

Supplement to Chapter 3

REVIEW QUESTIONS

- 3.1 For a system of N particles in three dimensions, what are the variables x_1, x_2, \dots, x_K and p_1, p_2, \dots, p_K ?
- 3.2 What is the meaning of the Hamiltonian function $H(x, p)$?
- 3.3 What is the form of the Hamiltonian function for a system of N three-dimensional particles in an external potential $U(\mathbf{r})$ and with two-particle interactions $\phi(r_{ij})$?
- 3.4 What are Hamilton's equations?
- 3.5 How is the energy surface $\omega(E)$ defined?
- 3.6 What is the dimensionality of $\omega(E)$?
- 3.7 How are one-body observables defined? Give one example.
- 3.8 How are two-body observables defined? Give one example.
- 3.9 What are the necessary mathematical properties of a microstate probability density?
- 3.10 What is the probability density function for the uniform ensemble?
- 3.11 Given that the volume of an N -dimensional sphere of radius R is $\pi^{N/2}R^N/(N/2)!$, calculate the normalization constant for a uniform ensemble for a system of noninteracting particles in a box of volume V .
- 3.12 What is the microcanonical ensemble probability density?
- 3.13 Given the microstate probability density $P(x, p)$, how can we calculate $n(\mathbf{r})$, the average particle density at position \mathbf{r} ?
- 3.14 Given the microstate probability density $P(x, p)$, how can we calculate $F_1(\mathbf{r}, \mathbf{p})$, the phase-space density function?
- 3.15 Given the microstate probability density $P(x, p)$, how can we calculate $F_2(\mathbf{r}, \mathbf{p}, \mathbf{r}', \mathbf{p}')$, the two-particle phase-space density function?
- 3.16 Express the average value of a one-body observable in terms of $F_1(\mathbf{r}, \mathbf{p})$.
- 3.17 Explain what is meant by the "thermodynamic limit."
- 3.18 What is a uniform intensive observable?
- 3.19 What is the property of asymptotic factorization?
- 3.20 Show that $\Delta A^2 \rightarrow 0$ for any uniform intensive observable if a system has the property of asymptotic factorization.
- 3.21 With respect to a uniform intensive observable, what is an exceptional point on the energy surface?
- 3.22 How does Chebyshev's inequality show that the fraction of points on the energy surface that are exceptional goes to zero in the thermodynamic limit?
- 3.23 Why does the property that was discussed in the last question justify the use of the microcanonical ensemble?

- 3.24** Describe a three-dimensional Ising model, giving an expression for the energy in terms of the spin variables.
- 3.25** How is the mean magnetization defined for an Ising model?
- 3.26** What happens to the probability distribution for the mean magnetization m at low temperatures?
- 3.27** How is the phenomenon discussed in the previous question related to the no-fluctuation theorem?
- 3.28** Describe the Standard Computational Procedure.
- 3.29** How was an “extra” conservation law defined?
- 3.30** Why would an extra conservation law make calculations based on a microcanonical ensemble unreliable?
- 3.31** What does the ergodic theorem say?
- 3.32** What is a “complex system” and why does such a system take an extremely long time to come to equilibrium?
- 3.33** If two thermodynamic systems are in contact, what is the condition that determines how the total energy will be shared between them?
- 3.34** A system is composed of two weakly interacting parts, so that its Hamiltonian can be approximated by $H = H_1(x_1, p_1) + H_2(x_2, p_2)$. Using a microcanonical ensemble for the total system, calculate $P_1(E_1)$, the probability that subsystem 1 has energy E_1 .
- 3.35** What is the condition that $P_1(E_1)$ be a maximum (consistent with energy conservation)?
- 3.36** How do the results of the previous three questions relate the thermodynamic entropy and the microcanonical partition function $Q(E)$?
- 3.37** How are the absolute temperature and the mechanical pressure related to the entropy function?

EXERCISES

Exercise 3.1 Two particles, each of mass m , are attached by a massless spring of force constant k and equilibrium length l . The particles are constrained to the x - y plane. Using center-of-mass and relative coordinates, write the Hamiltonian function and Hamilton's equations.

Solution Let the coordinates of the two particles be (x_1, y_1) and (x_2, y_2) . The kinetic energy of the system is

$$K = \frac{m}{2}(\dot{x}_1^2 + \dot{y}_1^2 + \dot{x}_2^2 + \dot{y}_2^2) \tag{S3.1}$$

where, as usual, $\dot{x} \equiv dx/dt$. Center-of-mass and relative coordinates are defined by the equations

$$X = \frac{x_1 + x_2}{2}, Y = \frac{y_1 + y_2}{2}, x = x_1 - x_2, \text{ and } y = y_1 - y_2. \tag{S3.2}$$

In terms of the center-of-mass and relative velocities,

$$\dot{x}_1 = \dot{X} + \frac{\dot{x}}{2}, \dot{y}_1 = \dot{Y} + \frac{\dot{y}}{2}, \dot{x}_2 = \dot{X} - \frac{\dot{x}}{2}, \text{ and } \dot{y}_2 = \dot{Y} - \frac{\dot{y}}{2} \tag{S3.3}$$

Using these relations in order to write the kinetic energy in terms of center-of-mass and relative velocities, we get

$$K = \frac{1}{2}M(\dot{X}^2 + \dot{Y}^2) + \frac{1}{2}\mu(\dot{x}^2 + \dot{y}^2) \tag{S3.4}$$

where $M = 2m$ and $\mu = m/2$. The momenta that are canonical to X and Y are

$$P_X = \frac{\partial K}{\partial \dot{X}} = M\dot{X} \quad \text{and} \quad P_Y = \frac{\partial K}{\partial \dot{Y}} = M\dot{Y} \tag{S3.5}$$

The momenta canonical to x and y are

$$p_x = \frac{\partial K}{\partial \dot{x}} = \mu\dot{x} \quad \text{and} \quad p_y = \frac{\partial K}{\partial \dot{y}} = \mu\dot{y} \tag{S3.6}$$

The potential energy is proportional to the square of the displacement from equilibrium of the spring.

$$V = \frac{1}{2}k(\sqrt{x^2 + y^2} - l)^2 \tag{S3.7}$$

The Hamiltonian function is simply $K + V$, written in terms of the coordinates and canonical momenta.

$$H = \frac{1}{2M}(P_X^2 + P_Y^2) + \frac{1}{2\mu}(p_x^2 + p_y^2) + \frac{k}{2}(\sqrt{x^2 + y^2} - l)^2 \tag{S3.8}$$

Hamilton's equations for this system are

$$\begin{aligned} \dot{X} &= \frac{\partial H}{\partial P_X} = \frac{P_X}{M} \\ \dot{x} &= \frac{\partial H}{\partial p_x} = \frac{p_x}{\mu} \\ \dot{P}_X &= -\frac{\partial H}{\partial X} = 0 \\ \dot{p}_x &= -\frac{\partial H}{\partial x} = -k \frac{x}{\sqrt{x^2 + y^2}}(\sqrt{x^2 + y^2} - l) \end{aligned} \tag{S3.9}$$

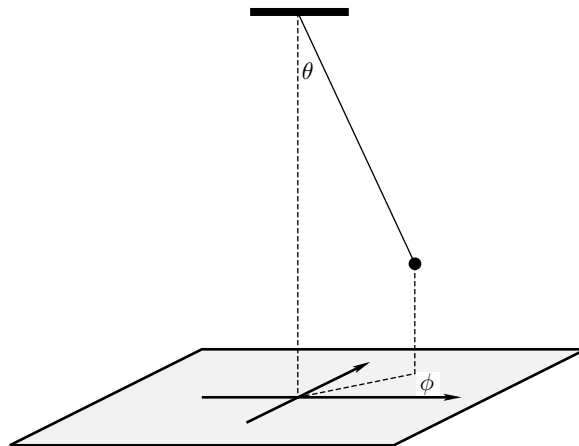


Fig. S3.1 The configuration of a hanging pendulum is defined by two angular coordinates.

and similar equations for Y, y, P_Y , and p_y .

