/2} \int_0^{\infty} e^{-\beta F u_1} du_1 \int_0^{\infty} e^{-\beta F u_2} du_2 \cdots \int_0^{\infty} e^{-\beta F u_N} du_N \\ &= (2\pi m/\beta h^2)^{N/2} (\beta F)^{-N} \end{aligned} \quad (\text{S4.138})$$

(b) The canonical potential is

$$\phi = N \left[\frac{1}{2} \log(2\pi m/h^2) - \frac{3}{2} \log \beta - \log F \right] \quad (\text{S4.139})$$

The energy of the system at temperature T is

$$E = -\frac{\partial\phi}{\partial\beta} = \frac{3}{2}kT \tag{S4.140}$$

which gives, for the specific heat,

$$C = \frac{\partial E}{\partial T} = \frac{3}{2}k \tag{S4.141}$$

The average position of the N th particle is $\langle x_N \rangle$. From Eq. (S4.136), one can see that

$$\begin{aligned} \langle x_N - (N - 1)a \rangle &= -kT \frac{\partial Z / \partial F}{Z} \\ &= -kT \frac{\partial\phi}{\partial F} \\ &= NkT/F \end{aligned} \tag{S4.142}$$

Thus

$$\langle x_N \rangle = (N - 1)a + NkT/F \tag{S4.143}$$

(c) For large N , we can replace the $N-1$ in the previous equation by N . If we do that and use the fact that $p = F$, we obtain the pressure equation of state.

$$p = \frac{Nkt}{x_N - Na} = \frac{nkT}{1 - na} \tag{S4.144}$$

Since $\langle U \rangle = F\langle x_N - (N - 1)a \rangle$, we see that, of the $\frac{3}{2}NkT$ of thermal energy, two-thirds of it is in the form of potential energy and only $\frac{1}{2}NkT$ is kinetic energy. This agrees with the equipartition theorem.

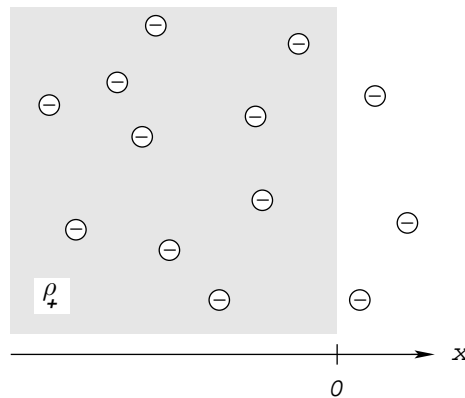


Fig. S4.6 Electrons diffuse out of a metal surface.

Exercise 4.18 A metal may be pictured as a rigid collection of positively charged ions plus a set of mobile conduction electrons. The ions are composed of the atomic nuclei plus their inner-shell electrons, which are tightly bound to the nuclei and play no role in electrical conductivity. A more simplified model of a metal, sometimes called the *jellium model*, is obtained by replacing the system of ions by a uniform positive background charge density of magnitude en_o within which moves a gas of electrons whose number is sufficient to make the whole system electrically neutral. Consider a classical jellium model of a metal surface. That is, take the background charge density to be

$$\rho_+(x) = \begin{cases} en_o, & \text{if } x < 0 \\ 0, & \text{if } x > 0 \end{cases} \tag{S4.145}$$

The charge density of the electrons is $\rho_- = -en(x)$, where $n(x)$ is the electron density—to be determined. Assume that the electrostatic potential $V(x)$ approaches zero deep inside the metal. Use Poisson's equation,

$$\frac{d^2V(x)}{dx^2} = -\frac{\rho(x)}{\epsilon_o} \quad (\text{S4.146})$$

and the Maxwell-Boltzmann equilibrium density function (remember that $U = -eV$)

$$n(x) = Ce^{eV(x)/kT} \quad (\text{S4.147})$$

along with the assumption that $kT \gg eV$, to determine $V(x)$ and $n(x)$ everywhere.

