Solutions Manual for Introduction to Statistical Physics (draft)

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Preface

We give some schematic solutions of exercises from chapters 1 to 10 of "Introduction to Statistical Physics", by Silvio R. A. Salinas, first published by Springer, New York, in 2001. We also add a number of corrections and some new exercises. Additional corrections and suggestions are warmly welcomed.

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Introduction to Statistical Physics

1- Obtain the probability of adding up six points if we toss three distinct dice.

*** Let´s consider an easier problem, two dice, for example. In this (simpler) case, there are $6 \times 6 = 36$ configurations (events), but only 5 of them correspond to 6 points. Since all of the configurations are equally probable, we have $P\left(6\right) = 5/36$.

2- Consider a binomial distribution for a one-dimensional random walk, with $N = 6$, $p = 2/3$, and $q = 1 - p = 1/3$.

(a) Draw a graph of $P_N(N_1)$ versus N_1/N.

(b) Use the values of $\langle N_1 \rangle$ and $\langle N_1^2 \rangle$ to obtain the corresponding Gaussian distribution, $p_G(N_1)$. Draw a graph of $p_G(N_1)$ versus N_1/N to compare with the previous result.

(c) Repeat items (a) and (b) for $N = 12$ and $N = 36$. Are the new answers too different?

*** The "equivalent Gaussian" distribution has the same first and second moments as the binomial distribution,

$$p_G\left(N_1\right) = C \exp\left[-\frac{\left(N_1 - \langle N_1 \rangle\right)^2}{2\left\langle \left(N_1 - \langle N_1 \rangle\right)^2 \right\rangle}\right] = C \exp\left[-\frac{\left(N_1 - pN\right)^2}{2Npq}\right],$$

where the "normalization factor" C comes from

$$\int_{-\infty}^{+\infty} C \exp\left[-\frac{(N_1 - pN)^2}{2Npq}\right] dN_1 = 1 \Longrightarrow C = (2\pi Npq)^{-1/2} .$$

It is instructive to draw graphs of $p_G(N_1)$ versus N_1 for some values of N.

In the figure, we show some graphs of $P_N(N_1)$ versus N_1/N.

3- Obtain an expression for the third moment of a binomial distribution. What is the behavior of this moment for large N?

*** Using the tricks introduced in the text, it is easy to see that

$$\left\langle (N_1 - \langle N_1 \rangle)^3 \right\rangle = Npq\,(q-p) .$$

Note that $\left\langle (\Delta N_1)^3 \right\rangle = 0$ for $p = q$ (same probabilities). Also, note the dependence of $\left\langle (\Delta N_1)^3 \right\rangle$ on N, so that

$$\frac{\left[\left\langle (\Delta N_1)^3 \right\rangle\right]^{1/3}}{\left[\left\langle (\Delta N_1)^2 \right\rangle\right]^{1/2}} \sim \frac{1}{N^{1/6}},$$

for large N.

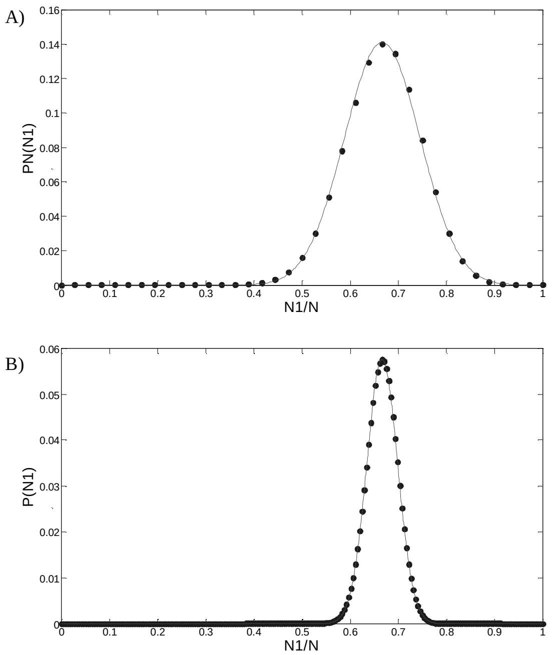
4- Consider an event of probability p. The probability of n occurrences of this event out of N trials is given by the binomial distribution,

$$W_N(n) = \frac{N!}{n!(N-n)!} p^n (1-p)^{N-n}.$$

If p is small ($p << 1$), $W_N(n)$ is very small, except for $n << N$. In this limit, show that we obtain the Poisson distribution,

$$W_N(n) \to P(n) = \frac{\lambda^n}{n!} \exp(-\lambda) ,$$

where $\lambda = np$ is the mean number of events. Check that $P(n)$ is normalized. Calculate $\langle n \rangle$ and $\left\langle (\Delta n)^2 \right\rangle$ for this Poisson distribution. Formulate a statistical problem to be solved in terms of this distribution.



Graphs of $P_N(N_1)$ (dots) versus N_1/N, and the corresponding Gaussian distribution (solid line), for N=36 (top figure) and N=216 (at bottom).

*** It is easy to see that

$$\sum_{n=0}^{\infty} P(n) = \exp(-\lambda) \sum_{n=0}^{\infty} \frac{\lambda^n}{n!} = 1,$$

$$\langle n \rangle = \sum_{n=0}^{\infty} nP(n) = \exp(-\lambda) \sum_{n=0}^{\infty} n \frac{\lambda^n}{n!} =$$

$$= \exp(-\lambda) \left(\lambda \frac{\partial}{\partial \lambda} \right) \sum_{n=0}^{\infty} \frac{\lambda^n}{n!} = \lambda,$$

and

$$\left\langle (\Delta n)^2 \right\rangle = \left\langle (n - \langle n \rangle)^2 \right\rangle = \lambda.$$

5- Consider an experiment with N equally likely outcomes, involving two events A and B. Let N_1 be the number of events in which A occurs, but not B; N_2 be the number of events in which B occurs, but not A; N_3 be the number of events in which both A and B occur; and N_4 be the number of events in which neither A nor B occur.

(i) Check that $N_1 + N_2 + N_3 + N_4 = N$.

(ii) Check that

$$P(A) = \frac{N_1 + N_3}{N} \text{ and } P(B) = \frac{N_2 + N_3}{N},$$

where $P(A)$ and $P(B)$ are the probabilities of occurrence of A and B, respectively.

(iii) Calculate the probability $P(A + B)$ of occurrence of either A or B.

(iv) Calculate the probability $P(AB)$ of occurrence of both A and B.

(v) Calculate the conditional probability $P(A \mid B)$ that A occurs given that B occurs.

(vi) Calculate the conditional probability $P(B \mid A)$ that B occurs given that A occurs.

(vii) Show that

$$P(A + B) = P(A) + P(B) - P(AB)$$

and

$$P(AB) = P(B)\,P(A \mid B) = P(A)\,P(B \mid A).$$

(viii) Considering a third event C, show that

$$\frac{P(B \mid A)}{P(C \mid A)} = \frac{P(B)}{P(C)}\frac{P(A \mid B)}{P(A \mid C)},$$

which is an expression of Bayes' theorem.

6- A random variable x is associated with the probability density

$$p(x) = \exp(-x),$$

for $0 < x < \infty$.

(a) Find the mean value $\langle x \rangle$.

(b) Two values x_1 and x_2 are chosen independently. Find $\langle x_1 + x_2 \rangle$ and $\langle x_1 x_2 \rangle$.

(c) What is the probability distribution of the random variable $y = x_1 + x_2$?

*** Note that

$$\langle x \rangle = 1, \qquad \langle x_1 + x_2 \rangle = 2, \qquad \langle x_1 x_2 \rangle = 1,$$

and that

$$p(y) = \int\int dx_1 dx_2 p(x_1)\,p(x_2)\,\delta(y - x_1 - x_2).$$

Using an integral representations of the delta-function (see the Appendix), it is easy to see that

$$p(y) = y \exp(-y).$$

7- Consider a random walk in one dimension. After N steps from the origin, the position is given by

$$x = \sum_{j=1}^{N} s_j,$$

where $\{s_j\}$ is a set of independent, identical, and identically distributed random variables, given by the probability distribution

$$w(s) = \left(2\pi\sigma^2\right)^{-1/2} \exp\left[-\frac{(s-l)^2}{2\sigma^2}\right],$$

where σ and l are positive constants. After N steps, what is the average displacement from the origin? What is the standard deviation of the random variable x? In the large N limit, what is the form of the Gaussian distribution associated with this problem?

*** It is easy to see that

$$\langle x \rangle = N \langle s \rangle = Nl,$$

and

$$\left\langle (x - \langle x \rangle)^2 \right\rangle = N \left\langle (s - \langle s \rangle)^2 \right\rangle = N\sigma^2,$$

from which we write the Gaussian form

$$p_G(x) = \left(2\pi\sigma^2\right)^{-1/2} \exp\left[-\frac{(x-Nl)^2}{2N\sigma^2}\right].$$

*** Try to solve a similar problem with

$$w(s) = \begin{cases} 0, & s < -1/2, \\ 1, & -1/2 < s < +1/2, \\ 0, & s > +1/2. \end{cases}$$

Calculate $\langle x \rangle$, $\langle x^2 \rangle$, and the limiting Gaussian distribution $p_G(x)$ (for large N). Note that

$$\int_{-\infty}^{+\infty} w(s) ds = 1, \qquad \langle x \rangle = N \langle s \rangle = 0, \qquad \left\langle (\Delta x)^2 \right\rangle = \frac{N}{12}.$$

8- Consider again problem 7, with a distribution $w(s)$ of the Lorentzian form

$$w(s) = \frac{1}{\pi} \frac{a}{s^2 + a^2},$$

with $a > 0$. Obtain an expression for the probability distribution associated with the random variable x. Is it possible to write a Gaussian approximation for large N? Why?

*** You should be careful. It is immediate to see that $\langle s \rangle = 0$, but $\langle s^2 \rangle$ is associated with a diverging integral! The Lorentzian form does not obey the conditions for the validity of the central limit theorem.

Additional exercises

9- The Ehrenfest "urn model" provides an excellent illustration of statistical fluctuations, the role of large numbers, and the direction of the "time arrow". Take a look at Section 1 of Chapter 15. The "stochastic equation" associated with the simple urn model is linear (and exactly soluble). There are many works on the urn model. See, for example, the relatively recent work by C. Godrèche and J. M. Luck, J. Phys.: Condens. Matter **14**, 1601-1615 (2002), which contains a number of historical references.

In the simple urn model, we consider two boxes, N numbered balls, and a generator of N random numbers. Initially, there are N_1 balls in urn 1, and $N_2 = N - N_1$ balls in urn 2. Each time unit, we draw a random number, between 1 and N, and change the position (urn location) of the corresponding ball.

Choose a reasonable generator of random numbers, and perform time simulations for this simple urn model. Draw graphs of N_1 (number of balls in urn 1) as a function of time t (in uniform discrete steps Δt), from an initial situation in which $N_1 = N$ (all the balls are in urn 1), using two values of the total number of balls: (a) $N = 10$, and (b) $N = 100$. What can you say about the fluctuations of the value of N_1? What happens at long times, $t \to \infty$?