Exercise 3.2 A hanging pendulum of mass m and length L is free to move in two dimensions. (See Fig. S3.1.) (a) Using a system of spherical angles, θ and ϕ , write the Hamiltonian function, $H(\theta, \phi, p_\theta, p_\phi)$. (b) Write Hamilton's equations for the system.

Solution (a) A small change in the polar angle $d\theta$ gives a displacement of the mass equal to $ds = L d\theta$. A small change in the azimuthal angle, $d\phi$, gives a displacement of the mass equal to $ds = L \sin \theta d\phi$. Since the two displacements are in perpendicular directions, a simultaneous change of both angular coordinates gives a displacement $ds = (L^2 d\theta^2 + L^2 \sin^2 \theta d\phi^2)^{1/2}$. But the kinetic energy is given by $K = (m/2)(ds/dt)^2$. Therefore

$$\begin{aligned} K &= \frac{1}{2}mL^2 \left[\left(\frac{d\theta}{dt} \right)^2 + \sin^2 \theta \left(\frac{d\phi}{dt} \right)^2 \right] \\ &= \frac{1}{2}I(\dot{\theta}^2 + \sin^2 \theta \dot{\phi}^2) \end{aligned} \quad (\text{S3.10})$$

The momenta that are canonical to the coordinates θ and ϕ are

$$p_\theta = \frac{\partial K}{\partial \dot{\theta}} = I\dot{\theta} \quad \text{and} \quad p_\phi = \frac{\partial K}{\partial \dot{\phi}} = I \sin^2 \theta \dot{\phi} \quad (\text{S3.11})$$

The Hamiltonian function is just the energy expressed in terms of the coordinates and canonical momenta. The potential energy is equal to mgz . As we have defined our coordinates, $z = -L \cos \theta$. Making the substitutions $\dot{\theta} = p_\theta/I$ and $\dot{\phi} = p_\phi/I \sin^2 \theta$ in the kinetic energy, we obtain

$$H = \frac{1}{2I} \left(p_\theta^2 + \frac{p_\phi^2}{\sin^2 \theta} \right) - mgL \cos \theta \quad (\text{S3.12})$$

(b) Hamilton's equations are

$$\begin{aligned} \frac{d\theta}{dt} &= \frac{\partial H}{\partial p_\theta} = \frac{p_\theta}{I} \\ \frac{dp_\theta}{dt} &= -\frac{\partial H}{\partial \theta} = \frac{\cos \theta p_\theta^2}{I \sin^3 \theta} - mgL \sin \theta \\ \frac{d\phi}{dt} &= \frac{\partial H}{\partial p_\phi} = \frac{p_\phi}{I \sin^2 \theta} \\ \text{and} \quad \frac{dp_\phi}{dt} &= -\frac{\partial H}{\partial \phi} = 0 \end{aligned} \quad (\text{S3.13})$$

Exercise 3.3 For a simple pendulum: (a) Write the Hamiltonian function $H(\theta, p_\theta)$. (b) In the two-dimensional phase space, indicate some of the one-dimensional equal energy “surfaces,” noting the change in their structure from lower to higher energies. (c) Describe the “topology” or connectedness of the phase space. (See Fig. S3.2.)

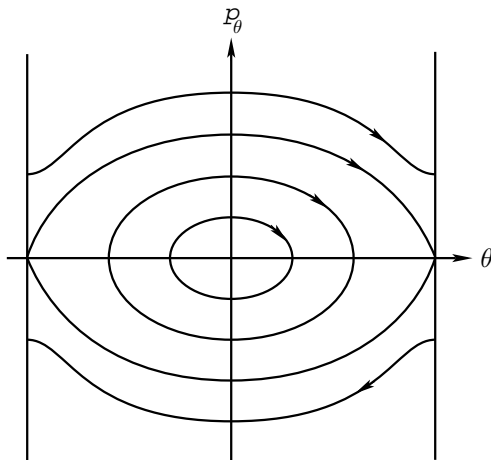


Fig. S3.2 The phase-space trajectories of a simple pendulum.

Solution (a) The kinetic energy is given by $K = \frac{1}{2}ml^2\dot{\theta}^2$, where l is the length of the pendulum. The canonical momentum is $p_\theta = \partial K/\partial \dot{\theta} = ml^2\dot{\theta}$. The potential energy is $V = -mgl \cos \theta$. The Hamiltonian is therefore

$$H = \frac{p_\theta^2}{2ml^2} - mgl \cos \theta \quad (\text{S3.14})$$

(b) The range of θ is $-\pi \leq \theta \leq \pi$. The range of p_θ is $-\infty < p_\theta < \infty$. The phase space can be shown as a vertical strip. (c) Since $\theta = -\pi$ and π really describe identical configurations of the system the representation shown maps, in some cases, a single physical state of the system into two points on the plane. In order to avoid such one-to-two mappings, one must bend the strip around and connect it so as to form an infinite cylinder. That is, the phase space of this system has the topology of a cylinder.

Exercise 3.4 For a system of N one-dimensional particles, write an observable whose value is equal to “the number of particles to the right of the origin.”

Solution Let us first try the simplest case, namely, $N = 1$. Since whether the particle is to the right of the origin depends only on its position and not its momentum, the observable will be only a function of x . The number of particles to the right of the origin can only be 0 or 1. Thus, for this single-particle system we want the observable to have the values

$$A(x) = \begin{cases} 1, & \text{if } x > 0 \\ 0, & \text{if } x < 0 \end{cases} \quad (\text{S3.15})$$

But this equation defines the unit step function. That is, for $N = 1$ the derived observable is $A(x) = \theta(x)$. Now that we have the trick, it is easy to do the same thing for an N -particle system. The one-body observable

$$A(x_1, \dots, x_N) = \sum_{n=1}^N \theta(x_n) \quad (\text{S3.16})$$

just counts the number of particles to the right of the origin.

Exercise 3.5 For a system of N one-dimensional massless particles in a one-dimensional “box” of length L , calculate the uniform ensemble normalization integral $C(E)$ and the entropy function of the system $S(N, E, L)$.

Solution For massless particles, $E = c|p|$, where c is the speed of light. Therefore, Eq. (3.18) for $C(E)$ must be replaced by

$$C(E) = L^N \int \theta\left(E - c \sum_n |p_n|\right) dp_1 \cdots dp_N \quad (\text{S3.17})$$

Making a transformation of variables, $q_1 = cp_1, q_2 = cp_2, \dots, q_N = cp_N$ and using the fact that the integrand is an even function of each variable we can write $C(E)$ as

$$C(E) = (2L/c)^N \int_0^\infty \theta\left(E - \sum_n q_n\right) dq_1 \cdots dq_N \quad (\text{S3.18})$$

The problem boils down to evaluating the N -dimensional integral

$$I_N(a) = \int_0^\infty dx_N \cdots \int_0^\infty dx_2 \int_0^\infty dx_1 \theta\left(a - \sum_n x_n\right) \quad (\text{S3.19})$$

since the integral is zero if any $x_n > a$, we can write $I_n(a)$ as

$$I_N(a) = \int_0^a dx_N \cdots \int_0^a dx_2 \int_0^a dx_1 \theta\left(a - \sum_n x_n\right) \quad (\text{S3.20})$$

Using the simple identity

$$\sum_n x_n = x_N + \sum_n^{N-1} x_n \quad (\text{S3.21})$$

we can derive the recursion relation

$$I_N(a) = \int_0^a dx_N I_{N-1}(a - x_N) \quad (\text{S3.22})$$

Making the change of variables, $y = a - x_N$, with $dy = -dx_N$, we can rewrite the recursion relation as

$$\begin{aligned} I_N(a) &= - \int_a^0 dy I_{N-1}(y) \\ &= \int_0^a I_{N-1}(y) dy \end{aligned} \quad (\text{S3.23})$$

It is obvious that $I_1(a) = a$. But, then

$$\begin{aligned} I_2(a) &= \int_0^a y dy = \frac{a^2}{2} \\ I_3(a) &= \frac{1}{2} \int_0^a y^2 dy = \frac{a^3}{3!} \end{aligned} \quad (\text{S3.24})$$

and it is easy to see that $I_N(a) = a^N/N!$. Using this result in Eq. (S3.18) we get

$$C(E) = \frac{(2LE/c)^N}{N!} \quad (\text{S3.25})$$

The entropy function of the system can be calculated using Eq. (3.86)

$$\begin{aligned} S &= k \log [C/h^N N!] \\ &= k \log [(2LE/hc)^N / (N!)^2] \\ &= kN [\log(E/N) + \log(L/N) + \text{const.}] \end{aligned} \quad (\text{S3.26})$$