Solution First let us determine the constant C in Eq. (S4.147). Deep inside the metal $V(x) \rightarrow 0$ and the background charge is en_o . But the total charge density must go to zero there. Thus $C = n_o$. Using the inequality $kT \gg eV$ we can expand the exponential and keep only the first two terms.

$$n(x) \approx n_o[1 + eV(x)/kT] \quad (\text{S4.148})$$

Inside the metal (that is, for $x < 0$) Poisson's equation is

$$\frac{d^2V(x)}{dx^2} = -\frac{1}{\epsilon_o}(\rho_+ + \rho_-) = \frac{n_o e^2}{\epsilon_o kT} V(x) \quad (\text{S4.149})$$

The solution to this equation that goes to zero as $x \rightarrow -\infty$ is

$$V(x) = V_o e^{\lambda x} \quad (\text{S4.150})$$

where $\lambda = e\sqrt{n_o/\epsilon_o kT}$. Outside the metal $\rho_+ = 0$ and Poisson's equation takes the form

$$\frac{d^2V(x)}{dx^2} = \frac{e}{\epsilon_o} n(x) = \frac{en_o}{\epsilon_o} \left(1 + \frac{e}{kT} V(x)\right) \quad (\text{S4.151})$$

The way to solve this equation is to notice that one can eliminate the constant term on the right-hand side by defining $f(x) = V(x) + kT/e$. Then $f(x)$ satisfies the equation

$$\frac{d^2f(x)}{dx^2} = \frac{e^2 n_o}{\epsilon_o kT} f(x) = \lambda^2 f(x) \quad (\text{S4.152})$$

The only solution to this equation that does not diverge as $x \rightarrow \infty$ is

$$f(x) = f_o e^{-\lambda x} \quad (\text{S4.153})$$

The constants V_o and f_o are determined by demanding that $V(x)$ and $V'(x)$ be continuous at $x = 0$. These conditions give the equations

$$V_o = f_o - kT/e \quad \text{and} \quad V_o = -f_o \quad (\text{S4.154})$$

which have the solution

$$V_o = -\frac{kT}{2e} \quad \text{and} \quad f_o = \frac{kT}{2e} \quad (\text{S4.155})$$

Thus

$$V(x) = \begin{cases} -(kT/2e)e^{\lambda x}, & \text{if } x < 0 \\ -(kT/2e)(2 - e^{-\lambda x}), & \text{if } x > 0 \end{cases} \quad (\text{S4.156})$$

The electron density is then given by Eq. (S4.148).

$$n(x) = \begin{cases} n_o(1 - \frac{1}{2}e^{\lambda x}), & \text{if } x < 0 \\ \frac{1}{2}n_o e^{-\lambda x}, & \text{if } x > 0 \end{cases} \quad (\text{S4.157})$$

Notice that the total charge density is an antisymmetric function, $\rho(-x) = -\rho(x)$.

Exercise 4.19 A perfect atomic crystal has exactly one atom at each lattice site. Such a configuration is only stable at zero temperature. At any finite temperature, due to the thermal fluctuations, various types of crystal imperfections develop. One of the simplest, called a *vacancy*, is an empty lattice point. In this example we want to determine the temperature dependence of the density of vacancies. We take the energy of the perfect crystal as zero and assume that the energy of the crystal with n vacancies is $n\varepsilon$. We also assume that n is much less than N , the number of atoms in the crystal. In doing this calculation we must be careful because there are two small quantities available. One of them is n/N , the density of vacancies. The other is N_s/N , where N_s is the number of sites on the surface of the perfect crystal. Assuming that $N_s/N \ll n/N \ll 1$, calculate n/N as a function of T . (Since $N_s/N \sim 1/N^{1/3}$ is an extremely small number for a macroscopic crystal, this is the condition that usually holds.)

Solution Imagine that we begin with a perfect crystal, with N particles filling N sites, and begin to warm it. Occasionally a particle near the surface will jump to the surface, leaving behind a vacancy. The vacancies will then migrate throughout the volume of the crystal. Because we are assuming that, at equilibrium, the total number of vacancies n is much larger than the original number of surface sites, many new surface layers will have to be created in order to make room for the particles that come from the vacancies. The number of lattice sites occupied by the new, imperfect crystal will be $N + n$. We can view the system as being composed of N particles and n vacancies, distributed over $N + n$ sites. The number of possible configurations is just the binomial coefficient.

$$K = \frac{(N+n)!}{N!n!} \quad (\text{S4.158})$$

The entropy is the logarithm of the number of configurations. Using Stirling's formula,

$$S^o = (N+n) \log(N+n) - N \log N - n \log n \quad (\text{S4.159})$$

Since $E = \varepsilon n$, $\beta = \partial S^o / \partial E = (1/\varepsilon) \partial S^o / \partial n$. Thus

$$\frac{\varepsilon}{kT} = \frac{\partial S^o}{\partial n} = \log\left(\frac{N+n}{n}\right) \quad (\text{S4.160})$$

or

$$\frac{N+n}{n} = e^{\varepsilon/kT} \quad (\text{S4.161})$$

which can easily be solved for n/N .

$$\frac{n}{N} = \frac{1}{e^{\varepsilon/kT} - 1} \approx e^{-\varepsilon/kT} \quad (\text{S4.162})$$

where the last step uses the fact that $e^{\varepsilon/kT}$ must be much larger than one if $n/N \ll 1$.