It is reasonable to assume the "stochastic equation"

$$P(N_1, t + \Delta t) = P(N_1 - 1, t)\, W_1 + P(N_1 + 1, t)\, W_2,$$

where $P(N_1, t)$ is the probability of finding N_1 balls in urn 1 at time t, Δt is the discrete time interval between draws, and W_1 and W_2 are "probabilities of transition". Show that it is reasonable to assume that

$$W_1 = \frac{N - (N_1 - 1)}{N} \quad \text{and} \quad W_2 = \frac{N_1 + 1}{N}.$$

What are the assumptions involved in this choice? Check that the binomial distribution is a an "equilibrium solution" of this equation (in other words, a solution for $t \to \infty$).

Use this equation to obtain the time evolution $\langle N_1 \rangle_t$ of the average value of N_1. Compare this analytical form with the results of your simulations.

*** Note that

$$\langle N_1 \rangle_t = \sum_{N_1} N_1 P(N_1, t).$$

Using the stochastic equation, it is easy to see that

$$\langle N_1 \rangle_{t+\Delta t} = \left(1 - \frac{2}{N}\right) \langle N_1 \rangle_t + 1,$$

which leads to the solution

$$\langle N_1 \rangle_t = C \left(1 - \frac{2}{N}\right)^t + \frac{N}{2},$$

where the prefactor C comes from the initial condition.

In figure 1 we show a simulation of N_1 versus discrete time t.

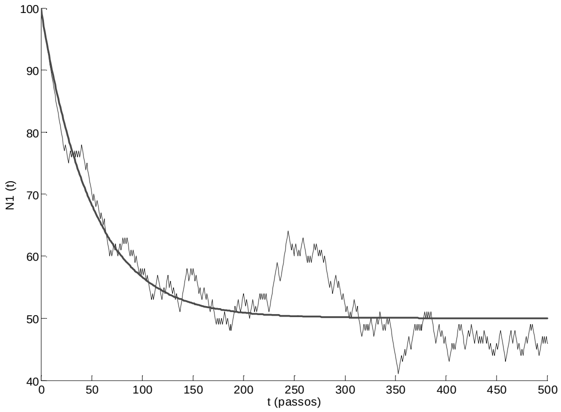


Figura 1: Simulation for the Ehrenfest urn model. Graph of N_1 versus the discrete time t, for N=100 and the initial condition N_{10}=N. The solid line represents the theoretical result for the time evolution of the average value of N_1.

2

Statistical Description of a Physical System

1. Neglect the complexities of classical phase space, and consider a system of N distinguishable and noninteracting particles, which may be found in two states of energy, with $\epsilon = 0$ and $\epsilon > 0$, respectively. Given the total energy U of this system, obtain an expression for the associated number of microscopic states.

*** Suppose that there are N_0 particles in the ground state and N_e particles in the excited state. The number of accessible microscopic states of this system is given by

$$\Omega\left(U,N\right) = \frac{N!}{N_0!N_e!},$$

where $N_0 + N_e = N$ and $U = \epsilon N_e$.

2. Calculate the number of accessible microscopic states of a system of two localized and independent quantum oscillators, with fundamental frequencies ω_o and $3\omega_o$, respectively, and total energy $E = 10\hbar\omega_o$.

*** There are three microscopic states:
$(n_1 = 2; n_2 = 2)$, $(n_1 = 5; n_2 = 1)$, and $(n_1 = 8; n_2 = 0)$.

3. Consider a classical one-dimensional system of two non-interacting particles of the same mass m. The motion of the particles is restricted to a region of the x axis between $x = 0$ and $x = L > 0$. Let x_1 and x_2 be the position coordinates of the particles, and p_1 and p_2 be the canonically conjugated momenta. The total energy of the system is between E and $E + \delta E$. Draw the projection of phase space in a plane defined by position coordinates. Indicate the region of this plane that is accessible to the system. Draw similar graphs in the plane defined by the momentum coordinates.

4. The position of a one-dimensional harmonic oscillator is given by

$$x = A \cos(\omega t + \varphi),$$

where A, ω, and φ are positive constants. Obtain $p(x)\,dx$, that is, the probability of finding the oscillator with position between x and $x + dx$. Note that it is enough to calculate dT/T, where T is a period of oscillation, and dT is an interval of time, within a period, in which the amplitude remains between x and $x + dx$. Draw a graph of $p(x)$ versus x.

*** It is easy to show that

$$p(x) = \frac{1}{2\pi A}\left[1 - \left(\frac{x}{A}\right)^2\right]^{-1/2}.$$

Now consider the classical phase space of an ensemble of identical one-dimensional oscillators with energy between E and $E + \delta E$. Given the energy E, we have an ellipse in phase space. So, the accessible region in phase space is a thin elliptical shell bounded by the ellipses associated with energies E and $E + \delta E$, respectively. Obtain an expression for the small area δA of this elliptical shell between x and $x + dx$. Show that the probability $p(x)dx$ may also be given by $\delta A/A$, where A is the total area of the elliptical shell. This is one of the few examples where we can check the validity of the ergodic hypothesis and the postulate of equal *a priori* probabilities.

5. Consider a classical system of N localized and weakly interacting one-dimensional harmonic oscillators, whose Hamiltonian is written as

$$\mathcal{H} = \sum_{j=1}^{N} \left(\frac{1}{2m} p_j^2 + \frac{1}{2} k x_j^2 \right),$$

where m is the mass and k is an elastic constant. Obtain the accessible volume of phase space for $E \leq \mathcal{H} \leq E + \delta E$, with $\delta E << E$. This classical model for the elastic vibrations of a solid leads to a constant specific heat with temperature (law of Dulong and Petit). The solid of Einstein is a quantum version of this model. The specific heat of Einstein's model decreases with temperature, in qualitative agreement with experimental data.

*** The volume in classical phase space is given by

$$\Omega = \underset{E \leq \mathcal{H} \leq E+\delta E}{\int \cdots \int} dx_1 ... dx_N dp_1 ... dp_N = \left(\frac{4m}{k} \right)^{N/2} \delta V_{sph,}$$

where δV_{sph} is the volume of a $2N$-dimensional hyperspherical shell (see Appendix) of radius $E^{1/2}$ and thickness proportional to δE. For large N, it is easy to write the asymptotic dependence of Ω on the energy E,

$$\delta V_{sph} \sim E^N.$$

The dependence on N is more delicate (it requires the calculation of the volume of the hypersphere).

6. The spin Hamiltonian of a system of N localized magnetic ions is given by

$$\mathcal{H} = D \sum_{j=1}^{N} S_j^2,$$

where $D > 0$ and the spin variable S_j may assume the values ± 1 or 0, for all $j = 1, 2, 3....$ This spin Hamiltonian describes the effects of the electrostatic environment on spin-1 ions. An ion in states ± 1 has energy $D > 0$, and an ion in state 0 has zero energy. Show that the number of accessible microscopic states of this system with total energy U can be written as

$$\Omega\left(U,N\right)=\frac{N!}{(N-\frac{U}{D})!}\sum_{N_-}\frac{1}{(\frac{U}{D}-N_-)!N_-!},$$

for N_- ranging from 0 to N, with $N>U/D$ and $N_-<U/D$. Thus, we have

$$\Omega\left(U,N\right)=N!2^{U/D}\left[\left(N-\frac{U}{D}\right)!\left(\frac{U}{D}\right)!\right]^{-1}.$$

Using Stirling's asymptotic series, show that

$$\frac{1}{N}\ln\Omega\rightarrow\frac{u}{D}\ln 2-\left(1-\frac{u}{D}\right)\ln\left(1-\frac{u}{D}\right)-\frac{u}{D}\ln\frac{u}{D},$$

for $N,U\rightarrow\infty$, with $U/N=u$ fixed. This last expression is the entropy per particle in units of Boltzmann's constant, k_B.

*** Let´s write the number of microscopic configurations with N_0 ions with spin $S=0$, N_+ ions with spin $+1$, and N_- ions with spin -1,

$$\Omega\left(N_0,N_+,N_-\right)=\frac{N!}{N_-!N_0!N_+!}.$$

It is easy to see that the number of microscopic configurations, with energy U and total number of ions N, is given by the sum

$$\Omega=\Omega\left(U,N\right)=\sum_{N_0,N_+,N_-}\frac{N!}{N_-!N_0!N_+!},$$

with the restrictions

$$N_0+N_++N_-=N$$

and

$$D\left(N_++N_-\right)=U.$$

We then use these restrictions to eliminate two variables, and write

$$\Omega\left(U,N\right)=\sum_{N_-=0}^{U/D}\frac{N!}{\left(N-\frac{U}{D}\right)!\left(\frac{U}{D}-N_-\right)!N_-!}=$$

$$=\frac{N!}{\left(N-\frac{U}{D}\right)!\left(\frac{U}{D}\right)!}\sum_{N_-=0}^{U/D}\frac{\left(\frac{U}{D}\right)!}{\left(\frac{U}{D}-N_-\right)!N_-!}.$$

Now it is easy to calculate the (binomial) sum and obtain the (exact) answer.

*** We usually look for results in the thermodynamic limit only. It is then acceptable to replace the sum by its maximum term. In fact, we can write

$$\Omega\left(U,N\right)=\sum_{N_0,N_+,N_-}\frac{N!}{N_-!N_0!N_+!}\sim\frac{N!}{\widetilde{N}_-!\widetilde{N}_0!\widetilde{N}_+!},$$

which is the asymptotic result in the limit $N,U\rightarrow\infty$, with $U/N=u$ fixed. In order to find the “occupation numbers” $\widetilde{N}_-$, $\widetilde{N}_0$, and $\widetilde{N}_+$, we use the technique of Lagrange multipliers. Let us define the function

$$f\left(N_-,N_0,N_+,\lambda_1,\lambda_2\right)=\ln\frac{N!}{N_-!N_0!N_+!}+$$

$$\lambda_1\left(N_0+N_++N_--N\right)+\lambda_2\left(DN_++DN_--U\right).$$

Using Stirling´s expansion, we take derivatives with respect to all of the arguments. It is easy to eliminate the Lagrange multipliers. The maximum is given by

$$\widetilde{N}_-=\widetilde{N}_+=\frac{U}{2D},\quad\widetilde{N}_0=N-\frac{U}{D},$$

from which we have the same asymptotic expression

$$\frac{1}{N}\ln\Omega\sim\frac{u}{D}\ln 2-\left(1-\frac{u}{D}\right)\ln\left(1-\frac{u}{D}\right)-\frac{u}{D}\ln\frac{u}{D},$$

in agreement with the limiting result from the previously obtained exact expression for Ω. In slightly more complicated problems, without an exact solution, we will be forced to resort to similar maximization techniques.

7. In a simplified model of a gas of particles, the system is divided into V cells of unit volume. Find the number of ways to distribute N distinguishable particles (with $0 \leq N \leq V$) within V cells, such that each cell may be either empty or filled up by only one particle. How would your answer be modified for indistinguishable particles?

*** If we consider distinguishable particles, we have

$$\Omega_d = \frac{V!}{(V-N)!}.$$

This result, however, does not make sense in the thermodynamic limit (see that $\ln \Omega_d / N$ does not exist in the limit $V, N \to \infty$, with $v = V/N$ fixed).