Exercise 3.6 The position of a two-dimensional diatomic molecule, with fixed distance between the atoms, can be described by the three coordinates, (x, y, θ) , where x and y are the coordinates of the molecule's center of mass and θ gives the orientation of the molecular axis with respect to the x axis. The momenta canonically conjugate to the coordinates are p_x , p_y , and p_θ where the first two are the Cartesian components of the center-of-mass momentum and the third is the angular momentum of the molecule about its center of mass. The energy of the molecule is

$$E = (p_x^2 + p_y^2)/2m + p_\theta^2/2I \quad (\text{S3.27})$$

Where I is the moment of inertia about the center of mass. (a) For a system of N noninteracting two-dimensional diatomic molecules confined to a two-dimensional area A , use the uniform ensemble to calculate the entropy function $S(N, E, A)$. (b) Using the entropy function, derive the equations of state of the system—that is, the equations that give the pressure and the energy per particle as functions of the temperature and density. Note: In two dimensions, the “pressure” is the force per unit length that is required to confine the particles to an area A . It is given by a formula analogous to the three-dimensional formula for p/T , namely $p/T = \partial S/\partial A$. (c) Calculate the constant volume (actually constant area) specific heat per particle, defined by $C_V = N^{-1} \partial E(N, T, A)/\partial T$.

Solution (a) S is related to the normalization integral for the uniform ensemble. For a system of N molecules, that integral is given by

$$C = \int \theta \left(E - \sum_{n=1}^N (p_{nx}^2 + p_{ny}^2)/2m - \sum_{n=1}^N p_{n\theta}^2/2I \right) \times dx_1 dy_1 d\theta_1 dp_{1x} dp_{1y} dp_{1\theta} \cdots dx_N dy_N d\theta_N dp_{Nx} dp_{Ny} dp_{N\theta} \quad (\text{S3.28})$$

For each molecule, (x_k, y_k) are integrated over the area A . These integrals give a factor of A^N . For each molecule, θ_k is integrated over 2π . Those integrals give a factor of $(2\pi)^N$. To do the momentum integrals, we define $3N$ variables, $u_1, \dots, u_N, v_1, \dots, v_N, w_1, \dots, w_N$, by

$$u_k = p_{kx}/\sqrt{2m}, \quad v_k = p_{ky}/\sqrt{2m}, \quad w_k = p_{k\theta}/\sqrt{2I} \quad (\text{S3.29})$$

for $k = 1, \dots, N$. The result is that

$$C = (2\pi A)^N (8m^2 I)^{N/2} \int \theta \left(E - \sum_{n=1}^N (u_n^2 + v_n^2 + w_n^2) \right) d^N u d^N v d^N w \quad (\text{S3.30})$$

The remaining integral is just the volume of a $3N$ -dimensional sphere of radius \sqrt{E} , which is equal to $(\pi E)^{3N/2}/(3N/2)!$. Thus

$$\begin{aligned} C &= (2\pi A)^N (8m^2 I)^{N/2} (\pi E)^{3N/2}/(3N/2)! \\ &= (2\pi m I^{1/2} A)^N (2\pi E)^{3N/2}/(3N/2)! \end{aligned} \quad (\text{S3.31})$$

In using the formula that relates C to S , we must remember that each molecule has three coordinates, and therefore $K = 3N$. Thus

$$\begin{aligned} S &= k \log(C/h^{3N} N!) \\ &= kN \left(\log A + \frac{3}{2} \log E - \frac{5}{2} \log N + \text{const.} \right) \end{aligned} \quad (\text{S3.32})$$

where the constant term has not been written explicitly because it will not contribute to the equations of state. (b) The relation

$$\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{3kN}{2E} \quad (\text{S3.33})$$

gives the energy equation

$$E = \frac{3}{2} NkT \quad (\text{S3.34})$$

Looking back over the derivation, one can see that each of the momentum variables p_x , p_y , and p_θ contribute $\frac{1}{2}kT$ to the energy per particle. This is an example of a general theorem that will be derived in Chapter 4,

called the equipartition theorem. It states that any term in the Hamiltonian function that is a simple square contributes $\frac{1}{2}kT$ to the thermal energy at temperature T . The pressure is given by

$$p = T \frac{\partial S}{\partial A} = kT \frac{N}{A} = nkT \quad (\text{S3.35})$$

which is the same as that for a gas without rotational degrees of freedom. (c) The specific heat per particle is easily calculated from Eq. (S3.34).

$$C_V = N^{-1} \frac{\partial E}{\partial T} = \frac{3}{2}k \quad (\text{S3.36})$$

Exercise 3.7 A one-dimensional particle in a harmonic oscillator potential has an energy $E = p^2/2m + k_o x^2/2$. A system of N particles in the same potential, using a microcanonical ensemble, has a probability function

$$P(x_1, p_1, \dots, x_N, p_N) = Q^{-1} \delta\left(E - \sum_n p_n^2/2m - \sum_n k_o x_n^2/2\right) \quad (\text{S3.37})$$

(a) For such a system, calculate the one-particle phase-space density function $F_1(x, p)$. (b) Assume that $E = N\varepsilon$, where ε is fixed, and show that, for large N , $F_1(x, p)$ is equal to the Maxwell–Boltzmann distribution function that was derived in the last chapter.

Solution By Eq. (3.34),

$$F_1(x, p) = \sum_{i=1}^N \int P(x_1, p_1, \dots, x_N, p_N) \delta(x - x_i) \delta(p - p_i) d^N x d^N p \quad (\text{S3.38})$$

Because the probability function P is symmetric under the exchange of the space and momentum coordinates of any two particles, each term in the sum over i makes the same contribution. Therefore, we can keep only the $i = 1$ term and multiply the result by N . One can then use the delta functions to do the integrals over x_1 and p_1 , obtaining

$$F_1(x, p) = N \int P(x, p, x_2, p_2, \dots, x_N, p_N) dx_2 dp_2 \cdots dx_N dp_N \quad (\text{S3.39})$$

This is really an obvious result. The integral, without the factor of N , is the probability of finding the first particle at phase-space point (x, p) , regardless of the states of the other particles. Multiplying that by N gives the probability of finding *any* particle at (x, p) . If we define E' by

$$E' = E - p^2/2m - k_o x^2/2 \quad (\text{S3.40})$$

then

$$\begin{aligned} F_1(x, p) &= N \frac{\int \delta(E' - \sum_2^N p_n^2/2m - \sum_2^N k_o x_n^2/2) dx_2 \cdots dp_N}{\int \delta(E - \sum_1^N p_n^2/2m - \sum_1^N x_n^2/2) dx_1 \cdots dp_N} \\ &= N \frac{Q_{N-1}(E')}{Q_N(E)} \end{aligned} \quad (\text{S3.41})$$

By making the transformation of coordinates $u_n = p_n/\sqrt{2m}$ and $v_n = x_n\sqrt{k_o/2}$, the integral $Q_N(E)$ can be written in terms of the surface area of a $2N$ -dimensional sphere, given in the Mathematical Appendix.

$$Q_N(E) = \frac{(2\pi/\omega)^N E^N}{N!} \quad (\text{S3.42})$$

where $\omega = \sqrt{k_o/m}$ is the oscillation frequency of a particle of mass m in the potential. The integral in the numerator can be done in a similar way.

$$Q_{N-1}(E') = \frac{(2\pi/\omega)^{N-1} (E - p^2/2m - k_o x^2/2)^{N-1}}{(N-1)!} \quad (\text{S3.43})$$

Using these in Eq. (S3.41) gives

$$F_1(x, p) = \frac{\omega N^2}{2\pi} \frac{(E - p^2/2m - k_o x^2/2)^{N-1}}{E^N} \tag{S3.44}$$

(b) Putting $E = N\varepsilon$, we can write this as

$$F_1(x, p) = \frac{\omega N}{2\pi\varepsilon} \left[1 - \frac{1}{N} \left(\frac{p^2}{2m\varepsilon} + \frac{k_o x^2}{2\varepsilon} \right) \right]^{N-1} \tag{S3.45}$$

But

$$\lim_{N \rightarrow \infty} \left(1 - \frac{x}{N} \right)^{N-1} = \lim_{N \rightarrow \infty} \left(1 - \frac{x}{N} \right)^N = e^{-x} \tag{S3.46}$$

Therefore, for large N ,

$$F_1(x, p) \approx \frac{\omega N}{2\pi kT} \exp\left(-\frac{p^2/2m + k_o x^2/2}{kT}\right) \tag{S3.47}$$

where $kT \equiv \varepsilon$. This is exactly the Maxwell–Boltzmann distribution given in Eq. (2.16), with $\phi(x) = k_o x^2/2$.