Exercise 4.20 Another type of crystal defect is an *interstitial atom*, that is, an atom squeezed into a space between filled lattice spaces. Such interstitial defects cause a local distortion of the crystal structure and therefore have fairly high energy. To study such defects let us consider a perfect crystal of N lattice sites that is rigidly constrained to its original volume and warmed to temperature T . At equilibrium, n particles will have jumped from their original positions to interstitial positions, creating n vacancies and n interstitial defects. Assuming that the energy of the configuration described is proportional to n and that there are N interstitial positions, calculate n/N as a function of T .

Solution The vacancies can be distributed among the N lattice sites in $N!/n!(N-n)!$ ways. The interstitial atoms can be distributed among the N interstitial sites in $N!/n!(N-n)!$ ways. Therefore, the total number of configurations of the system is

$$K = \left[N!/n!(N-n)! \right]^2 \quad (\text{S4.163})$$

The entropy is, using Stirling's approximation,

$$S^o = \log K = 2[N \log N - n \log n - (N-n) \log(N-n)] \quad (\text{S4.164})$$

The energy is given by $E = \varepsilon n$, and therefore $\beta = \partial S^o / \partial E = (1/\varepsilon) \partial S^o / \partial n$.

$$\frac{\varepsilon}{kT} = \frac{\partial S^o}{\partial n} = 2 \log \frac{N-n}{n} \quad (\text{S4.165})$$

This equation can be solved for n/N , giving

$$\frac{n}{N} = \frac{1}{e^{\varepsilon/2kT} + 1} \approx e^{-\varepsilon/2kT} \quad (\text{S4.166})$$

Exercise 4.21 The molecules of an imaginary ideal gas have internal energy levels that are equally spaced so that the n th energy eigenvalue is $E_n = n\varepsilon$, where $n = 0, 1, 2, \dots$. The degeneracy of the n th energy level is $n + 1$. Calculate the contribution to the thermal energy of the internal energy states.

Solution For a single molecule, the internal partition function is

$$\begin{aligned} z_{\text{int}} &= \sum_{n=0}^{\infty} (n+1) e^{-\beta \varepsilon n} \\ &= \sum_{n=0}^{\infty} (n+1) x^n \quad (x = e^{-\beta \varepsilon}) \\ &= \frac{d}{dx} \sum_{m=0}^{\infty} x^m \quad (m = n+1) \\ &= \frac{d}{dx} (1-x)^{-1} \\ &= (1-x)^{-2} \\ &= (1 - e^{-\beta \varepsilon})^{-2} \end{aligned} \quad (\text{S4.167})$$

The contribution of the internal states to the canonical potential of the molecule is

$$\phi_{\text{int}} = -2 \log(1 - e^{-\beta \varepsilon}) \quad (\text{S4.168})$$

The internal energy of the molecule is

$$E_{\text{int}} = -\frac{\partial \phi_{\text{int}}}{\partial \beta} = \frac{2\varepsilon}{e^{\beta \varepsilon} - 1} \quad (\text{S4.169})$$

The total energy of the N -particle gas would be

$$E = \frac{3}{2} N k T + \frac{2N\varepsilon}{e^{\varepsilon/kT} - 1} \quad (\text{S4.170})$$

Notice that Eq. (S4.169) has the same form as the thermal energy of a harmonic oscillator with angular frequency $\omega = \varepsilon/\hbar$ except for the factor of 2. This is easy to understand. If the internal energy states were composed of two independent harmonic oscillators with the same angular frequency, then the energy levels, measured from the ground state, would be given by

$$E(n_1, n_2) = \hbar \omega (n_1 + n_2) \quad (\text{S4.171})$$

But it is easy to see that there are just $n + 1$ combinations of n_1 and n_2 that add up to n . Thus the spectrum and degeneracies of the molecule are those of a pair of harmonic oscillators and so the thermal energy is twice that of a single oscillator.

Exercise 4.22 The total dipole moment of a gas of dipolar molecules in an electric field directed along the z axis is defined as $P = N\bar{\mu}_z$. In Eq. (4.78) it is shown that $P = kT \partial \phi / \partial \mathcal{E}$, where ϕ is the canonical potential

and \mathcal{E} is the electric field strength. Derive a similar (but different) formula for $(\Delta P)^2$, the mean-square fluctuation in P .