If the particles are indistinguishable, we have

$$\Omega_i = \frac{V!}{(V-N)!N!},$$

so that

$$\frac{1}{N} \ln \Omega_i \sim v \ln v - (v-1) \ln (v-1),$$

in the thermodynamic limit (note that $v = V/N \geq 1$). This is a simplified, and fully respectable, model of a non-interacting lattice gas. The entropy per particle is given by

$$s = s(v) = k_B \left[v \ln v - (v-1) \ln (v-1) \right],$$

from which we obtain the pressure,

$$\frac{p}{T} = \frac{\partial s}{\partial v} = k_B \ln \frac{v}{v-1}.$$

It is more instructive to write the pressure in terms of the particle density, $\rho = 1/v$,

$$\frac{p}{T} = -k_B \ln (1-\rho) = k_B \left[\rho + \frac{1}{2}\rho^2 + ... \right].$$

This is a virial expansion. The low-density limit gives the well-known expression for the ideal gas.

8. The atoms of a crystalline solid may occupy either a position of equilibrium, with zero energy, or a displaced position, with energy $\epsilon > 0$. To each equilibrium position, there corresponds a unique displaced position. Given the number N of atoms, and the total energy U, calculate the number of accessible microscopic states of this system.

*** It easy to see that

$$\Omega\left(U,N\right) = \frac{N!}{\left(\frac{U}{\epsilon}\right)!\left(N-\frac{U}{\epsilon}\right)!}.$$

Additional exercises

9. Obtain an expression for the volume of a hypersphere of radius R in d dimensions. Use this expression for obtaining t$_{i=1}$he volume $\Omega\left(E,V,N;\delta E\right)$ in phase space associated with a gas of N non-interacting classical monatomic particles, inside a box of volume V, with energy between E and $E+\delta E$ (with $\delta E << E$). What is the entropy $S = S\left(E,V,N\right)$ of this system? Is there any trouble in the thermodynamic limit?: How to correct this trouble? What is the "Gibbs paradox"?

*** The volume of the hypersphere is calculated in Appendix A4. We then present an alternative calculation. The element of volume of a d-dimensional hypersphere can be written as

$$A\,dR = \int_{-\infty}^{+\infty} dx_1 ... \int_{-\infty}^{+\infty} dx_d\,\delta\left(R - x_1^2 - x_2^2 - ...x_d^2\right) d\left(R^2\right),$$

where we have used a Dirac delta-function (see the Appendix A3). Note that it is easy to check this result for 2 or 3 dimensions. We now insert an extra term in this integral,

$$A\,dR = \left(\prod_{i=1}^{d}\int_{-\infty}^{+\infty} dx_i\right)\exp\left(-\alpha\sum_{i=1}^{N} x_i^2\right)\delta\left(R-\sum_{i=1}^{N} x_i^2\right) d\left(R^2\right),$$

and make $\alpha = 0$ at the end of the calculations. Using an integral representation of the delta-function (see the Appendix), we have

$$A = 2R\left(\prod_{i=1}^{d}\int_{-\infty}^{+\infty} dx_i\right)\exp\left(-\alpha\sum_{i=1}^{N} x_i^2\right)\times$$

$$\times\frac{1}{2\pi}\int_{-\infty}^{+\infty} dk\,\exp\left[-ik\left(R-\sum_{i=1}^{N} x_i^2\right)\right] =$$

$$=\frac{R}{\pi}\int_{-\infty}^{+\infty} dk\,\exp\left(-ikR^2\right)\left[\frac{\pi}{d-ik}\right]^{d/2}.$$

Changing variables, $kR^2 = z$, and resorting to the method of residues in the complex plane, we have

$$A = \frac{1}{\pi}R^{d-1}\left(i\pi\right)^{d/2}\int dz\frac{\exp\left(-iz\right)}{\left[z+i\alpha R^2\right]^{d/2}}.$$

Closing the contour around a pole of order $d/2$, we obtain the final result

$$A = \frac{2\pi^d}{\left(\frac{d}{2}-1\right)!}R^{d-1}.$$

Now it is easy to write the volume Ω in phase space, and to see that we have to divide this volume by the Boltzmann counting factor $N!$ in order to obtain an extensive entropy in the thermodynamic limit.

10. Stirling´s asymptotic expansion, given by

$$\ln N! = N\ln N - N + O\left(\ln N\right),$$

which works very well for large N ($N \to \infty$), is a most useful trick in statistical mechanics, in connection with the thermodynamic limit.

(i) Show that

$$\int_0^\infty x^n e^{-x}dx = n!$$

for $n = 0, 1, 2, ...$ (and assuming an analytic continuation related to the Gamma function).

(ii) Using this integral and the Laplace method of asymptotic integration, derive the first two terms of Stirling´s expansion.

(ii) Prove that

$$\lim_{n\rightarrow\infty} \frac{1}{n} \ln \left\{ \int_a^b \exp\left[nf\left(x\right)\right] dx \right\} = f\left(x_0\right),$$

where x_0 is the maximum of a continuous function $f\left(x\right)$ in the interval between a and $b > a$. This results gives a good degree of confidence in the usual replacements of certain sums by their maximum term!

*** For integer n, we can used the induction method to prove the that

$$\int_0^\infty x^n e^{-x} dx = n!$$

It is simple to check that it works for $n = 1$ (and $n = 0$, with $0! = 1$). Supposing that if holds for $n-1$, it is easy to show that it holds for n as well.

*** The use of Laplace´s method to find the first few terms in the asymptotic expansion of $\ln n!$ is fully described in Appendix A1.

*** The mathematical proof that has been asked is based on a sequence of very reasonable steps. Since $f\left(x_0\right)$ is the maximum of $f\left(x\right)$ in the interval between a and b, it is immediate to see that

$$I_n = \int_a^b \exp\left\{n\left[f\left(x\right) - f\left(x_0\right)\right]\right\} dx \leq$$

$$\leq \int_a^b \exp\left\{\left[f\left(x\right) - f\left(x_0\right)\right]\right\} dx = C,$$

where C is a well-defined constant value.

Let us find an inequality in the reversed direction. It is always possible to write

$$I_n = \int_a^b \exp\left\{n\left[f\left(x\right) - f\left(x_0\right)\right]\right\} dx \geq$$

$$\geq \int_{x_o-\frac{1}{2}\varepsilon}^{x_o+\frac{1}{2}\varepsilon} \exp\left\{n\left[f\left(x\right)-f\left(x_0\right)\right]\right\} dx.$$

Supposing that $f\left(x\right)$ is a continuous function, it is clear that, given $\delta > 0$, there exists $\varepsilon > 0$ such that $\left|f\left(x\right)-f\left(x_0\right)\right| < \delta$, for all δ. Thus,

$$I_n \geq \int_{x_o-\frac{1}{2}\varepsilon}^{x_o-\frac{1}{2}\varepsilon} \exp\left\{n\left[f\left(x\right)-f\left(x_0\right)\right]\right\} dx \geq$$

$$\geq \int_{x_o-\frac{1}{2}\varepsilon}^{x_o-\frac{1}{2}\varepsilon} \exp\left[-n\delta\right] dx = \varepsilon \exp\left[-n\delta\right].$$

Therefore,

$$\varepsilon \exp\left[-n\delta\right] \leq I_n \leq C,$$

which leads to

$$\varepsilon \exp\left[-n\delta\right] \exp\left[nf\left(x_0\right)\right] \leq \int_a^b \exp\left[nf\left(x\right)\right] dx \leq C \exp\left[nf\left(x_0\right)\right].$$

Taking the logarithm and dividing by n, we have

$$\frac{1}{n}\ln\varepsilon-\delta+f\left(x_0\right) \leq \frac{1}{n}\ln\left\{\int_a^b \exp\left[nf\left(x\right)\right] dx\right\} \leq \frac{1}{n}\ln C+f\left(x_0\right).$$

In the limit $n \to \infty$, and taking into account that ε is fixed, we have

$$-\delta + f\left(x_0\right) \leq \lim_{n\to\infty}\frac{1}{n}\ln\left\{\int_a^b \exp\left[nf\left(x\right)\right] dx\right\} \leq f\left(x_0\right).$$

Since $\delta > 0$ is arbitrary, we can take the limit $\delta \to 0$, which leads to the expected result. Note that the only requirements are the existence of the integral and the continuity of the function $f\left(x\right)$.

3

Overview of Classical Thermodynamics

1. The chemical potential of a simple fluid of a single component is given by the expression

$$\mu = \mu_o(T) + k_B T \ln \frac{p}{p_o(T)},$$

where T is the temperature, p is the pressure, k_B is the Boltzmann constant, and the functions $\mu_o(T)$ and $p_o(T)$ are well behaved. Show that this system obeys Boyle's law, $pV = Nk_BT$. Obtain an expression for the specific heat at constant pressure. What are the expressions for the thermal compressibility, the specific heat at constant volume, and the thermal expansion coefficient? Obtain the density of Helmholtz free energy, $f = f(T, v)$.

**** Note that $\mu(T,p) = g(T,p)$, where $g(T,p)$ is the Gibbs free energy per particle. Thus,

$$v = \left(\frac{\partial \mu}{\partial p}\right)_T = \frac{k_B T}{p},$$

which is the expression of Boyle's law, and

$$-s = \left(\frac{\partial \mu}{\partial T}\right)_p = \frac{d\mu_o}{dT} + k_B \ln \frac{p}{p_o(T)} - \frac{k_B T}{p_o(T)} \frac{dp_o}{dT},$$

from which we obtain the specific heat at constant pressure. All other expressions are straightforward. In particular,

$$f = g - pv.$$

You should give f in terms of T and v, $f = f\left(T, v\right)$.

2. Consider a pure fluid of one component. Show that

$$\left(\frac{\partial c_V}{\partial v}\right)_T = T\left(\frac{\partial^2 p}{\partial T^2}\right)_v.$$

Use this result to show that the specific heat of an ideal gas does not depend on volume. Show that

$$\left(\frac{\partial \alpha}{\partial p}\right)_{T,N} = -\left(\frac{\partial \kappa_T}{\partial T}\right)_{p,N}.$$

*** From the definition of the specific heat, we have

$$c_V = T\left(\frac{\partial s}{\partial T}\right)_v \Longrightarrow$$

$$\Longrightarrow \left(\frac{\partial c_V}{\partial v}\right)_T = T\frac{\partial^2 s}{\partial T \partial v} = T\frac{\partial^2 s}{\partial v \partial T} = T\left[\frac{\partial}{\partial T}\left(\frac{\partial s}{\partial v}\right)_T\right]_v.$$

Note that $s = s\left(T, v\right)$ is an equation of state in the Helmholtz representation. Then, we write

$$df = -sdT - pdv \Longrightarrow -s = \left(\frac{\partial f}{\partial T}\right)_v; \; -p = \left(\frac{\partial f}{\partial v}\right)_T$$

$$\Longrightarrow \left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v,$$

which leads to the first identity.

The proof of the second identity requires similar tricks.