Exercise 3.8 In Chapter 3 it is stated that the entropy may be calculated by Eq. (3.84), using either the function $C(E)$, associated with the uniform ensemble, or the function $Q(E)$, associated with the microcanonical ensemble. Let S_U be the entropy, calculated with the uniform ensemble, and S_M be that calculated with the microcanonical ensemble. Show that, for large N , $(S_M - S_U)/S_U$ is of order $1/N$.

Solution

$$S_M = k \log(Q/h^k N!) \tag{S3.48}$$

and

$$S_U = k \log(C/h^k N!) \tag{S3.49}$$

where

$$Q = \int \delta(E - H) d^k x d^k p \tag{S3.50}$$

and

$$C = \int \theta(E - H) d^k x d^k p \tag{S3.51}$$

We can see that $Q(E) = \partial C(E)/\partial E$, which means that

$$S_M - S_U = k \log\left(\frac{\partial C/\partial E}{C}\right) \tag{S3.52}$$

But

$$\frac{\partial C/\partial E}{C} = \frac{\partial}{\partial E} \log C = \frac{\partial(S_U/k)}{\partial E} = \frac{1}{kT} \tag{S3.53}$$

Thus

$$S_M - S_U = -k \log(kT) \tag{S3.54}$$

For a large system, the right-hand side is independent of N , but S_U is proportional to N . Therefore $(S_M - S_U)/S_U \sim 1/N$.

Exercise 3.9 Suppose the Hamiltonian function has one term that is proportional to some scalar parameter λ . That is,

$$H(x, p) = H_o(x, p) + \lambda h(x, p) \tag{S3.55}$$

An example is a set of particles in an external gravitational field. Then the parameter is g , the gravitational acceleration, and $h = m \sum z_i$. In that case the entropy will depend on the value of the parameter. Show that the microcanonical average of the observable $h(x, p)$ is given by the formula

$$\langle h \rangle = -T \frac{dS}{d\lambda} \tag{S3.56}$$

Solution

$$\begin{aligned}
 S &= k \log \left(\frac{1}{h^K N!} \int \theta(E - H_o - \lambda h) d^K x d^K p \right) \\
 &= k \log \left(\int \theta(E - H_o - \lambda h) d^K x d^K p \right) - k \log(h^K N!)
 \end{aligned}
 \tag{S3.57}$$

Using the fact that $d\theta(E - H_o - \lambda h)/d\lambda = -h\delta(E - H_o - \lambda h)$, we see that

$$\begin{aligned}
 \frac{dS}{d\lambda} &= k \frac{\left[\frac{d}{d\lambda} \int \theta(E - H_o - \lambda h) d^K x d^K p \right]}{\int \theta(E - H_o - \lambda h) d^K x d^K p} \\
 &= -k \frac{\int h(x, p) \delta(E - H_o - \lambda h) d^K x d^K p}{\int \theta(E - H_o - \lambda h) d^K x d^K p} \\
 &= -k \frac{\int h \delta(E - H) d^K x d^K p}{\int \delta(E - H) d^K x d^K p} \frac{\int \delta(E - H) d^K x d^K p}{\int \theta(E - H) d^K x d^K p}
 \end{aligned}
 \tag{S3.58}$$

But the microcanonical average of h is

$$\langle h \rangle = \frac{\int h \delta(E - H) d^K x d^K p}{\int \delta(E - H) d^K x d^K p}
 \tag{S3.59}$$

and

$$\begin{aligned}
 \frac{1}{T} &= k \frac{\partial}{\partial E} \log \left[\int \theta(E - H) d^K x d^K p \right] \\
 &= k \frac{\int \delta(E - H) d^K x d^K p}{\int \theta(E - H) d^K x d^K p}
 \end{aligned}
 \tag{S3.60}$$

which gives the desired result.

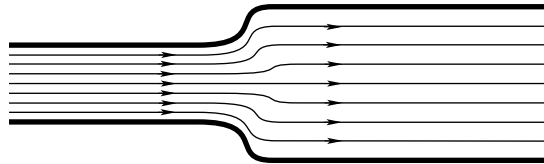


Fig. S3.3 The flow lines of a two-dimensional fluid.

Exercise 3.10 Fig. S3.3 shows the flow lines for the steady (that is, time-independent) flow of a two-dimensional fluid. The flow velocity at position (x_1, x_2) is $\mathbf{u}(x_1, x_2)$. If the volume occupied by a certain amount of fluid remains constant under the flow, then the flow is called *incompressible*. The mathematical condition for incompressible flow is that the divergence of the velocity field vanish everywhere.

$$\nabla \cdot \mathbf{u} = \frac{\partial u_1}{\partial x_1} + \frac{\partial u_2}{\partial x_2} = 0
 \tag{S3.61}$$

(a) For a two-dimensional phase space, the variables (x, p) could be identified with a pair of Cartesian coordinates (z_1, z_2) . Then Hamilton's equations would define a velocity field

$$\begin{aligned}
 u_1 &= \frac{dz_1}{dt} = \frac{dx}{dt} = \frac{\partial H}{\partial p} = \frac{\partial H(z_1, z_2)}{\partial z_2} \\
 u_2 &= \frac{dz_2}{dt} = \frac{dp}{dt} = -\frac{\partial H}{\partial x} = -\frac{\partial H(z_1, z_2)}{\partial z_1}
 \end{aligned}
 \tag{S3.62}$$

and

Show that this Hamiltonian flow is incompressible. (b) using the fact that $\nabla \cdot \mathbf{u} = 0$ is the condition for incompressible flow in any number of dimensions, generalize (a) to a $2K$ -dimensional phase space. The result is known as Liouville's theorem.

Solution (a)

$$\nabla \cdot \mathbf{u}(z_1, z_2) = \frac{\partial u_1}{\partial z_1} + \frac{\partial u_2}{\partial z_2} = \frac{\partial^2 H}{\partial z_1 \partial z_2} - \frac{\partial^2 H}{\partial z_2 \partial z_1} = 0 \tag{S3.63}$$

(b) For a $2K$ -dimensional phase space, we identify the $2K$ variables $(z_1, z_2, \dots, z_{2K})$ with the phase-space variables $(x_1, \dots, x_K, p_1, \dots, p_K)$. Then Hamilton's equations give the $2K$ -dimensional velocity field defined as follows. For $k = 1$ to K ,

$$u_k = \frac{dz_k}{dt} = \frac{dx_k}{dt} = \frac{\partial H}{\partial p_k} = \frac{\partial H}{\partial z_{K+k}} \tag{S3.64}$$

and

$$u_{K+k} = \frac{dz_{K+k}}{dt} = \frac{dp_k}{dt} = -\frac{\partial H}{\partial x_k} = -\frac{\partial H}{\partial z_k} \tag{S3.65}$$

Then

$$\begin{aligned} \nabla \cdot \mathbf{u} &= \sum_{k=1}^K \left(\frac{\partial u_k}{\partial z_k} + \frac{\partial u_{K+k}}{\partial z_{K+k}} \right) \\ &= \sum_{k=1}^K \left(\frac{\partial^2 H}{\partial z_k \partial z_{K+k}} - \frac{\partial^2 H}{\partial z_{K+k} \partial z_k} \right) = 0 \end{aligned} \tag{S3.66}$$

Exercise 3.11 According to Liouville's theorem, the motion of phase-space points defined by Hamilton's equations conserves phase-space volume. In this exercise we will illustrate this conservation of phase-space volume with a particular case. The Hamiltonian for a single particle in one dimension, subjected to a constant force F , is

$$H(x, p) = p^2/2m - Fx \tag{S3.67}$$

Consider the phase-space rectangle defined by $0 < x < A$ and $0 < p < B$. (a) Letting the points in the rectangle move for a time t according to Hamilton's equations, show the region into which the rectangle develops. (b) Show that the area of the region is AB , which is the area of the initial rectangle.