Solution We know that

$$(\Delta P)^2 = \langle P^2 \rangle - \langle P \rangle^2 \tag{S4.172}$$

But, $P = \sum \mu \cos \theta_i$, and therefore

$$\langle P^2 \rangle = \left\langle \mu^2 \sum_{i,j} \cos \theta_i \cos \theta_j \right\rangle \tag{S4.173}$$

Also, $H = H_o - \mathcal{E} \mu \sum \cos \theta_i$. If we define the normalization integral

$$I = \int \exp\left(-\beta H_o - \beta \mu \mathcal{E} \sum_n \cos \theta_n\right) d^K x d^K p \tag{S4.174}$$

then

$$\begin{aligned} \langle P^2 \rangle &= \frac{\int (\mu \sum \cos \theta_i)^2 \exp[-\beta H_o - \beta \mu \mathcal{E} \sum \cos \theta_n] d^K x d^K p}{I} \\ &= (kT)^2 \frac{\partial^2 I / \partial \mathcal{E}^2}{I} \end{aligned} \tag{S4.175}$$

and

$$\begin{aligned} \langle P^2 \rangle - \langle P \rangle^2 &= (kT)^2 \left[\frac{\partial^2 I / \partial \mathcal{E}^2}{I} - \left(\frac{\partial I / \partial \mathcal{E}}{I} \right)^2 \right] \\ &= (kT)^2 \frac{\partial}{\partial \mathcal{E}} \left(\frac{\partial I / \partial \mathcal{E}}{I} \right) \\ &= (kT)^2 \frac{\partial^2 \phi}{\partial \mathcal{E}^2} \end{aligned} \tag{S4.176}$$

where, in the final step, we have used the fact that

$$\phi = \log(I/h^K N!) = \log I - \log(h^K N!) \tag{S4.177}$$

which shows that $\partial \phi / \partial \mathcal{E} = \partial(\log I) / \partial \mathcal{E}$. Notice that this analysis does not really depend on the detailed form of the observable P . In fact, if any observable A and some parameter λ satisfy the relation $\langle A \rangle = \partial \phi / \partial \lambda$, then the fluctuation in A is given by $(\Delta A)^2 = \partial^2 \phi / \partial \lambda^2$.

Exercise 4.23 This exercise concerns another way of deriving the canonical ensemble for a quantum mechanical system. Consider a system that is composed of a very large number N of weakly interacting identical subsystems. The total system is isolated and has energy E . Each subsystem has discrete energy eigenstates with eigenvalues $E_n (n = 1, 2, \dots)$. Let N_n be the number of subsystems that are in the n th quantum state. Calculate the most probable distribution of the subsystems among their possible quantum states. That is, calculate the distribution N_n that corresponds to the maximum number of states for the complete system.

Solution The microstate of the complete system is defined by specifying the exact quantum state of each subsystem. This can be done by giving the quantum numbers n_1, n_2, \dots, n_N that tell the quantum states of each subsystem. The macrostates of the system are defined by specifying how many subsystems are in each possible quantum state, that is, by giving N_1, N_2, \dots . The number of microstates that correspond to a particular macrostate is given by the usual formula

$$I = \frac{N!}{N_1! N_2! \dots} \tag{S4.178}$$

There are two restrictions on the possible choice of macrostates. The sum over all the N_i s must give the total number of subsystems N and the sum of N_i times E_i must give the fixed total energy of the complete system. Thus

$$\sum_i N_i = N \quad \text{and} \quad \sum_i N_i E_i = E \tag{S4.179}$$

Maximizing $\log I$, using Lagrange's method to handle the constraints and Stirling's approximation for $\log(N_i!)$, leads to the problem of maximizing the function

$$F = N(\log N - 1) - \sum_i N_i(\log N_i - 1) - \alpha \sum N_i - \beta \sum N_i E_i \quad (\text{S4.180})$$

Setting $\partial F/\partial N_i = 0$ gives the relation

$$\log N_i = -\alpha - \beta E_i \quad (\text{S4.181})$$

or

$$N_i = C e^{-\beta E_i} \quad (\text{S4.182})$$

where $C = e^{-\alpha}$. The normalization condition $\sum N_i = N$ fixes the value of the constant C .

$$N_i = N \frac{e^{-\beta E_i}}{\sum e^{-\beta E_k}} \quad (\text{S4.183})$$

But the probability of finding any particular subsystem in its n th quantum state is N_n/N . Thus

$$P_n = Z^{-1} e^{-\beta E_n} \quad (\text{S4.184})$$

which is exactly the canonical probability density. What we have done is simply to choose, as our reservoir, $(N - 1)$ copies of the sample system.