3. Consider a pure fluid characterized by the grand thermodynamic potential

$$\Phi = V f_o\left(T\right) \exp\left(\frac{\mu}{k_B T}\right),$$

where $f_o(T)$ is a well-behaved function. Write the equations of state in this thermodynamic representation. Obtain an expression for the internal energy as a function of T, V, and N. Obtain an expression for the Helmholtz free energy of this system. Calculate the thermodynamic derivatives κ_T and α as a function of temperature and pressure.

*** From Euler's relation, we have

$$p = -\frac{\Phi}{V} = -f_o(T)\exp\left(\frac{\mu}{k_B T}\right).$$

Thus, we can write

$$\mu = k_B T \ln\frac{p}{-f_o(T)},$$

which is identical to the expression for the chemical potential in the first exercise, if we make $\mu_o = 0$ and $p_o(T) = -f_o(T)$. Therefore, we have Boyle's law and the usual expressions for κ_T and α.

4. Obtain an expression for the Helmholtz free energy per particle, $f = f(T, v)$, of a pure system given by the equations of state

$$u = \frac{3}{2}pv \quad \text{and} \quad p = avT^4,$$

where a is a constant.

*** These equations of state can be explicitly written in the entropy representation,

$$\frac{1}{T} = \left(\frac{3a}{2}\right)^{1/4} v^{1/2}u^{-1/4} \quad \text{and} \quad \frac{p}{T} = \frac{2}{3}\left(\frac{3a}{2}\right)^{1/4} v^{-1/2}u^{3/4},$$

from which we obtain the fundamental equation

$$s = \frac{4}{3}\left(\frac{3a}{2}\right)^{1/4} v^{1/2}u^{3/4} + c,$$

where c is a constant. The Helmholtz free energy per particle is given by

$$f(T, v) = u - Ts =$$

$$= \frac{3a}{2} v^2 T^4 - T \left[\frac{4}{3} \left(\frac{3a}{2} \right)^{1/4} v^{1/2} \left(\frac{3a}{2} v^2 T^4 \right)^{3/4} + c \right].$$

*** Let us consider a similar problem, with a slight modification in one of the equations of state,

$$u = \frac{3}{2} pv \qquad \text{and} \qquad p = avT^n.$$

Note that, instead of T^4, we are writing T^n, where n is an arbitrary integer. Is this a bona fide thermodynamic system? Is it possible to have $n \neq 4$?

Again, we rewrite the equations of state in the entropy representation,

$$\frac{1}{T} = \left(\frac{3a}{2} \right)^{1/n} v^{2/n} u^{-1/n} \quad \text{and} \quad \frac{p}{T} = \frac{2}{3} \left(\frac{3a}{2} \right)^{1/n} v^{-1+2/n} u^{1-1/n}.$$

In this representation we have

$$\frac{1}{T} = \left(\frac{\partial s}{\partial u} \right)_v ; \; \frac{p}{T} = \left(\frac{\partial s}{\partial v} \right)_u \Longrightarrow \left[\frac{\partial}{\partial v} \frac{1}{T} \right]_u = \left[\frac{\partial}{\partial u} \frac{p}{T} \right]_v ,$$

from which we obtain

$$\left(\frac{3a}{2} \right)^{1/n} \frac{2}{n} v^{-1+2/n} u^{-1/n} = \frac{2}{3} \left(\frac{3a}{2} \right)^{1/n} v^{-1+2/n} \left(1 - \frac{1}{n} \right) u^{-1/n},$$

leading to the only thermodynamic bona fide solution, $n = 4$.

5. Obtain an expression for the Gibbs free energy per particle, $g = g(T, p)$, for a pure system given by the fundamental equation

$$\left(\frac{S}{N} - c \right)^4 = a \frac{VU^2}{N^3},$$

where a and c are constants.

*** From the fundamental equation

$$s = a^{1/4} v^{1/4} u^{1/2} + c,$$

we write the equations of state

$$\frac{1}{T}=\left(\frac{\partial s}{\partial u}\right)_v=\frac{1}{2}a^{1/4}v^{1/4}u^{-1/2}$$

and

$$\frac{p}{T}=\left(\frac{\partial s}{\partial v}\right)_u=\frac{1}{4}a^{1/4}v^{-3/4}u^{1/2}.$$

The Gibbs free energy per particle is given by the Legendre transformation

$$-\frac{g}{T}=s-\frac{1}{T}u-\frac{p}{T}v,$$

where u and v come from the equations of state. Note that g has to be given in terms of T and p.

6. Consider an elastic ribbon of length L under a tension f. In a quasi-static process, we can write

$$dU=TdS+fdL+\mu dN.$$

Suppose that the tension is increased very quickly, from f to $f+\Delta f$, keeping the temperature T fixed. Obtain an expression for the change of entropy just after reaching equilibrium. What is the change of entropy per mole for an elastic ribbon that behaves according to the equation of state $L/N=cf/T$, where c is a constant?

*** Using the Gibbs representation, we have the Maxwell relation

$$\left(\frac{\partial S}{\partial f}\right)_T=\left(\frac{\partial L}{\partial T}\right)_f.$$

From the equation of state, $L/N=cf/T$, we have

$$\frac{\Delta S}{N}=-\frac{cf}{T^2}\Delta f.$$

7. A magnetic compound behaves according to the Curie law, $m=CH/T$, where C is a constant, H is the applied magnetic field, m is the magnetization per particle (with corrections due to presumed surface effects), and T is temperature. In a quasi-static process, we have

$$du = Tds + Hdm,$$

where $u = u\,(s, m)$ plays the role of an internal energy. For an infinitesimal adiabatic process, show that we can write

$$\Delta T = \frac{CH}{c_H T}\Delta H,$$

where c_H is the specific heat at constant magnetic field.

*** We have to calculate the partial derivative $(\partial T/\partial H)$ at fixed entropy. Using Jacobians, it is easy to write

$$\left(\frac{\partial T}{\partial H}\right)_s = \frac{\partial\,(T,s)}{\partial\,(H,s)} = \frac{\partial\,(T,s)}{\partial\,(T,H)}\frac{\partial\,(T,H)}{\partial\,(H,s)} = \left(\frac{\partial s}{\partial H}\right)_T \frac{-1}{\left(\frac{\partial s}{\partial T}\right)_H}.$$

All derivatives are written in terms of the independent variables T and H. We then introduce the Legendre transformation

$$g = u - Ts - Hm \Longrightarrow dg = -sdT - mdH,$$

from which we have

$$-s = \left(\frac{\partial g}{\partial T}\right)_H, -m = \left(\frac{\partial g}{\partial H}\right)_T \Longrightarrow \left(\frac{\partial s}{\partial H}\right)_T = \left(\frac{\partial m}{\partial T}\right)_H.$$

Inserting the equation of state in this Maxwell relation, it is easy to complete the proof.

8. From stability arguments, show that the enthalpy of a pure fluid is a convex function of entropy and a concave function of pressure.

*** The entalpy per particle is given by

$$h = u + pv,$$

from which we have

$$dh = Tds + vdp \Longrightarrow T = \left(\frac{\partial h}{\partial s}\right)_p \text{ and } v = \left(\frac{\partial h}{\partial p}\right)_s .$$

It is easy to show that

$$\left(\frac{\partial^2 h}{\partial s^2}\right)_p = \left(\frac{\partial T}{\partial s}\right)_p = \frac{T}{c_p} > 0.$$

Also, we have

$$\left(\frac{\partial^2 h}{\partial p^2}\right)_s = \left(\frac{\partial v}{\partial p}\right)_s = -v\kappa_s < 0.$$

It is straightforward to use standard tricks (Jacobians, for example) to write an expression for the adiabatic modulus of compressibility,

$$\kappa_s = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_s ,$$

in terms of positive quantities.

***9.** Show that the entropy per mole of a pure fluid, $s = s\left(u, v\right)$, is a concave function of its variables. Note that we have to analyze the sign of the quadratic form

$$d^2 s = \frac{1}{2}\frac{\partial^2 s}{\partial u^2}\left(du\right)^2 + \frac{\partial^2 s}{\partial u \partial v} du dv + \frac{1}{2}\frac{\partial^2 s}{\partial v^2}\left(dv\right)^2 .$$

*** This quadratic form can be written in the matrix notation

$$d^2 s = \frac{1}{2}\begin{pmatrix} du & dv \end{pmatrix}\begin{pmatrix} \frac{\partial^2 s}{\partial u^2} & \frac{\partial^2 s}{\partial u \partial v} \\ \frac{\partial^2 s}{\partial u \partial v} & \frac{\partial^2 s}{\partial v^2} \end{pmatrix}\begin{pmatrix} du \\ dv \end{pmatrix}.$$

The eigenvalues of the 2×2 matrix are the roots of the quadratic equation

$$\lambda^2 - \left[\frac{\partial^2 s}{\partial u^2} + \frac{\partial^2 s}{\partial v^2}\right]\lambda + \frac{\partial^2 s}{\partial u^2}\frac{\partial^2 s}{\partial v^2} - \left[\frac{\partial^2 s}{\partial u \partial v}\right]^2 = 0.$$

For a concave function, the eigenvalues are negative, that is,

$$\frac{\partial^2 s}{\partial u^2}\frac{\partial^2 s}{\partial v^2} - \left[\frac{\partial^2 s}{\partial u \partial v}\right]^2 > 0$$

and

$$\frac{\partial^2 s}{\partial u^2} + \frac{\partial^2 s}{\partial v^2} > 0.$$

Now it is straightforward to relate these derivatives of the entropy with positive physical quantities (as the compressibilities and the specific heats).

4

Microcanonical Ensemble

1. Consider a model of N localized magnetic ions, given by the spin Hamiltonian

$$\mathcal{H} = D \sum_{j=1}^{N} S_j^2,$$

where the spin variable S_j may assume the values -1, 0, or $+1$, for all j (see exercise **6** of Chapter 2). Given the total energy E, use the expression for the number of accessible microstates, $\Omega\left(E, N\right)$, to obtain the entropy per particle, $s = s\left(u\right)$, where $u = E/N$. Obtain an expression for the specific heat c in terms of the temperature T. Sketch a graph of c versus T. Check the existence of a broad maximum associated with the Schottky effect. Write an expression for the entropy as a function of temperature. What are the limiting values of the entropy for $T \rightarrow 0$ and $T \rightarrow \infty$?

*** The number of accessible microscopic states, $\Omega\left(E, N\right)$, has already been calculated in exercise **6** of Chapter 2. The entropy per magnetic ion is given by

$$s = s\left(u\right) = k_B \lim \frac{1}{N} \ln \Omega\left(E, N\right),$$

in the thermodynamic limit, $E, N \to \infty$, with $u = E/N$ fixed. We thus have

$$\frac{1}{k_B} s = \frac{u}{D} \ln 2 - \left(1 - \frac{u}{D}\right) \ln \left(1 - \frac{u}{D}\right) - \frac{u}{D} \ln \frac{u}{D},$$

from which we obtains the equation of state

$$\frac{1}{k_B T} = \frac{1}{D} \ln \frac{2\left(1 - u/D\right)}{u/D}.$$

The inversion of this equation leads to the dependence of the energy on the temperature,

$$u = \frac{2D \exp\left(-\beta D\right)}{1 + 2 \exp\left(-\beta D\right)},$$

where $\beta = 1/\left(k_B T\right)$. The specific heat $c = c\left(T\right)$ is given by the derivative of u with respect to T. Check the broad maximum in the graph of c versus T.