Solution First we have to determine the phase-space position at time t of a point that starts out at (x_o, p_o) . Hamilton's equations are

$$\frac{dx}{dt} = \frac{\partial H}{\partial p} = \frac{p(t)}{m} \tag{S3.68}$$

and

$$\frac{dp}{dt} = -\frac{\partial H}{\partial x} = F \tag{S3.69}$$

The second equation can be easily integrated to give

$$p(t) = p_o + Ft \tag{S3.70}$$

Using this result, we can integrate the first equation.

$$x(t) = x_o + \frac{1}{m} \int_o^t p(t) dt = x_o + \frac{p_o}{m}t + \frac{F}{2m}t^2 \tag{S3.71}$$

In Fig. S3.4 the four sides of the initial rectangle are numbered. Side 1 consists of the phase-space points $(x_o, 0)$, where $0 < x_o < A$. An initial point $(x_o, 0)$ goes to a point

$$(x_o, 0) \rightarrow \left(x_o + \frac{F}{2m}t^2, Ft\right) \tag{S3.72}$$

Side 2 consists of the points $(0, p_o)$, where $0 < p_o < B$. These points are carried, by Hamilton's equations, into

$$(0, p_o) \rightarrow \left(\frac{p_o}{m}t + \frac{F}{2m}t^2, p_o + Ft \right) \tag{S3.73}$$

Side 3 consists of the points (x_o, B) , where $0 < x_o < A$. These go to

$$(x_o, B) \rightarrow \left(x_o + \frac{B}{m}t + \frac{F}{2m}t^2, B + Ft \right) \tag{S3.74}$$

Side 4 consists of the points (A, p_o) , with $0 < p_o < B$. These go to

$$(A, p_o) \rightarrow \left(A + \frac{p_o}{m}t + \frac{F}{2m}t^2, p_o + Ft \right) \tag{S3.75}$$

In particular, the four corners of the rectangle are transformed as follows:

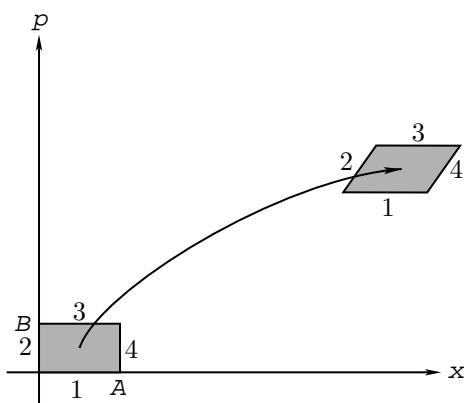


Fig. S3.4 The motion of a region in phase space under Hamiltonian flow.

$$\begin{aligned} (0, 0) &\rightarrow \left(\frac{F}{2m}t^2, Ft \right) \\ (A, 0) &\rightarrow \left(A + \frac{F}{2m}t^2, Ft \right) \\ (0, B) &\rightarrow \left(\frac{B}{m}t + \frac{F}{2m}t^2, B + Ft \right) \\ \text{and } (A, B) &\rightarrow \left(A + \frac{B}{m}t + \frac{F}{2m}t^2, B + Ft \right) \end{aligned} \tag{S3.76}$$

The rectangle is transformed into a parallelogram with a base of A and an altitude of B , which has an area AB .

Exercise 3.12 Given any probability density in phase space $P(x, p)$ a statistical ensemble associated with that probability density is a very large but finite collection of points in phase space that has the property that the density of ensemble points $N(x, p)$, is, at every location, proportional to the probability function $P(x, p)$. The ensemble may be pictured as a vast collection of exact replicas of the system, each in a different physical state (having different values of particle positions and/or velocities). For example, if the system is a simple pendulum, then the ensemble is a vast warehouse of identical pendula, each with its own combination of angle and rotational velocity. But this picture of an ensemble immediately suggests the question: What happens to the ensemble density as all the pendula move according to Hamilton's equations? The answer is given by the following remarkable theorem.

Theorem: As the system points move according to Hamilton's equations, the ensemble density at the location of any moving phase space-point remains constant.

(a) Prove the theorem, which is also due to Liouville. (b) Show that, as the system points move, the ensemble density $N(x, p, t)$ satisfies *Liouville's equation*,

$$\frac{\partial N(x, p, t)}{\partial t} + \sum_{k=1}^K \left(\frac{\partial N}{\partial x_k} \frac{\partial H}{\partial p_k} - \frac{\partial N}{\partial p_k} \frac{\partial H}{\partial x_k} \right) = 0 \quad (\text{S3.77})$$

Solution (a) Let us consider the case of a simple pendulum. As each pendulum moves, its system point in the two-dimensional phase space moves like a speck of dust caught in the Hamiltonian flow. Suppose at time 0 we consider a small region δV_0 in the phase space. That small region will contain a number of ensemble points, δN . Now let all the points of δV_0 (not only the ensemble points) move for a time t according to Hamilton's equations. The region δV_0 will then be transformed into the region δV_t . But, because Hamiltonian flow is incompressible, the volume of δV_t will equal the volume of δV_0 . The ensemble points, like dust particles, remain in δV as it moves. Thus at time t the number of ensemble points in δV_t will be the same as the original number of ensemble points in δV_0 . Since the volume of the region has not changed, the density of ensemble points in δV_t at time t will equal the density of ensemble points in δV_0 at time 0. That is, the density at the location of a moving ensemble point remains constant. (b) Let $N(x, p, t)$ be the ensemble density at time t and let $(x(t), p(t))$ be a solution of Hamilton's equations of motion. What we have just shown can be written as

$$N(x(t), p(t), t) = N(x(0), p(0), 0) \quad (\text{S3.78})$$

Taking a time derivative of this equation gives

$$\frac{\partial N}{\partial t} + \sum_{k=1}^K \left(\frac{\partial N}{\partial x_k} \frac{dx_k}{dt} + \frac{\partial N}{\partial p_k} \frac{dp_k}{dt} \right) = 0 \quad (\text{S3.79})$$

Using Hamilton's equations to eliminate dx_k/dt and dp_k/dt gives Liouville's equation.

Exercise 3.13 For a uniform ensemble, the ensemble density is $N(x, p) = N_o \theta(E - H(x, p))$, where N_o is a constant that is proportional to the number of system points in the ensemble. For a microcanonical ensemble, the density is of the form $N(x, p) = N_o \delta(E - H(x, p))$. If these density functions are to describe the time-independent equilibrium state of a complex system, then one characteristic that we would certainly want them to have is that the ensemble density function would not change in time as the ensemble points moved according to Hamilton's equations. Show that a time-independent ensemble density that is *any* function of the system Hamiltonian [that is, $N(x, p, t) = F(H(x, p))$] is a solution of Liouville's equation.

Solution If $N(x, p, t) = F(H(x, p))$ then

$$\begin{aligned} \frac{\partial N}{\partial t} + \sum_{k=1}^K \left(\frac{\partial N}{\partial x_k} \frac{\partial H}{\partial p_k} - \frac{\partial N}{\partial p_k} \frac{\partial H}{\partial x_k} \right) &= \frac{dF}{dH} \sum_{k=1}^K \left(\frac{\partial H}{\partial x_k} \frac{\partial H}{\partial p_k} - \frac{\partial H}{\partial p_k} \frac{\partial H}{\partial x_k} \right) \\ &= 0 \end{aligned} \quad (\text{S3.80})$$

Exercise 3.14 For any observable, let $\langle A \rangle$ represent the time average of $A(t)$ over the time period $0 < t < \infty$. That is,

$$\langle A \rangle \equiv \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T A(t) dt \quad (\text{S3.81})$$

For any isolated system of point particles in a fixed volume, prove the *Virial Theorem of Clausius*,

$$\langle E_K \rangle = \left\langle -\frac{1}{2} \sum \mathbf{r}_i \cdot \mathbf{F}_i \right\rangle \quad (\text{S3.82})$$

where E_K is the kinetic energy of the system and \mathbf{F}_i is the instantaneous force on the i th particle.