Exercise 4.24 A solid is composed of N atoms whose nuclei have angular momentum $\hbar/2$. Associated with the nuclear angular momentum is a nuclear magnetic moment of magnitude μ . When the solid is placed in a magnetic field the component of the magnetic moment of any nucleus, in the direction of the field, can have the two values $\pm\mu$. The interactions between the nuclear magnetic moments are completely negligible. In many real solids, the interaction between the nuclear magnetic moments and all other degrees of freedom of the solid, such as lattice vibrations and electronic motions, is so weak that the collection of nuclei can be considered as an isolated system.

Using the canonical ensemble, calculate the energy and entropy of the system of nuclear magnetic moments in a magnetic field B at temperature T .

Solution For the i th nucleus we introduce a variable σ_i that is equal to -1 if the magnetic moment is parallel to B and $+1$ if it is antiparallel. The configuration of the system is then defined by the set of variables $(\sigma_1, \sigma_2, \dots, \sigma_N)$. The energy associated with a given configuration is

$$E = \mu B \sum_n \sigma_n \quad (\text{S4.185})$$

Since the energy is a sum of independent terms, the partition function is the N th power of the partition function for one nucleus. Thus $Z = z^N$, where

$$\begin{aligned} z &= \sum_{\sigma} e^{-\beta E(\sigma)} \\ &= \sum_{\sigma=\pm 1} e^{-\beta \mu B \sigma} \\ &= 2 \cosh(\beta \mu B) \end{aligned} \quad (\text{S4.186})$$

The canonical potential is

$$\phi = N \log[2 \cosh(\beta \mu B)] \quad (\text{S4.187})$$

and the energy at inverse temperature β is

$$E = -\frac{\partial \phi}{\partial \beta} = -N \mu B \tanh(\beta \mu B) \quad (\text{S4.188})$$

The entropy is related to the canonical potential and the energy by $\phi = S^\circ - \beta E$. Therefore

$$S^\circ = N \{ \log[2 \cosh(\beta\mu B)] - \beta\mu B \tanh(\beta\mu B) \} \quad (\text{S4.189})$$

This system is exactly the noninteracting Ising model that was analyzed in Exercise 3.14. A comparison of this short calculation with that much longer one shows again the advantage of the canonical versus the microcanonical ensemble.

Exercise 4.25 We can define an unrealistic but solvable model of a molecular gas by assuming that the gas consists of N diatomic molecules and that the two atoms in the i th molecule have masses m and m' and are described by position and momentum vectors \mathbf{r}_i , \mathbf{r}'_i , \mathbf{p}_i , and \mathbf{p}'_i . The atoms in any given molecule are bound together with a harmonic oscillator potential $v(|\mathbf{r}_i - \mathbf{r}'_i|) = k_o |\mathbf{r}_i - \mathbf{r}'_i|^2/2$, but they do not interact with the atoms in any other molecule. With such a model, the Hamiltonian is

$$H = \sum_{i=1}^N \left(\frac{p_i^2}{2m} + \frac{p_i'^2}{2m'} + \frac{k_o}{2} |\mathbf{r}_i - \mathbf{r}'_i|^2 \right) \quad (\text{S4.190})$$

Calculate the thermal energy of the system, using classical mechanics, and show that it agrees with the equipartition theorem.

Solution The canonical partition function is

$$Z = \frac{1}{h^{6N} N!} \int e^{-\beta H} d^{3N} p d^{3N} p' d^{3N} r d^{3N} r' \quad (\text{S4.191})$$

The momentum integrals are straightforward, giving a factor of $(2\pi\sqrt{mm'}/\beta)^{3N}$. The coordinate integrals factor into N six-dimensional integrals. The i th integral involves the coordinates of the i th molecule only. Each of the integrals is of the form

$$I = \int_V e^{-\beta k_o |\mathbf{r} - \mathbf{r}'|^2/2} d^3 r d^3 r' \quad (\text{S4.192})$$