We now write the entropy s in terms of the temperature, $s = s\left(T\right)$. Check that $c = T\left(\partial s/\partial T\right)$. Draw a graph of $s\left(T\right)$ versus T. Check that $s\left(T\right) \to 0$ as $T \to 0$, and that $s\left(T\right) \to k_B \ln 3$ as $T \to \infty$ (for $D > 0$). What happens if $D < 0$?

2. In the solid of Einstein, we may introduce a volume coordinate if we make the phenomenological assumption that the fundamental frequency ω as a function of $v = V/N$ is given by

$$\omega = \omega\left(v\right) = \omega_o - A \ln\left(\frac{v}{v_o}\right),$$

where ω_o, A, and v_o are positive constants. Obtain expressions for the expansion coefficient and the isothermal compressibility of this model system.

*** Taking ω as a function of v, $\omega = \omega\left(v\right)$, the entropy of Einstein's solid can be written as a function of energy and volume, $s = s\left(u, v\right)$. From the equations of state, it is straightforward to obtain the expansion coefficient α and the compressibility κ_T.

3. Consider the semiclassical model of N particles with two energy levels (0 and $\epsilon > 0$). As in the previous exercise, suppose that the volume of the gas may be introduced by the assumption that the energy of the excited level depends on $v = V/N$,

$$\epsilon = \epsilon\left(v\right) = \frac{a}{v^{\gamma}},$$

where a and γ are positive constants. Obtain an equation of state for the pressure, $p = p\left(T, v\right)$, and an expression for the isothermal compressibility (note that the constant γ plays the role of the Grüneisen parameter of the solid).

*** Again, as $\epsilon = \epsilon\left(v\right)$, we can write $s = s\left(u, v\right)$. From the equations of state, it is easy to obtain the isothermal compressibility.

4. The total number of the accessible microscopic states of the Boltzmann gas, with energy E and number of particles N, may be written as

$$\Omega\left(E, N\right) = \sum_{N_1, N_2, \ldots} \frac{N!}{N_1! N_2! \cdots},$$

with the restrictions

$$\sum_j N_j = N \quad \text{and} \quad \sum_j \epsilon_j N_j = E.$$

Except for an additive constant, show that the entropy per particle is given by

$$s = -k_B \sum_j \left(\frac{\tilde{N}_j}{N}\right) \ln \left(\frac{\tilde{N}_j}{N}\right),$$

where $\left\{\tilde{N}_j\right\}$ is the set of occupation numbers at equilibrium. Using the continuum limit of the Boltzmann gas, show that the entropy depends on temperature according to a term of the form $k_B \ln T$ (note the correction!).

*** In the thermodynamic limit, we replace the sum by its largest term,

$$\Omega\left(E,N\right)\sim\frac{N!}{\widetilde{N}_1!\widetilde{N}_2!\cdots},$$

so the entropy per particle is written as

$$s=k_B\frac{1}{N}\ln\Omega\left(E,N\right)\sim-k_B\sum_j\left(\frac{\tilde{N}_j}{N}\right)\ln\left(\frac{\tilde{N}_j}{N}\right),$$

which resembles the H-function of Boltzmann (see chapter 15). Also, note the similarity with Shannon´s entropy of information theory (see chapter 5).

In order to find $\left\{\widetilde{N}_j\right\}$, we resort to the method of Lagrange multipliers. Let´s introduce the multipliers λ_1 and λ_2, and minimize the function

$$f\left(\left\{N_j\right\},\lambda_1,\lambda_2\right)=\ln\frac{N!}{\prod\limits_j N_j!}+$$

$$+\lambda_1\left(N-\sum_j N_j\right)+\lambda_2\left(E-\sum_j\epsilon_jN_j\right).$$

It is straightforward to see that

$$\widetilde{N}_j=\exp\left(-\lambda_1-\lambda_2\epsilon_j\right),$$

so that

$$\frac{\widetilde{N}_j}{N}=\frac{\exp\left(-\lambda_2\epsilon_j\right)}{\sum\limits_j\exp\left(-\lambda_2\epsilon_j\right)}.$$

The second Lagrange multiplier comes form the energy,

$$\sum_j\epsilon_j\frac{\widetilde{N}_j}{N}=\frac{E}{N}=u,$$

from which we have

$$u = -\frac{\partial}{\partial \lambda_2} Z_1, \qquad Z_1 = \sum_j \exp\left(-\lambda_2 \epsilon_j\right).$$

In the continuum limit, we have

$$Z_1 = \sum_j \exp\left(-\lambda_2 \epsilon_j\right) \sim \int d^3\overrightarrow{p} \exp\left(-\lambda_2 \frac{p^2}{2m}\right) = \left(\frac{2\pi m}{\lambda_2}\right)^{3/2},$$

which leads to the energy,

$$u = \frac{3}{2}\frac{1}{\lambda_2} = \frac{3}{2} k_B T,$$

and to the identification of the Lagrange multiplier $\lambda_2 \equiv \beta$ with the inverse of the temperature.

Now it is easy to write the continuum form of the entropy per particle,

$$s \sim -k_B \int d^3\overrightarrow{p} \frac{\exp\left(-\beta \frac{p^2}{2m}\right)}{Z_1} \ln \frac{\exp\left(-\beta \frac{p^2}{2m}\right)}{Z_1} =$$

$$= k_B \frac{3}{2} \ln T + \text{ constant},$$

which should be compared with the entropy per particle for the ideal gas ($pv = k_B T$, $u = 3k_B T/2$),

$$s = k_B \frac{3}{2} \ln T + k_B \ln v + \text{ constant}.$$

Note that $s \to -\infty$ for $T \to 0$, which is a well-known difficulty of classical statistical mechanics.

5. Consider a lattice gas of N particles distributed among V cells (with $N \leq V$). Suppose that each cell may be either empty or occupied by a single particle. The number of microscopic states of this system will be given by

$$\Omega\left(V, N\right) = \frac{V!}{N!\left(V-N\right)!}.$$

Obtain an expression for the entropy per particle, $s = s(v)$, where $v = V/N$. From this fundamental equation, obtain an expression for the equation of state p/T. Write an expansion of p/T in terms of the density $\rho = 1/v$. Show that the first term of this expansion gives the Boyle law of the ideal gases. Sketch a graph of μ/T, where μ is the chemical potential, in terms of the density ρ. What is the behavior of the chemical potential in the limits $\rho \to 0$ and $\rho \to 1$?

*** Look at the solution of exercise 7 of Chapter 2. The entropy particle of this lattice gas model is given by

$$s = k_B \left[v \ln v - (v-1) \ln (v-1) \right],$$

from which we have the equation of state

$$\frac{p}{k_B T} = -\ln\left(1 - \frac{1}{v}\right) = \frac{1}{v} + \frac{1}{2v^2} + \frac{1}{3v^3} + ...$$

Note that Bolyle's law is already given by the first term is this expansion.

In order to find μ/T, we write the thermodynamic entropy $S = Ns = S(V,N)$, and take the partial derivative with respect to N. Note that we can find ratios, as p/T and μ/T, but we cannot find an independent expression for the temperature (since there is no mention to the energy in the definition of this very simple and schematic model).

It is instructive to draw a graph of μ/T versus the particle density $\rho = 1/v$ (remember that $0 < \rho < 1$). Note that μ is an increasing function of ρ. Also, note that $\mu/T \to \infty$ for $\rho \to 0, 1$ (in the vacuum).

*** This lattice gas model can be alternatively defined in terms of a set variables $\{t_i\}$, $i = 1, ..., V$, such that $t_i = 1$ if cell i is occupied, and $t_i = 0$ if cell i is empty. The total number of accessible states $\Omega(V,N)$ is given by a (restricted) sum over the configurations of these occupation variables,

$$\Omega(V,N) = \sum_{\{t_i\},\text{restriction}} 1,$$

with the restriction

$$\sum_{i=1}^{V} t_i = N.$$

Of course, we obtain the same result, $\Omega\,(V, N) = V!/N!\,(V-N)!$

This problem becomes more difficult (and much more realistic) if we include interactions between particles. For example, we can mimic the short-range attraction between particles by assigning an energy $-\epsilon$, with $\epsilon > 0$, to each nearest-neighbor pair of occupied lattice sites. We then write the Hamiltonian

$$\mathcal{H} = -\epsilon \sum_{(i,j)} t_i t_j,$$

where the sum is over nearest-neighbor pairs of lattice sites. Given the total energy U, the calculation of the number of accessible microstates, $\Omega\,(U, V, N)$, becomes a formidable mathematical problem (related to the well-known Ising model of magnetism, as we shall see in the forthcoming chapters).

5

Canonical Ensemble

“We consider especially ensembles of systems in which the index (or logarithm) of probability of phase is a linear function of energy. The distribution, on account of its unique importance in the theory of statistical equilibrium, I have ventured to call *canonical*, and the divisor of the energy, the *modulus* of the distribution. The moduli of ensembles have properties analogous to temperature, in that equality of the moduli is a condition of equilibrium with respect to exchange of energy, when such exchange is made possible.” - J. W. Gibbs, “Elementary Principles In Statistical Mechanics: Developed With Especial Reference To The Rational Foundation Of Thermodynamics”, Scribner´s, New York, 1902.

1. The energy of a system of N localized magnetic ions, at temperature T, in the presence of a field H, may be written as

$$\mathcal{H} = D\sum_{i=1}^{N} S_i^2 - \mu_o H \sum_{i=1}^{N} S_i,$$

where the parameters D, μ_o, and H are positive, and $S_i = +1$, 0, or -1, for all sites i. Obtain expressions for the internal energy, the entropy, and the magnetization per site. In zero field ($H =$

0), sketch graphs of the internal energy, the entropy, and the specific heat versus temperature. Indicate the behavior of these quantities in the limits $T \to 0$ and $T \to \infty$. Calculate the expected value of the "quadrupole moment,"

$$Q = \frac{1}{N} \left\langle \sum_{i=1}^{N} S_i^2 \right\rangle ,$$

as a function of field and temperature.

*** The canonical partition function is given by

$$Z = \sum_{\{S_i\}} \exp \left[-\beta D \sum_{i=1}^{N} S_i^2 + \beta \mu_o H \sum_{i=1}^{N} S_i \right] =$$

$$= \sum_{S_1, S_2, \ldots, S_N} \exp \left[-\beta D \sum_{i=1}^{N} S_i^2 + \beta \mu_o H \sum_{i=1}^{N} S_i \right] =$$

$$= \left\{ \sum_{S} \exp \left[-\beta D S^2 + \beta \mu_o H S \right] \right\}^N =$$

$$= \left\{ 2 \exp \left(-\beta D \right) \cosh \left(\beta \mu_o H \right) + 1 \right\}^N .$$

In this simple case, the thermodynamic limit is trivial. The internal energy per ion comes from

$$u = -\frac{1}{N} \frac{\partial}{\partial \beta} \ln Z.$$

The magnetization per spin is given by

$$m = \frac{1}{\beta N} \frac{\partial}{\partial H} \ln Z,$$

and the "quadrupolar moment" by

$$Q = -\frac{1}{\beta D} \frac{\partial}{\partial D} \ln Z.$$

In zero field, we have $u\left(T=0\right)=0$, $u\left(T\rightarrow\infty\right)=2D/3$, $s\left(T=0\right)=0$, and $s\left(T\rightarrow\infty\right)=k_{B}\ln 3$. What happens for $D<0$?