Solution Consider the observable

$$S(t) = \sum_i \mathbf{r}_i \cdot \mathbf{p}_i \quad (\text{S3.83})$$

The time derivative of S is

$$\begin{aligned} \frac{dS}{dt} &= \sum_i \mathbf{v}_i \cdot \mathbf{p}_i + \sum_i \mathbf{r}_i \cdot \mathbf{F}_i \\ &= 2E_K + \sum_i \mathbf{r}_i \cdot \mathbf{F}_i \end{aligned} \quad (\text{S3.84})$$

Averaging this equation over the time interval $(0, T)$ gives

$$\frac{1}{T} \int_0^T \frac{dS}{dt} dt = \frac{S(T) - S(0)}{T} = \frac{1}{T} \int_0^T \left(2E_K + \sum_i \mathbf{r}_i \cdot \mathbf{F}_i \right) dt \quad (\text{S3.85})$$

For a system in a fixed volume, $S(T)$ is bounded and, therefore, $[S(T) - S(0)]/T \rightarrow 0$ as $T \rightarrow \infty$. In the same limit, the last term approaches $2\langle E_K \rangle + \langle \sum_i \mathbf{r}_i \cdot \mathbf{F}_i \rangle$, which proves the theorem.

Exercise 3.15 For a gas with no interparticle interactions, in a rectangular volume, show that the virial theorem leads to the well-known result, $pV = \frac{2}{3}E_K$.

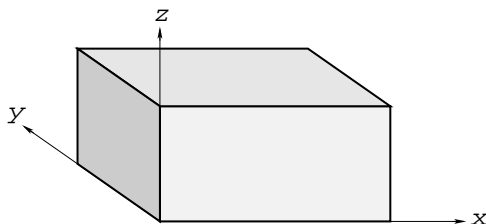


Fig. S3.5 The coordinate system origin is at the corner of a rectangular volume of sides L_x , L_y , and L_z .

Solution Assume that the dimensions of the volume are L_x , L_y , and L_z (Fig. S3.5). Take a coordinate system whose origin is located at one corner of the volume. Let X_i , Y_i , and Z_i be the rectangular components of the force on particle i . Then

$$\langle E_K \rangle = -\frac{1}{2} \left\langle \sum (x_i X_i + y_i Y_i + z_i Z_i) \right\rangle \quad (\text{S3.86})$$

In the absence of interparticle interactions, forces are exerted on the particles only when they are microscopically close to one of the walls. Thus, at any instant of time, the sum on the right-hand side of Eq. (S3.86) has six contributions associated with the sets of particles that, at that instant, are very close to each of the six walls.

For every particle near the wall at $x=0$, the x coordinate is essentially zero. The total force that those particles exert on that wall is, by definition of the pressure, equal to the instantaneous pressure times the area of the wall, namely $L_y L_z$. Thus, for that wall,

$$\sum_i x_i X_i = 0 \cdot \sum_i X_i = 0 \cdot L_y L_z = 0 \quad (\text{S3.87})$$

For simplicity, we will assume that the forces exerted on the particles by the walls are always normal to the walls. Then, the y and z components of the forces exerted on the particles by the wall at $x=0$ are zero. (This assumption could be replaced by the weaker assumption that the tangential components of the forces were statistically independent of position on the wall. Their sum would then be zero by cancellation.) In a similar way, the contribution of the particles near the wall at $x=L_x$ is

$$\sum (x_i X_i + y_i Y_i + z_i Z_i) = L_x (-L_y L_z p) = -L_x L_y L_z p \quad (\text{S3.88})$$

Taking into account the other four walls, one obtains

$$-\sum(x_i X_i + y_i Y_i + z_i Z_i) = 3L_x L_y L_z p = 3Vp \quad (\text{S3.89})$$

giving

$$2\langle E_K \rangle = 3V\langle p \rangle \quad (\text{S3.90})$$

If we neglect the fluctuations in the macroscopic observables E_K and p , we may drop the time average symbols.

Exercise 3.16 In the last exercise, it was shown that, for a gas without interparticle interactions, $pV = \frac{2}{3}E_K$. Assume that a nonideal gas has interparticle forces derivable from a two-body interaction potential $v(r_{ij})$. That is, that the Hamiltonian function is

$$H = \sum_i \frac{p_i^2}{2m} + \frac{1}{2} \sum_{i \neq j} v(r_{ij}) \quad (\text{S3.91})$$

The quantity $pV - \frac{2}{3}E_K$ we will call the deviation from the ideal gas law. (a) Using the Virial Theorem, and assuming that the system has no extra conservation laws, so that time averages can be replaced by microcanonical ensemble averages, show that the deviation from the ideal gas law can be written as the average value of a two-particle observable involving the interaction potential $v(r)$. (b) The function

$$n_2(\mathbf{r}_1, \mathbf{r}_2) = \int F_2(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2) d^3\mathbf{p}_1 d^3\mathbf{p}_2 \quad (\text{S3.92})$$

gives the probability density for finding a particle at \mathbf{r}_1 and another particle at \mathbf{r}_2 , regardless of their momenta. (F_2 is the two-particle phase space density function, defined in Section 3.10.) In a rotationally and translationally invariant system, $n_2(\mathbf{r}_1, \mathbf{r}_2)$ is a function of $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ only. We write it as

$$n_2(\mathbf{r}_1, \mathbf{r}_2) = n^2 g(r_{12}) \quad (\text{S3.93})$$

where n is the particle density and $g(r)$ is called the *two-particle correlation function*. Using the result of (a), write $pV - \frac{2}{3}E_K$ as a one-dimensional integral involving $v(r)$ and $g(r)$.

Solution (a) According to the Virial Theorem, $\langle E_K \rangle = \langle -\frac{1}{2} \sum \mathbf{r}_i \cdot \mathbf{F}_i \rangle$. Assuming that the system has no extra conservation laws, we can interpret the averages as microcanonical averages. The force on the i th particle is a sum of the forces exerted on that particle by all the other particles in the system plus the force on that particle by the walls (in case it is sufficiently close to one of the walls). Let us write the force of the walls on the i th particle as \mathbf{W}_i . The force exerted on the i th particle by the j th particle is given by

$$\mathbf{F}_{ij} = -v'(r_{ij})\mathbf{n}_{ij} \quad (\text{S3.94})$$

where $\mathbf{n}_{ij} = \mathbf{r}_{ij}/r_{ij}$ is a unit vector, pointing from particle j to particle i . Then, ignoring fluctuations in E_K ,

$$E_K = \left\langle -\frac{1}{2} \sum_i \mathbf{r}_i \cdot \mathbf{W}_i \right\rangle + \frac{1}{2} \left\langle \sum_{i \neq j} \mathbf{r}_i \cdot \mathbf{n}_{ij} v'(r_{ij}) \right\rangle \quad (\text{S3.95})$$

The first term on the right, by the argument of the previous exercise, gives $\frac{3}{2}pV$. The pair of particles labeled 1 and 2 contribute two terms to the double sum in Eq. (S3.95). Using the fact that $\mathbf{n}_{ij} = -\mathbf{n}_{ji}$, they can be written as

$$(\mathbf{r}_1 - \mathbf{r}_2) \cdot \mathbf{n}_{12} v'(r_{12}) = r_{12} v'(r_{12}) \quad (\text{S3.96})$$

Doing the same for the other pairs of particles, we get

$$\begin{aligned} E_K &= \frac{3}{2}pV + \frac{1}{2} \left\langle \sum_{i < j} r_{ij} v'(r_{ij}) \right\rangle \\ &= \frac{3}{2}pV + \frac{1}{4} \left\langle \sum_{i \neq j} r_{ij} v'(r_{ij}) \right\rangle \end{aligned} \quad (\text{S3.97})$$