We transform to center-of-mass and relative variables, $\mathbf{R} = (\mathbf{r} + \mathbf{r}')/2$ and $\mathbf{q} = \mathbf{r} - \mathbf{r}'$. We have seen before that the Jacobian of this transformation is one. The integral is then

$$I = \int e^{-\beta k_o q^2/2} d^3 R d^3 q \quad (\text{S4.193})$$

The exponential factor goes rapidly to zero as q becomes large. Therefore, we can extend the q integral to infinity, making negligible error. The molecular center of mass must be integrated over the system volume. Using the fact that $q^2 = q_x^2 + q_y^2 + q_z^2$, the integral over the relative variable can be factored into three Gaussian integrals,

$$I = V (2\pi/\beta k_o)^{3/2} \quad (\text{S4.194})$$

Putting these all together, the partition function is

$$\begin{aligned} Z &= \frac{(2\pi\sqrt{mm'}/\beta)^{3N} V^N (2\pi/\beta k_o)^{3N/2}}{h^{6N} N!} \\ &= \left(8\pi^3 mm'/h^4 \sqrt{k_o} \right)^{3N/2} V^N / \beta^{9N/2} N! \end{aligned} \quad (\text{S4.195})$$

and

$$\phi = N \left[\log(V/N) - \frac{9}{2} \log \beta + \text{const.} \right] \quad (\text{S4.196})$$

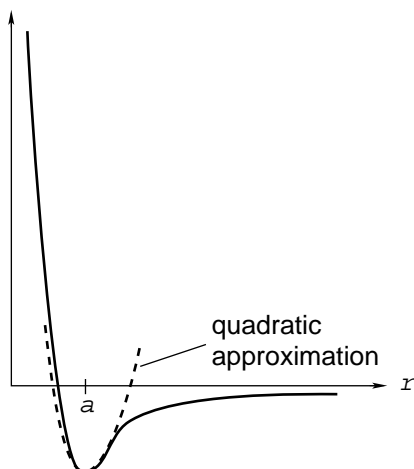


Fig. S4.7 The interaction potential between two atoms.

The thermal energy is

$$E = -\frac{\partial \phi}{\partial \beta} = \frac{9}{2}NkT \quad (\text{S4.197})$$

Since the Hamiltonian function is composed of $9N$ simple squares (remember that $p^2 = p_x^2 + p_y^2 + p_z^2$, etc.), this result could have been predicted by the equipartition theorem.

Exercise 4.26 The most unrealistic characteristic of the model of a diatomic ideal gas used in the last example is the fact that the equilibrium distance between the atoms in the molecule is zero. In reality the interaction potential between two atoms in a diatomic molecule is similar to the function shown in Fig. S4.7. For such an interaction potential, if we still ignore the interactions between atoms in different molecules, the Hamiltonian function is

$$H = \sum_{i=1}^N \left(\frac{p_i^2}{2m} + \frac{p_i'^2}{2m'} + v(|\mathbf{r}_i - \mathbf{r}_i'|) \right) \quad (\text{S4.198})$$

(a) Treating the system by classical mechanics, derive a formula for the thermal energy per molecule in terms of one-dimensional integrals involving $v(r)$. (b) Approximate $v(r)$ by a displaced harmonic oscillator potential with a minimum $-\varepsilon_o$ at $r = a$ and a force constant k_o

$$v(r) = -\varepsilon_o + \frac{1}{2}k_o(r - a)^2 \quad (\text{S4.199})$$

Assume that $kT \ll ka^2/2$ and show that the simple modification of displacing the minimum of the potential has an effect on the temperature dependence of the thermal energy. Actually, the Hamiltonian in Eq. (S4.198), combined with the displaced harmonic oscillator approximation, gives a reasonably accurate description of many diatomic molecules if the vibrational degrees of freedom are treated quantum mechanically.

Solution (a) All of the analysis used in the preceding example is still valid, but the integral for the internal partition function of a single molecule must be changed to

$$I = V \int e^{-\beta v(q)} d^3q = 4\pi V \int_o^\infty e^{-\beta v(q)} q^2 dq \quad (\text{S4.200})$$

With this modification, Eq. (S4.195) for the partition function of the system becomes

$$Z = \frac{(2\pi\sqrt{mm'}/\beta)^{3N} V^N (4\pi \int_o^\infty e^{-\beta v} q^2 dq)^N}{h^{6N} N!} \quad (\text{S4.201})$$

and the equation for the canonical potential becomes

$$\phi = N \left[\log \left(\frac{V}{N} \right) - 3 \log \beta + \log \left(\int_0^\infty e^{-\beta v} q^2 dq \right) + C \right] \quad (\text{S4.202})$$

The energy per molecule is

$$\frac{E}{N} = - \frac{\partial(\phi/N)}{\partial \beta} = 3kT + \frac{\int v e^{-\beta v} q^2 dq}{\int e^{-\beta v} q^2 dq} \quad (\text{S4.203})$$

This is an obvious formula. The $3kT$ comes, via the equipartition theorem, from the six momentum degrees of freedom per molecule. The term involving the interaction potential simply shows that the probability distribution for the interatomic distance within a molecule is the Maxwell–Boltzmann function, $C e^{-\beta v(q)}$.