2. Consider a one-dimensional magnetic system of N localized spins, at temperature T, associated with the energy

$$\mathcal{H}=-J\sum_{i=1,3,5,...,N-1}\sigma_{i}\sigma_{i+1}-\mu_{o}H\sum_{i=1}^{N}\sigma_{i},$$

where the parameters J, μ_{o}, and H are positive, and $\sigma_{i}=\pm1$ for all sites i. Assume that N is an even number, and note that the first sum is over odd integers.

(a) Obtain an expression for the canonical partition function and calculate the internal energy per spin, $u=u\left(T,H\right)$. Sketch a graph of $u\left(T,H=0\right)$ versus temperature T. Obtain an expression for the entropy per spin, $s=s\left(T,H\right)$. Sketch a graph of $s\left(T,H=0\right)$ versus T.

(b) Obtain expressions for the magnetization per particle,

$$m=m\left(T,H\right)=\frac{1}{N}\left\langle\mu_{o}\sum_{i=1}^{N}\sigma_{i}\right\rangle,$$

and for the magnetic susceptibility,

$$\chi=\chi\left(T,H\right)=\left(\frac{\partial m}{\partial H}\right)_{T}.$$

Sketch a graph of $\chi\left(T,H=0\right)$ versus temperature.

*** The canonical partition function is given by

$$Z=\sum_{\{\sigma_{i}\}}\exp\left[\beta J\sum_{i\text{ odd}}\sigma_{i}\sigma_{i+1}+\beta\mu_{o}H\sum_{i=1}^{N}\sigma_{i}\right]=$$

$$=\left\{\sum_{\sigma_{1},\sigma_{2}}\exp\left[\beta J\sigma_{1}\sigma_{2}+\beta\mu_{o}H\left(\sigma_{1}+\sigma_{2}\right)\right]\right\}^{N/2}=$$

$$= \left[2\exp\left(\beta J\right)\cosh\left(2\beta\mu_o H\right) + 2\exp\left(-\beta J\right)\right]^{N/2}.$$

Note the factorization of this sum.

The magnetization per particle is given by

$$m = \lim_{N\to\infty}\frac{1}{N}\frac{1}{Z}\sum_{\{\sigma_i\}}\left(\sum_{i=1}^{N}\sigma_i\right)\exp\left(-\beta\mathcal{H}\right) = \frac{1}{N\beta}\frac{\partial}{\partial H}\ln Z =$$

$$= \mu_o\frac{\sinh\left(2\beta\mu_o H\right)}{\cosh\left(2\beta\mu_o H\right) + \exp\left(-2\beta J\right)},$$

whose derivative with respect to H yields the susceptibility.

From the free energy,

$$f = -\frac{1}{\beta N}\ln Z,$$

we calculate the entropy,

$$s = s\left(T, H\right) = -\left(\frac{\partial f}{\partial T}\right)_H.$$

Check that, in zero field, $H = 0$, the entropy is given by

$$s\left(T, H = 0\right) = \frac{1}{2}k_B\ln\left(4\cosh\beta J\right) - \frac{1}{2}k_B\beta J\tanh\beta J,$$

with the limiting values

$$s\left(T, H = 0\right) \to \frac{1}{2}k_B\ln 2,$$

for $T \to 0$ $(\beta J \to \infty)$, and

$$s\left(T, H = 0\right) \to k_B\ln 2,$$

for $T \to \infty$ $(\beta J \to 0)$. How do you explain the residual entropy at $T = 0$?

3. Consider a system of N classical and noninteracting particles in contact with a thermal reservoir at temperature T. Each particle may have energies 0, $\epsilon > 0$, or 3ϵ. Obtain an expression for the canonical partition function, and calculate the internal energy per particle, $u = u(T)$. Sketch a graph of u versus T (indicate the values of u in the limits $T \to 0$ and $T \to \infty$). Calculate the entropy per particle, $s = s(T)$, and sketch a graph of s versus T. Sketch a graph of the specific heat versus temperature.

*** The canonical partition function is given by

$$Z = \left[1 + \exp(-\beta\epsilon) + \exp(-3\beta\epsilon)\right]^N .$$

For $T \to \infty$, we have $u = 4\epsilon/3$ and $s = k_B \ln 3$. Indicate the slopes of the graph of $u(T)$ versus T, for $T \to 0$ and $T \to \infty$. Calculate the asymptotic form of the specific heat $c(T)$ for $T \to 0$ and $T \to \infty$. Note that the graph of $c(T)$ versus T displays a broad maximum at the typical value $k_B T \sim \epsilon$.

4. A system of N localized and independent quantum oscillators is in contact with a thermal reservoir at temperature T. The energy levels of each oscillator are given by

$$\epsilon_n = \hbar\omega_o \left(n + \frac{1}{2}\right), \text{ with } n = 1, 3, 5, 7, ...$$

Note that n is an odd integer.

(a) Obtain an expression for the internal energy u per oscillator as a function of temperature T. What is the form of u in the classical limit ($\hbar\omega_o << k_B T$)?

(b) Obtain an expression for the entropy per oscillator as a function of temperature. Sketch a graph of entropy versus temperature. What is the expression of the entropy in the classical limit?

(c) What is the expression of the specific heat in the classical limit?

*** The answers come from the expression

$$Z_1 = \frac{\exp\left(-\frac{3}{2}\beta\hbar\omega_o\right)}{1 - \exp(-2\beta\hbar\omega_o)}.$$

The internal energy is given by

$$u=-\frac{\partial}{\partial\beta}\ln Z_1=\frac{3}{2}\hbar\omega_o+\frac{2\hbar\omega_o}{\exp\left(2\beta\hbar\omega_o\right)-1}.$$

Note that $u\rightarrow k_BT$ in the classical limit (the classical specific, $c=k_B$, behaves according to the law of Dulong and Petit).

5. Consider a system of N noninteracting classical particles. The single-particle states have energies $\epsilon_n=n\epsilon$, and are n times degenerate ($\epsilon>0$; $n=1,2,3,...$). Calculate the canonical partition function and the entropy of this system. Obtain expressions for the internal energy and the entropy as a function of temperature. What are the expressions for the entropy and the specific heat in the limit of high temperatures?

*** The thermodynamic functions come from canonical partition function, given by $Z=Z_1^N$, where

$$Z_1=\sum_{n=1,2,3,...}n\exp\left(-\beta n\epsilon\right)=\frac{\exp\left(\beta\epsilon\right)}{\left[\exp\left(\beta\epsilon\right)-1\right]^2}.$$

6. A set of N classical oscillators in one dimension is given by the Hamiltonian

$$\mathcal{H}=\sum_{i=1}^{N}\left(\frac{1}{2m}p_i^2+\frac{1}{2}m\omega^2q_i^2\right).$$

Using the formalism of the canonical ensemble in classical phase space, obtain expressions for the partition function, the energy per oscillator, the entropy per oscillator, and the specific heat. Compare with the results from the classical limit of the quantum oscillator. Calculate an expression for the quadratic deviation of the energy as a function of temperature.

*** The thermodynamic functions come from canonical partition function,

$$Z=\int_{-\infty}^{+\infty}dq_1...\int_{-\infty}^{+\infty}dq_N\int_{-\infty}^{+\infty}dp_1...\int_{-\infty}^{+\infty}dp_N\exp\left[-\beta\mathcal{H}\right]=$$

$$= \left\{ \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} dp dq \exp\left[-\frac{\beta}{2m} p^2 - \frac{\beta m \omega^2}{2} q^2 \right] \right\}^N = \left(\frac{2\pi}{\beta\omega} \right)^N .$$

***7.** Consider again the preceding problem. The canonical partition function can be written as an integral form,

$$Z(\beta) = \int_0^\infty \Omega(E) \exp(-\beta E)\, dE,$$

where $\Omega(E)$ is the number of accessible microscopic states of the system with energy E. Note that, in the expressions for $Z(\beta)$ and $\Omega(E)$, we are omitting the dependence on the number N of oscillators. Using the expression for $Z(\beta)$ obtained in the last exercise, perform a **reverse** Laplace transformation to obtain an asymptotic form (in the thermodynamic limit) for $\Omega(E)$. Compare with the expression calculated in the framework of the microcanonical ensemble.

*** First, we use an integral representation of the δ-function (see Appendix) to write

$$\frac{1}{2\pi} \int_{-i\infty}^{+i\infty} Z(\beta) \exp(\beta E')\, d\beta =$$

$$= \int_0^\infty dE \Omega(E) \frac{1}{2\pi} \int_{-i\infty}^{+i\infty} \exp\left[\beta (E' - E)\right] d\beta = \Omega(E') .$$

Inserting the result of the previous exercise, we have

$$\Omega(E) = \frac{1}{2\pi} \int_{-i\infty}^{+i\infty} \left(\frac{2\pi}{\beta\omega} \right)^N \exp(\beta E)\, d\beta,$$

which can be written in the form of a saddle-point integration (see Appendix),

$$\Omega(E) = \frac{1}{2\pi} \int_{-i\infty}^{+i\infty} \exp\left\{ N \left[\ln\left(\frac{2\pi}{\omega} \right) - \ln\beta + u\beta \right] \right\} d\beta,$$

where $u = E/N$. Using the asymptotic integration techniques of the Appendix, we locate the saddle point at $\beta = 1/u$ and write the asymptotic form (for $N \to \infty$),

$$\Omega\left(E\right) \sim \left(2\pi u^2\right)^{-1/2} \exp\left\{N\left[\ln\left(\frac{2\pi}{\omega}\right) + \ln u + 1\right]\right\}.$$

Therefore, we have the entropy per oscillator,

$$\frac{1}{k_B} s = \ln\left(\frac{2\pi}{\omega}\right) + \ln u + 1,$$

which should be compared with the well-known result for the classical one-dimensional harmonic oscillator in the microcanonical ensemble.

8. A system of N one-dimensional localized oscillators, at a given temperature T, is associated with the Hamiltonian

$$\mathcal{H} = \sum_{i=1}^{N}\left[\frac{1}{2m} p_i^2 + V\left(q_i\right)\right],$$

where

$$V\left(q\right) = \begin{cases} \frac{1}{2} m\omega^2 q^2; & \text{for } q > 0, \\ \frac{1}{2} m\omega^2 q^2 + \epsilon; & \text{for } q < 0, \end{cases}$$

with $\epsilon > 0$.

(a) Obtain the canonical partition function of this classical system. Calculate the internal energy per oscillator, $u = u\left(T\right)$. What is the form of $u\left(T\right)$ in the limits $\epsilon \to 0$ and $\epsilon \to \infty$?

(b) Consider now the quantum analog of this model in the limit $\epsilon \to \infty$. Obtain an expression for the canonical partition function. What is the internal energy per oscillator of this quantum analog?