From the definition of $n_2(\mathbf{r}_1, \mathbf{r}_2)$,

$$\left\langle \sum_{i \neq j} r_{ij} v'(r_{ij}) \right\rangle = \int d^3 \mathbf{r}_1 d^3 \mathbf{r}_2 r_{12} v'(r_{12}) n_2(\mathbf{r}_1, \mathbf{r}_2) \quad (\text{S3.98})$$

We transform the integral to center-of-mass and relative coordinates, $\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2$ and $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$, and use the fact that $n_2(\mathbf{r}_1, \mathbf{r}_2) = n^2 g(r)$. The term $v'(r)$ is zero unless r is very small; thus we can extend the \mathbf{r} integral to infinity. The integral over \mathbf{R} gives a factor of V . Introducing polar coordinates in the \mathbf{r} integral gives

$$\left\langle \sum_{i \neq j} r_{ij} v'(r_{ij}) \right\rangle = 4\pi V n^2 \int_0^\infty r^3 v'(r) g(r) dr \quad (\text{S3.99})$$

and therefore,

$$E_K - \frac{3}{2} pV = \pi V n^2 \int_0^\infty r^3 v'(r) g(r) dr \quad (\text{S3.100})$$

In the next chapter it will be shown that, for a classical system, even one with interparticle interactions, $E_K = \frac{3}{2} NkT$. When this is used in Eq. (S3.100), one obtains an exact equation for the pressure of a nonideal gas in terms of the two-particle correlation function.

$$p = nkT - \frac{2}{3} \pi n^2 \int_0^\infty r^3 v'(r) g(r) dr \quad (\text{S3.101})$$

Exercise 3.17 The three-dimensional Ising model described in Section 3.13, in which the energy depends on the relative orientation of nearest-neighbor spins, cannot be solved exactly. That is, no one has been able to derive an analytic expression for the thermodynamic functions, such as the entropy, associated with the model. There is a simpler model that can easily be solved exactly. It is called the noninteracting Ising model. The configurations of the model are still described by N spin variables, $\sigma_1, \dots, \sigma_N$, but the model attempts to describe a system of N noninteracting magnetic moments in an external magnetic field. For a given configuration, the energy is given by

$$E = H(\sigma_1, \sigma_2, \dots, \sigma_N) = \sum_{i=1}^N mB\sigma_i \quad (\text{S3.102})$$

where m is the magnetic moment of the particle, B is the magnetic field strength, and σ_i tells whether the i th magnetic moment is parallel or antiparallel to the field. For any energy value of the form $E = mBK$, where K is an integer, we can construct a microcanonical ensemble with a probability density

$$P(\sigma_1, \sigma_2, \dots, \sigma_N) = Q^{-1} \delta(E - H(\sigma_1, \sigma_2, \dots, \sigma_N)) \quad (\text{S3.103})$$

where $\delta(0) = 1$ and $\delta(x) = 0$ for $x \neq 0$. (a) Calculate the microcanonical normalization sum

$$Q(N, E) = \sum_{\sigma_1} \dots \sum_{\sigma_N} \delta(E - H(\sigma_1, \sigma_2, \dots, \sigma_N)) \quad (\text{S3.104})$$

(b) Using the relation, $S = k \log(Q/h^N)$, calculate the thermal energy per particle as a function of the temperature. Note: For particles that are fixed in place in a lattice, there is no possibility of particle exchange and therefore there is no need to include the $N!$ factor in the entropy expression. Such particles are said to be *distinguishable*.

Solution (a)

$$Q = \sum_{\sigma_1} \dots \sum_{\sigma_N} \delta\left(E - mB \sum \sigma_i\right) \quad (\text{S3.105})$$

where $E = mBK$. For a given configuration, let N_+ be the number of up spins and N_- be the number of down spins. Then $mB \sum \sigma_i = E$ iff $N_+ - N_- = K$. But we also know that $N_+ + N_- = N$. Therefore, $N_+ = (N + K)/2$ and $N_- = (N - K)/2$. Q is equal to the number of configurations with given values of N_+ and N_- . That is

$$Q = \frac{N!}{N_+!N_-!} = \frac{N!}{[(N + K)/2]![(N - K)/2]!} \quad (\text{S3.106})$$

(b) Using Stirling's approximation

$$S/k = N \log N - \frac{N + K}{2} \log \left(\frac{N + K}{2} \right) - \frac{N - K}{2} \log \left(\frac{N - K}{2} \right) - N \log h \quad (\text{S3.107})$$

The relation $E = mBK$ allows us to express S in terms of N and E .

$$\begin{aligned} \frac{S}{k} = & N \log N - \frac{1}{2} \left(N + \frac{E}{mB} \right) \log \left(N + \frac{E}{mB} \right) \\ & - \frac{1}{2} \left(N - \frac{E}{mB} \right) \log \left(N - \frac{E}{mB} \right) - N \log \left(\frac{h}{2} \right) \end{aligned} \quad (\text{S3.108})$$

The temperature is related to the energy by

$$\frac{1}{kT} = \frac{\partial(S/k)}{\partial E} = \frac{1}{2mB} \log \left(\frac{N - E/mB}{N + E/mB} \right) \quad (\text{S3.109})$$

or

$$\frac{N + E/mB}{N - E/mB} = e^{-2mB/kT} \quad (\text{S3.110})$$

Letting $x = E/mBN$ and $y = e^{-2mB/kT}$, this equation can be written as

$$1 + x = y(1 - x) \quad (\text{S3.111})$$

which has the solution $x = (y - 1)/(y + 1)$, or

$$\begin{aligned} \frac{E}{N} &= mB \frac{e^{-2mB/kT} - 1}{e^{-2mB/kT} + 1} \\ &= -mB \frac{e^{mB/kT} - e^{-mB/kT}}{e^{mB/kT} + e^{-mB/kT}} \\ &= -mB \tanh(mB/kT) \end{aligned} \quad (\text{S3.112})$$

Exercise 3.18 Consider a set of N particles in two dimensions in a symmetrical harmonic oscillator potential $V(x, y) = \frac{1}{2}k(x^2 + y^2)$. Because of the perfect rotational symmetry of the potential the angular momentum about the origin is an extra conserved quantity. Assume that the angular momentum L and the total energy E are given. (a) Use the method of Chapter 2 to determine the phase-space particle density $f(x, y, p_x, p_y)$ at equilibrium. (b) Determine the spatial particle density $n(r)$ as a function of distance from the origin. (c) Determine the average velocity of particles at position (x, y) and show that it is consistent with the velocity field of rigid body rotation. (Warning: This is a very long and difficult exercise.)

Solution (a) We break up the four-dimensional phase space (x, y, p_x, p_y) into little four-dimensional cubes, which we number with an integer $i = 1, 2, \dots$. The center of the i th cube is at $(x_i, y_i, p_{xi}, p_{yi})$. A particle in the i th cube has an energy E_i and an angular momentum L_i , where

$$E_i = \frac{1}{2m} (p_{xi}^2 + p_{yi}^2) + \frac{k}{2} (x_i^2 + y_i^2) \quad (\text{S3.113})$$

and

$$L_i = x_i p_{yi} - y_i p_{xi} \quad (\text{S3.114})$$

We describe a macrostate by assigning occupation numbers, N_1, N_2, \dots , to all cubes. We describe a microstate by saying which cube each particle is in. For a given macrostate, there correspond I microstates where

$$I = \frac{N!}{\prod_i N_i!} \quad (\text{S3.115})$$

We maximize $\log I$, subject to the three constraints

$$\sum_i N_i = N \quad (\text{S3.116})$$

$$\sum_i N_i E_i = E \quad (\text{S3.117})$$

and

$$\sum_i N_i L_i = L \quad (\text{S3.118})$$

This is done by maximizing the function

$$\begin{aligned} F &= \log I - \alpha \sum_i N_i - \beta \sum_i N_i E_i - \gamma \sum_i N_i L_i \\ &= \log N! - \sum_i N_i (\log N_i - 1) - \sum_i (\alpha + \beta E_i + \gamma L_i) N_i \end{aligned} \quad (\text{S3.119})$$

with no constraints. Setting $\partial F / \partial N_i = 0$ gives the equation

$$\log N_i = -\alpha - \beta E_i - \gamma L_i \quad (\text{S3.120})$$

If ω is the four-dimensional volume of one of the phase-space cubes, then the definition of the phase-space distribution function is

$$f(x_i, y_i, p_{xi}, p_{yi}) = \frac{N_i}{\omega} \quad (\text{S3.121})$$

This shows that

$$f(x, y, p_x, p_y) = C \exp \left[-\beta \left(\frac{1}{2m} (p_x^2 + p_y^2) + \frac{k}{2} (x^2 + y^2) \right) - \gamma (xp_y - yp_x) \right] \quad (\text{S3.122})$$