(b) Using the displaced harmonic oscillator approximation, the integral in the denominator in Eq. (S4.203) becomes

$$\begin{aligned} \int_0^\infty e^{-\beta v(q)} q^2 dq &= e^{\beta \varepsilon_o} \int_{-a}^\infty e^{-\beta k_o x^2 / 2} (x+a)^2 dx \\ &\approx e^{\beta \varepsilon_o} \int_{-\infty}^\infty e^{-\beta k_o x^2 / 2} (x^2 + a^2) dx \\ &= \sqrt{2} e^{\beta \varepsilon_o} [(\beta k_o)^{-3/2} + a^2 (\beta k_o)^{-1/2}] \end{aligned} \quad (\text{S4.204})$$

In going from the first to the second line, we have used the fact that $\beta k_o a^2 / 2 \gg 1$ to extend the integral to $-\infty$ and the fact that the term $2ax$ gives a zero integral. The other necessary integral is

$$\begin{aligned} \int_0^\infty v(q) e^{-\beta v(q)} q^2 dq &= - \frac{d}{d\beta} \int_0^\infty e^{-\beta v(q)} q^2 dq \\ &= - \frac{d}{d\beta} \left\{ \sqrt{2} e^{\beta \varepsilon_o} [(\beta k_o)^{-3/2} + a^2 (\beta k_o)^{-1/2}] \right\} \\ &= - \sqrt{2} \varepsilon_o e^{\beta \varepsilon_o} [(\beta k_o)^{-3/2} + a^2 (\beta k_o)^{-1/2}] \\ &\quad + \sqrt{2} k_o e^{\beta \varepsilon_o} \left[\frac{3}{2} (\beta k_o)^{-5/2} + \frac{1}{2} a^2 (\beta k_o)^{3/2} \right] \end{aligned} \quad (\text{S4.205})$$

Using these values for the integrals in Eq. (S4.203), we get, after some simple algebra,

$$\frac{E}{N} = 3kT - \varepsilon_o + \frac{1}{2} kT \frac{1 + 3kT/k_o a^2}{1 + kT/k_o a^2} \quad (\text{S4.206})$$

If $kT \ll k_o a^2$, as we have already assumed, then

$$\frac{E}{N} \approx \frac{7}{2} kT - \varepsilon_o \quad (\text{S4.207})$$

The $-\varepsilon_o$ comes from a trivial shift in the zero of our interatomic potential. The change of the factor in front of kT from $9/2$ to $7/2$ shows that displacing the harmonic oscillator potential has changed it from a three-dimensional to a one-dimensional harmonic oscillator, thus eliminating two contributions of $\frac{1}{2} kT$. Notice that letting $a \rightarrow 0$ in Eq. (S4.206) makes the two suppressed terms reappear.

Exercise 4.27 In this example we want to show that the temperature coefficient of expansion of a solid is related to the anharmonic terms in the interatomic potential. We take as our model a one-dimensional solid in which only nearest-neighbor particles interact and they interact with a potential

$$v(x) = \frac{k_o}{2} (x-a)^2 - \gamma (x-a)^3 \quad (\text{S4.208})$$

where the second term is assumed to be much smaller than the first. The minimum of the potential occurs at $x = a$, and thus at zero temperature the configuration of the system will be a perfect lattice of spacing a . The Hamiltonian for the system is

$$H = \sum_{n=1}^N \frac{p_n^2}{2m} + \sum_{n=1}^N v(x_n - x_{n-1}) \quad (\text{S4.209})$$

In order to fix one end of the crystal, we assume that the first particle interacts with a completely stationary particle at $x_o = 0$. That accounts for the $n = 1$ term in the potential sum in Eq. (S4.209). Using classical mechanics, determine the length of the N -particle crystal as a function of temperature and show that it is constant if $\gamma = 0$.

Solution The probability of a given configuration is

$$P(x_1, x_2, \dots, x_N) = I^{-1} \exp\left(-\beta \sum v(x_n - x_{n-1})\right) \quad (\text{S4.210})$$

where $x_o = 0$. The normalization integral is

$$I = \int_{-\infty}^{\infty} \exp\left(-\beta \sum v(x_n - x_{n-1})\right) dx_1 \cdots dx_N \quad (\text{S4.211})$$