*** The classical partition function is given by $Z = Z_1^N$, where

$$Z_1 = \frac{\pi}{\beta\omega}\left[\exp\left(-\beta\epsilon\right) + 1\right].$$

Note that $u \to k_BT$ at both limits, $\epsilon \to 0$ and $\epsilon \to \infty$.

The quantum results are simple in the limit of an infinite potential barrier ($\epsilon \to \infty$). in this limit, we have to discard all of the harmonic oscillator states with even values of n (which are associated with even wave functions; wave functions that do not vanish at the origin, $q = 0$).

6

The Classical Gas in the Canonical Formalism

1. A system of N classical ultrarelativistic particles, in a container of volume V, at temperature T, is given by the Hamiltonian

$$\mathcal{H} = \sum_{i=1}^{N} c\,|\vec{p}_i|\,,$$

where c is a positive constant. Obtain an expression for the canonical partition function. Calculate the entropy per particle as a function of temperature and specific volume. What is the expression of the specific heat at constant volume?

*** The thermodynamic quantities are easily obtained from the classical canonical partition function, given by

$$Z = \frac{1}{h^{3N}N!}V^N\left[\int d^3p \exp\left(-\beta c\,|\overrightarrow{p}\,|\right)\right]^N = \frac{1}{h^{3N}N!}\left[\frac{8\pi V}{(\beta c)^3}\right]^N .$$

2. Consider a set of N one-dimensional harmonic oscillators, described by the Hamiltonian

$$\mathcal{H} = \sum_{i=1}^{N}\left[\frac{1}{2m}\vec{p}_i^{\,2} + \frac{1}{2}m\omega^2 x_i^n\right],$$

where n is a positive and even integer. Use the canonical formalism to obtain an expression for the classical specific heat of this system.

*** Note that the canonical partition function may be written as $Z = Z_1^N$, where

$$Z_1 = \left(\frac{2\pi m}{\beta}\right)^{1/2} \left(\frac{2}{\beta m \omega^2}\right)^{n/2} \int_{-\infty}^{+\infty} dy \exp\left(-y^n\right).$$

Thus,

$$u = -\frac{\partial}{\partial \beta} \ln Z_1 = \frac{n+2}{2n} k_B T.$$

3. Consider a classical system of N very weakly interacting diatomic molecules, in a container of volume V, at a given temperature T. The Hamiltonian of a single molecule is given by

$$\mathcal{H}_m = \frac{1}{2m}\left(\vec{p}_1^{\,2} + \vec{p}_2^{\,2}\right) + \frac{1}{2}\kappa \left|\vec{r}_1 - \vec{r}_2\right|^2,$$

where $\kappa > 0$ is an elastic constant. Obtain an expression for the Helmholtz free energy of this system. Calculate the specific heat at constant volume. Calculate the mean molecular diameter,

$$D = \left\{\left\langle \left|\vec{r}_1 - \vec{r}_2\right|^2 \right\rangle\right\}^{1/2}.$$

Now consider another Hamiltonian, of the form ϵ

$$\mathcal{H}_m = \frac{1}{2m}\left(\vec{p}_1^{\,2} + \vec{p}_2^{\,2}\right) + \epsilon \left|r_{12} - r_o\right|,$$

where ϵ and r_o are positive constants, and $r_{12} = |\vec{r}_1 - \vec{r}_2|$. What are the changes in your previous answers?

*** Taking into account the thermodynamic limit ($V \to \infty$), the first Hamiltonian is associated with the partition function

$$Z_1 = \left(\frac{2\pi m}{\beta}\right)^3 \int d^3 r_1 \int d^3 r_2 \exp\left[-\frac{\beta\kappa}{2}\left|\overrightarrow{r_1} - \overrightarrow{r_2}\right|^2\right] \sim$$

$$\sim \left(\frac{2\pi m}{\beta}\right)^3 V \left(\frac{2\pi}{\beta\kappa}\right)^{3/2},$$

from which we obtain the Helmholtz free energy (and the value of D). It interesting to check the constant value of the molecular specific heat, $c = (9/2)\, k_B$.

The second Hamiltonian represents a more complicated model of a diatomic molecule. The partition function is given by

$$Z_1 = \left(\frac{2\pi m}{\beta}\right)^3 \int d^3r_1 \int d^3r_2 \exp\left[-\beta\epsilon\left|\left(\left|\overrightarrow{r_1} - \overrightarrow{r_2}\right| - r_o\right)\right|\right] \sim$$

$$\sim \left(\frac{2\pi m}{\beta}\right)^3 V\, I,$$

where

$$I = 4\pi \int_0^{r_o} r^2 \exp\left[-\beta\epsilon\left(r_o - r\right)\right] dr + 4\pi \int_{r_o}^{\infty} r^2 \exp\left[-\beta\epsilon\left(r - r_o\right)\right] dr =$$

$$= \frac{2r_o^2}{\beta\epsilon} + \frac{4}{(\beta\epsilon)^3} - \frac{2}{(\beta\epsilon)^4} \exp\left(-\beta\epsilon r_o\right).$$

Now it is interesting to obtain the specific heat as a function of temperature.

4. Neglecting the vibrational motion, a diatomic molecule may be treated as a three-dimensional rigid rotator. The Hamiltonian $\mathcal{H}_m$ of the molecule is written as a sum of a translational, $\mathcal{H}_{tr}$, plus a rotational, $\mathcal{H}_{rot}$, term (that is, $\mathcal{H}_m = \mathcal{H}_{tr} + \mathcal{H}_{rot}$). Consider a system of N very weakly interacting molecules of this kind, in a container of volume V, at a given temperature T.

(a) Obtain an expression for $\mathcal{H}_{rot}$ in spherical coordinates. Show that there is a factorization of the canonical partition function of this system. Obtain an expression for the specific heat at constant volume.

(b) Now suppose that each molecule has a permanent electric dipole moment $\vec{\mu}$ and that the system is in the presence of an external electric field $\vec{E}$ (with the dipole $\vec{\mu}$ along the axis of the rotor). What is the form of the new rotational part of the Hamiltonian? Obtain an expression for the polarization of the molecule as a function of field and temperature. Calculate the electric susceptibility of this system.

*** The Lagrangian of a free rotator (two atoms of mass m and a fixed interatomic distance a) is given by

$$L_{rot} = \frac{ma^2}{4}\left[\left(\frac{d\theta}{dt}\right)^2 + \left(\frac{d\varphi}{dt}\right)^2 \sin^2\theta\right],$$

from which we have the Hamiltonian

$$\mathcal{H}_{rot} = \frac{p_\theta^2}{ma^2} + \frac{p_\varphi^2}{ma^2\sin^2\theta}.$$

Therefore,

$$u_{rot} = \langle H_{rot}\rangle = \frac{1}{2}k_BT + \frac{1}{2}k_BT = k_BT.$$

In the presence on an electric field (taken along the z direction), and with the magnetic moment along the axis of the rotator, we have

$$\mathcal{H} = \frac{p_\theta^2}{ma^2} + \frac{p_\varphi^2}{ma^2\sin^2\theta} - E\mu\cos\theta.$$

The associated partition function is given by

$$Z_1 = \int\limits_0^\pi d\theta \int\limits_0^{2\pi} d\varphi \int\limits_{-\infty}^{+\infty} dp_\theta \int\limits_{-\infty}^{+\infty} dp_\varphi \exp\left[- \frac{\beta p_\theta^2}{ma^2} - \frac{\beta p_\varphi^2}{ma^2\sin^2\theta} + \right.$$

$$\left. + \beta E\mu\cos\theta\right] = \frac{4\pi^2 ma^2}{\beta}\frac{2\sinh(\beta\mu E)}{\beta\mu E}.$$

Thus, we have

$$\langle\mu\cos\theta\rangle = \mu\left[\coth(\beta\mu E) - \frac{1}{\beta\mu E}\right] = \mu\mathcal{L}(\beta\mu E),$$

where $\mathcal{L}(x)$ is known as the Langevin function.

5. Consider a classical gas of N weakly interacting molecules, at temperature T, in an applied electric field $\vec{E}$. Since there is no permanent electric dipole moment, the polarization of this system comes from the induction by the field. We then suppose that the Hamiltonian of each molecule will be given by the sum of a standard translational term plus an "internal term." This internal term involves an isotropic elastic energy, which tends to preserve the shape of the molecule, and a term of interaction with the electric field. The configurational part of the internal Hamiltonian is be given by

$$\mathcal{H} = \frac{1}{2} m\omega_o^2 r^2 - q\vec{E}\cdot\vec{r}.$$

Obtain the polarization per molecule as a function of field and temperature. Obtain the electric susceptibility. Compare with the results of the last problem. Make some comments about the main differences between these results. Do you know any physical examples corresponding to these models?

*** First, we calculate the configurational partition function

$$Z_1 = \int\limits_0^\infty r^2 dr \int\limits_0^\pi \sin\theta d\theta \int\limits_0^{2\pi} d\varphi \exp\left[-\frac{\beta m\omega_o^2}{2} r^2 + \beta q E r\cos\theta\right] =$$

$$= \left(\frac{2\pi}{\beta m\omega_o^2}\right)^{3/2} \exp\left(\frac{\beta q^2 E^2}{2m\omega_o^2}\right).$$

The polarization is given by

$$\langle qr\cos\theta\rangle = \frac{1}{\beta}\frac{\partial}{\partial E}\ln Z_1 = \frac{q^2 E}{m\omega_o^2},$$

so the dielectric susceptibility is just a constant (in sharp contrast to the previous result for permanent electric dipoles!)

6. The equation of state of gaseous nitrogen at low densities may be written as

$$\frac{pv}{RT} = 1 + \frac{B(T)}{v},$$

where v is a molar volume, R is the universal gas constant, and $B(T)$ is a function of temperature only. In the following table we give some experimental data for the second virial coefficient, $B(T)$, as a function of temperature.

T (K)	B (cm^3/mol)
100	-160.0
273	-10.5
373	6.2
600	21.7

Suppose that the intermolecular potential of gaseous nitrogen is given by

$$V(r) = \begin{cases} \infty, & 0 < r < a, \\ -V_0, & a < r < b, \\ 0, & r > b. \end{cases}$$

Use the experimental data of this table to determine the best values of the parameters a, b, and V_0.

*** According to Section 6.4 (although Nitrogen is a gas of diatomic molecules), the virial coefficient is given by

$$B = -2\pi \int_0^\infty r^2 \left\{\exp\left[-\beta V(r)\right] - 1\right\} =$$

$$= 2\pi \int_0^a r^2 dr - 2\pi \int_a^b r^2 \left[\exp\left(\beta V_o\right) - 1\right] dr.$$

Now it is straightforward to fit the parameters a, b and V_o.

7

The Grand Canonical and Pressure Ensembles

1. Show that the entropy in the grand canonical ensemble can be written as

$$S = -k_B \sum_j P_j \ln P_j,$$

with probability P_j given by,

$$P_j = \Xi^{-1} \exp\left(-\beta E_j + \beta \mu N_j\right).$$

Show that this same form of entropy still holds in the pressure ensemble (with a suitable probability distribution).