Next, we must evaluate the constants C , β , and γ in terms of N , E , and L .

$$\begin{aligned} C^{-1} N &= \int \exp \left[-\beta \left(\frac{1}{2m} (p_x^2 + p_y^2) + \frac{k}{2} (x^2 + y^2) \right) \right. \\ &\quad \left. - \gamma (xp_y - yp_x) \right] dx dy dp_x dp_y \end{aligned} \quad (\text{S3.123})$$

Notice that the integral factors into equivalent two-dimensional integrals involving (x, p_y) and (y, p_x) .

$$\frac{N}{C} = \left[\int \exp(-\beta p_y^2 / 2m - \beta k x^2 / 2 - \gamma x p_y) dy dp_x \right]^2 \quad (\text{S3.124})$$

The two-dimensional integral needed is of the form

$$I = \int e^{-(Ax^2 + 2Bxp + Cp^2)} dx dp \quad (\text{S3.125})$$

But

$$Ax^2 + 2Bxp + Cp^2 = A \left(x + \frac{B}{A} p \right)^2 + \left(C - \frac{B^2}{A} \right) p^2 \quad (\text{S3.126})$$

Changing variables from x to $u = x + (B/A)p$, the integral separates into two Gaussian integrals, giving

$$I = \frac{\pi}{\sqrt{A(C - B^2/A)}} = \frac{\pi}{\sqrt{AC - B^2}} \quad (\text{S3.127})$$

In the case at hand, $A = \beta k/2$, $B = \gamma/2$, and $C = \beta/2m$. The final result is

$$C^{-1}N = \frac{4\pi^2}{\beta^2\omega^2 - \gamma^2} \quad (\text{S3.128})$$

where $\omega = \sqrt{k/m}$. This gives the constant C in terms of N , β , and γ .

$$C = \frac{\beta^2\omega^2 - \gamma^2}{4\pi^2} N \quad (\text{S3.129})$$

To do the integrals for the energy and angular momentum, it is best to use the following trick:

$$\begin{aligned} \left\langle \frac{p_x^2 + p_y^2}{2m} + \frac{k}{2}(x^2 + y^2) \right\rangle &= -C \frac{\partial}{\partial \beta} \int \exp \left[-\beta \left(\frac{1}{2m}(p_x^2 + p_y^2) + \frac{k}{2}(x^2 + y^2) \right) \right. \\ &\quad \left. - \gamma(xp_y - yp_x) \right] dx dy dp_x dp_y \quad (\text{S3.130}) \\ &= -N \frac{\beta^2\omega^2 - \gamma^2}{4\pi^2} \frac{\partial}{\partial \beta} \left(\frac{4\pi^2}{\beta^2\omega^2 - \gamma^2} \right) \\ &= N \frac{2\beta\omega^2}{\beta^2\omega^2 - \gamma^2} \end{aligned}$$

Also

$$\begin{aligned} \langle xp_y - yp_x \rangle &= -N \frac{\beta^2\omega^2 - \gamma^2}{4\pi^2} \frac{\partial}{\partial \gamma} \left(\frac{4\pi^2}{\beta^2\omega^2 - \gamma^2} \right) \quad (\text{S3.131}) \\ &= -N \frac{2\gamma}{\beta^2\omega^2 - \gamma^2} \end{aligned}$$

Letting $\varepsilon = E/N$ and $l = L/N$ be the energy and angular momentum per particle, we get the following two equations for β and γ .

$$\frac{2\beta\omega^2}{\beta^2\omega^2 - \gamma^2} = \varepsilon \quad (\text{S3.132})$$

and

$$\frac{2\gamma}{\beta^2\omega^2 - \gamma^2} = -l \quad (\text{S3.133})$$

It is easy to see that these equations imply that

$$\gamma\varepsilon + \beta\omega^2 l = 0 \quad (\text{S3.134})$$

and

$$\gamma l + \beta\varepsilon = 2 \quad (\text{S3.135})$$

which are two linear equations for γ and β , with the solution

$$\gamma = -\frac{2\omega^2 l}{\varepsilon^2 - \omega^2 l^2} \quad \text{and} \quad \beta = \frac{2\varepsilon}{\varepsilon^2 - \omega^2 l^2} \quad (\text{S3.136})$$

(b) Because the system has rotational symmetry about the origin, it is sufficient to calculate the spatial density along the x axis.

$$n(x, 0) = C \int \exp \left(-\beta \left[\frac{p_x^2 + p_y^2}{2m} + kx^2/2 \right] - \gamma xp_y \right) dp_x dp_y \quad (\text{S3.137})$$

The integral over p_x gives a factor of $(2\pi m/\beta)^{1/2}$. The integral over p_y can be done by completing the square, as was done previously. It then gives a factor of $(2\pi m/\beta)^{1/2} \exp[(m\gamma^2/2\beta)x^2]$. Using Eq. (S3.108) for C , we get

$$\begin{aligned} n(x, 0) &= N \frac{m}{2\pi\beta} (\beta^2\omega^2 - \gamma^2) \exp\left[-\left(\frac{\beta k}{2} - \frac{m\gamma^2}{2\beta}\right)x^2\right] \\ &= \frac{N}{\pi} \frac{k}{\varepsilon} e^{-(k/\varepsilon)x^2} \end{aligned} \quad (\text{S3.138})$$

where we have used Eq. (S3.111) and the fact that $\omega^2 = k/m$. Since both k and ε must be positive, it is clear that the density decreases at large distances, as it must for normalization. (c) The average velocity at position (x, y) is defined by saying that

$$mn(x, y)\mathbf{u}(x, y) = \int f(x, y, p_x, p_y)\mathbf{p} dp_x dp_y \quad (\text{S3.139})$$

Again we can utilize the rotational symmetry and calculate only u_y on the x axis, knowing that the velocity field must point in circles around the origin.

$$\begin{aligned} mn(x, 0)u_y(x) &= \int f(x, 0, p_x, p_y)p_y dp_x dp_y \\ &= -(C/x) \frac{\partial}{\partial \gamma} \int \exp\left[-\beta(p_x^2 + p_y^2)/2m - \beta kx^2/2 - \gamma xp_y\right] dp_x dp_y \end{aligned} \quad (\text{S3.140})$$

The integral factors into an integral over p_x times an integral over p_y .

$$\begin{aligned} \int e^{-\beta p_x^2/2m} dp_x &= (2\pi m/\beta)^{1/2} \\ \int e^{-\beta p_y^2/2m - \gamma xp_y} dp_y &= \exp\left(\frac{m\gamma^2}{2\beta}x^2\right) (2\pi m/\beta)^{1/2} \end{aligned} \quad (\text{S3.141})$$

Using this in Eq. (S3.119) and using Eq. (S3.117) for $n(x, 0)$, we get

$$\begin{aligned} \frac{m^2 N}{2\pi\beta} (\beta^2\omega^2 - \gamma^2) \exp\left[-\left(\frac{\beta k}{2} - \frac{m\gamma^2}{2\beta}\right)x^2\right] u(x) \\ - \frac{N}{4\pi^2} (\beta^2\omega^2 - \gamma^2) \frac{m\gamma}{\beta} x \frac{2\pi m}{\beta} \exp\left[-\left(\frac{\beta k}{2} - \frac{m\gamma^2}{2\beta}\right)x^2\right] \end{aligned} \quad (\text{S3.142})$$

which gives the velocity field

$$u(x) = -(\gamma/\beta)x = (l\omega^2/\varepsilon)x \equiv \Omega x \quad (\text{S3.143})$$

This is the velocity field of a rigid body that rotates about the origin with an angular velocity $\Omega = l\omega^2/\varepsilon$.