We make a transformation of variables, $y_1 = x_1$, $y_2 = x_2 - x_1$, $y_3 = x_3 - x_2$, \dots , $y_N = x_N - x_{N-1}$. Then

$$I = \left(\int \exp[-\beta v(y)] dy \right)^N \quad (\text{S4.212})$$

The length of the crystal is the average value of the position of the last particle. That is $L = \langle x_N \rangle$. Using the fact that, with the transformation defined, $y_1 + y_2 + \cdots + y_N = x_N$, we get

$$L(T) = \left\langle \sum y_n \right\rangle \quad (\text{S4.213})$$

Written in terms of the y variables

$$P(x_1, x_2, \dots, x_N) = I^{-1} \prod_{n=1}^N \exp[-\beta v(y_n)] \quad (\text{S4.214})$$

Using this fact, it is easy to see that

$$\left\langle \sum y_n \right\rangle = N \frac{\int y e^{-\beta v(y)} dy}{\int e^{-\beta v(y)} dy} \quad (\text{S4.215})$$

The integral in the denominator is

$$\begin{aligned} I_{\text{den}} &= \int_{-\infty}^{\infty} \exp[-\beta k_o(y-a)^2/2 + \beta\gamma(y-a)^3] dy \\ &= \int_{-\infty}^{\infty} \exp(-\beta k_o q^2/2) \exp(\beta\gamma q^3) dq \\ &\approx \int_{-\infty}^{\infty} \exp(-\beta k_o q^2/2) (1 + \beta\gamma q^3) dq \\ &= \sqrt{2\pi/\beta k_o} \end{aligned} \quad (\text{S4.216})$$

where, in the second line, we have used the definition $q = y - a$, and in the third line we have expanded the exponential to first order in the small parameter γ . The integral in the numerator is done in a similar way.

$$\begin{aligned} I_{\text{num}} &= \int_{-\infty}^{\infty} \exp[-\beta k_o(y-a)^2/2 + \beta\gamma(y-a)^3] y dy \\ &= \int_{-\infty}^{\infty} \exp(-\beta k_o q^2/2) \exp(\beta\gamma q^3) (a+q) dq \\ &\approx \int_{-\infty}^{\infty} \exp(-\beta k_o q^2/2) (1 + \beta\gamma q^3) (a+q) dq \\ &= \int_{-\infty}^{\infty} \exp(-\beta k_o q^2/2) (a + \beta\gamma q^4) dq \\ &= a\sqrt{2\pi/k_o\beta} + 3\sqrt{2\pi}\gamma(kT)^{3/2}/k_o^{5/2} \end{aligned} \quad (\text{S4.217})$$

$L(T)$ is equal to $NI_{\text{num}}/I_{\text{den}}$.

$$L(T) = N[a + 3\gamma(kT/k_o)^2] \quad (\text{S4.218})$$

Notice that if the anharmonic term is eliminated by setting $\gamma = 0$, then the length of the crystal becomes independent of temperature.

Exercise 4.28 A nonideal gas has an equation of state $p = p(n, T)$, where n is the particle density. The gas is at equilibrium in a uniform gravitational field g in the negative z direction. (a) Using hydrostatic arguments, obtain a differential equation for the density at height z . (b) Show that, for an ideal gas, the equation predicts the usual exponential atmosphere, $n(z) = n_0 \exp(-mgz/kT)$.

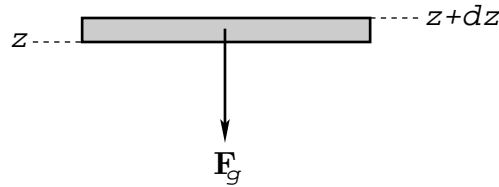


Fig. S4.8 A “slab” of gas, between z and $z + dz$.

Solution (a) We consider a horizontal slab of the gas (see Fig. S4.8) with its top surface at $z + dz$ and its bottom surface at z . The area of the slab is A . The z component of the pressure forces exerted on the top and bottom surfaces of the slab add up to

$$F_p = A[p(n(z), T) - p(n(z + dz), T)] \quad (\text{S4.219})$$

where we have used the fact that, at equilibrium, the temperature is uniform. The mass of the gas in the slab is $mn(z)A dz$. (For very small dz we can take the value of n at the bottom and ignore the variation of the density through the slab.) The z component of the gravitational force on the slab is

$$F_g = -mnAg dz \quad (\text{S4.220})$$

Setting $F_p + F_g$ equal to zero and dividing by dz gives the differential equation

$$\frac{\partial p}{\partial n} \frac{dn}{dz} + mgn = 0 \quad (\text{S4.221})$$

(b) For an ideal gas $p(n, T) = nkT$. Equation (S4.221) is then

$$\frac{dn}{dz} = -(mg/kT)n \quad (\text{S4.222})$$

which has the solution

$$n(z) = n(0)e^{-(mg/kT)z} \quad (\text{S4.223})$$