2. Consider a classical ultrarelativistic gas of particles, given by the Hamiltonian

$$\mathcal{H} = \sum_{i=1}^{N} c \left|\vec{p}_i\right|,$$

where c is a positive constant, inside a container of volume V, in contact with a reservoir of heat and particles (at temperature T and chemical potential μ). Obtain the grand partition function and the grand thermodynamic potential. From a Legendre transformation of the grand potential, write an expression for the Helmholtz free energy of this system. To check your result, use the integral in equation (**??**) for obtaining an asymptotic form for the canonical partition function.

*** As we have already calculated in a previous exercise, the canonical partition function is given by

$$Z_N = \frac{1}{N!}\left[\frac{8\pi V}{\left(h\beta c\right)^3}\right]^N .$$

Using this expression, we obtain the grand canonical partition function,

$$\Xi = \sum_{N=0}^{\infty} \exp\left(\beta\mu N\right) Z_N = \exp\left\{\frac{8\pi V}{\left(h\beta c\right)^3}\exp\left(\beta\mu\right)\right\},$$

from which we have the grand potential,

$$\Phi = -\frac{1}{\beta}\frac{8\pi V}{\left(h\beta c\right)^3}\exp\left(\beta\mu\right).$$

If we write $\exp\left(\beta\mu\right) = z$, the canonical partition function is given by

$$Z = \frac{1}{2\pi i}\oint \frac{\Xi\left(\beta, z, V\right)}{z^{N+1}} dz \sim \frac{1}{2\pi i}\oint \exp\left[N f\left(z\right)\right] dz,$$

with

$$f\left(z\right) = \frac{8\pi v}{\left(h\beta c\right)^3} z - \ln z,$$

where $v = V/N$. From a saddle-point integration (see Appendix), we have

$$\frac{1}{N}\ln Z \sim f\left(z_o\right) = 1 - \ln\frac{\left(h\beta c\right)^3}{8\pi v}.$$

It is interesting to note that the same expression comes from the asymptotic form

$$\frac{1}{N}\ln Z_N = \frac{1}{N}\ln\left\{\frac{1}{N!}\left[\frac{8\pi V}{\left(h\beta c\right)^3}\right]^N\right\}.$$

3. Obtain the grand partition function of a classical system of particles, inside a container of volume V, given by the Hamiltonian

$$\mathcal{H}=\sum_{i=1}^{N}\left[\frac{1}{2m}\vec{p}_i^{\,2}+u\left(\vec{r}_i\right)\right].$$

Write the equations of state in the representation of the grand potential. For all reasonable forms of the single-particle potential $u\left(\vec{r}\right)$, show that the energy and the pressure obey typical equations of an ideal gas.

4. Show that the average quadratic deviation of the number of particles in the grand canonical ensemble may be written as

$$\left\langle\left(\Delta N\right)^2\right\rangle=\left\langle N_j^2\right\rangle-\left\langle N_j\right\rangle^2=z\frac{\partial}{\partial z}\left[z\frac{\partial}{\partial z}\ln\Xi\left(\beta,z\right)\right].$$

Obtain an expression for the relative deviation $\sqrt{\left\langle\left(\Delta N\right)^2\right\rangle}/\left\langle N_j\right\rangle$ of an ideal gas of classical monatomic particles.

*** For a classical ideal gas of monatomic particles, we have

$$\left\langle N\right\rangle=z\frac{\partial}{\partial z}\ln\Xi\left(\beta,z\right)=\frac{zV}{h^3}\left(\frac{2\pi m}{\beta}\right)^{3/2}$$

and

$$\left\langle\left(\Delta N\right)^2\right\rangle=z\frac{\partial}{\partial z}\left[z\frac{\partial}{\partial z}\ln\Xi\left(\beta,z\right)\right]=\frac{zV}{h^3}\left(\frac{2\pi m}{\beta}\right)^{3/2}=\left\langle N\right\rangle.$$

The relative deviation is thus of order $1/\sqrt{N}$.

5. Show that the average quadratic deviation of energy in the grand canonical ensemble may be written as

$$\left\langle\left(\Delta E\right)^2\right\rangle=\left\langle E_j^2\right\rangle-\left\langle E_j\right\rangle^2=-\left(\frac{\partial U}{\partial\beta}\right)_{z,V},$$

where $U = \langle E_j \rangle$ is the thermodynamic internal energy in terms of β, z, and V. Hence, show that we may also write

$$\left\langle (\Delta E)^2 \right\rangle = k_B T^2 \left[\left(\frac{\partial U}{\partial T} \right)_{\mu,V} + \frac{\mu}{T} \left(\frac{\partial U}{\partial \mu} \right)_{T,V} \right]$$

(you may use the Jacobian transformations of Appendix A.5). From this last expression, show that

$$\begin{aligned} \left\langle (\Delta E)^2 \right\rangle &= \left\langle (\Delta E)^2 \right\rangle_{can} + k_B T^2 \left[\left(\frac{\partial U}{\partial N} \right)_{T,V} \left(\frac{\partial N}{\partial T} \right)_{V,\mu} \right. \\ &\quad \left. + \frac{\mu}{T} \left(\frac{\partial U}{\partial N} \right)_{T,V} \left(\frac{\partial N}{\partial \mu} \right)_{T,V} \right], \end{aligned}$$

where

$$\left\langle (\Delta E)^2 \right\rangle_{can} = N k_B T^2 c_V$$

is the average quadratic deviation of energy in the canonical ensemble. Finally, show that

$$\left[\left(\frac{\partial U}{\partial N} \right)_{T,V} \left(\frac{\partial N}{\partial T} \right)_{V,\mu} + \frac{\mu}{T} \left(\frac{\partial U}{\partial N} \right)_{T,V} \left(\frac{\partial N}{\partial \mu} \right)_{T,V} \right]$$

$$= \frac{1}{T} \left(\frac{\partial N}{\partial \mu} \right)_{T,V} \left[\left(\frac{\partial U}{\partial N} \right)_{T,V} \right]^2 > 0,$$

since

$$\left\langle (\Delta N)^2 \right\rangle = k_B T \left(\frac{\partial N}{\partial \mu} \right)_{T,V} > 0.$$

6. At a given temperature T, a surface with N_o adsorption centers has $N \leq N_o$ adsorbed molecules. Suppose that there are no interactions between molecules. Show that the chemical potential of the adsorbed gas is given by

$$\mu = k_B T \ln \frac{N}{(N_o - N)\, a(T)}.$$

What is the meaning of the function $a\left(T\right)$?

*** Suppose an adsorbed particle has energy $-\epsilon$. We then write the canonical partition function

$$Z=\frac{N_o!}{N!\left(N_o-N\right)!}\exp\left(\beta\epsilon N\right).$$

Now we can use the grand-canonical formalism to write

$$\Xi=\sum_N\frac{N_o!}{N!\left(N_o-N\right)!}\exp\left(\beta\epsilon N\right)z^N=\left[z\exp\left(\beta\epsilon\right)+1\right]^{N_o},$$

from which we have

$$N=\frac{N_oz}{z+\exp\left(-\beta\epsilon\right)},$$

and the expression for the chemical potential with $a=\exp\left(\beta\epsilon\right)$.

7. The grand partition function for a simplified statistical model is given by the expression

$$\Xi\left(z,V\right)=\left(1+z\right)^V\left(1+z^{\alpha V}\right),$$

where α is a positive constant. Write parametric forms of the equation of state. Sketch an isotherm of pressure versus specific volume (draw a graph to eliminate the variable z). Show that this system displays a (first-order) phase transition. Obtain the specific volumes of the coexisting phases at this transition. Find the zeros of the polynomial $\Xi\left(z,V\right)$ in the complex z plane, and show that there is a zero at $z=1$ in the limit $V\rightarrow\infty$.

*** Note the structures of zeroes at

$$z=-1\quad\text{and}\quad z=\exp\left[i\pi\left(2n+1\right)/\left(\alpha V\right)\right],$$

for $n=0,\pm1,....$

Also, note the thermodynamic limit,

$$\frac{1}{V}\ln\Xi\rightarrow\ln\left(1+z\right)+\alpha\ln z,\quad\text{for}\quad z>1$$

and

$$\frac{1}{V}\ln\Xi \to \ln(1+z), \quad \text{for} \quad z<1.$$

For $z>1$, we have the equations of state

$$\frac{p}{k_B T} = \ln(1+z) + \alpha \ln z, \quad \text{and} \quad \frac{1}{v} = \frac{z^2 + \alpha(1+z)}{z(1+z)}.$$

For $z<1$, we have

$$\frac{p}{k_B T} = \ln(1+z), \quad \text{and} \quad \frac{1}{v} = \frac{z}{1+z}.$$

There is a first-order transition $[\Delta v = 4\alpha/(1+2\alpha)]$ at $z=1$.

8

The Ideal Quantum Gas

1. Obtain the explicit forms of the ground state and of the first excited state for a system of two free bosons, with zero spin, confined to a one-dimensional region of length L. Repeat this problem for two fermions of spin 1/2.

*** The single-particle states are given by $\varphi\left(x\right)=A\sin\left(kx\right)$, where $k=\sqrt{2mE}/\hbar$ and $kL=n\pi$, with $n=1,2,3....$ Note that $\varphi\left(x\right)$ vanishes at $x=0$ and $x=L$.

The ground state is given by $C\sin\left(\pi x_1/L\right)\sin\left(\pi x_2/L\right)$, where C is a normalization constant.

The first excited state is given by

$$D\left[\sin\left(\pi x_1/L\right)\sin\left(2\pi x_2/L\right)+\sin\left(2\pi x_1/L\right)\sin\left(\pi x_2/L\right)\right].$$

2. Show that the entropy of an ideal quantum gas may be written as

$$S=-k_B\sum_j\left\{f_j\ln f_j\pm\left(1\mp f_j\right)\ln\left(1\mp f_j\right)\right\},$$

where the upper (lower) sign refers to fermions (bosons), and

$$f_j = \langle n_j \rangle = \frac{1}{\exp\left[\beta\left(\epsilon_j - \mu\right)\right] \pm 1}$$

is the Fermi–Dirac (Bose–Einstein) distribution. Show that we can still use these equations to obtain the usual results for the classical ideal gas.

3. Show that the equation of state

$$pV = \frac{2}{3}U$$

holds for both free bosons and fermions (and also in the classical case). Show that an ideal ultrarelativistic gas, given by the energy spectrum $\epsilon = c\hbar k$, still obeys the same equation of state.

*** For fermions, we have

$$\Phi = -pV = -\frac{1}{\beta}\sum_j \ln\left[1 + z\exp\left(-\beta\epsilon_j\right)\right].$$

In the thermodynamic limit, for free fermions, we can write

$$\sum_j \ln\left[1 + z\exp\left(-\beta\epsilon_j\right)\right] \sim$$

$$\sim \frac{V\gamma}{\left(2\pi\right)^3}\int\limits_0^\infty 4\pi k^2 dk \ln\left[1 + z\exp\left(-\frac{\beta\hbar^2 k^2}{2m}\right)\right] =$$

$$= \frac{V\gamma}{\left(2\pi\right)^3}\{\ \frac{4\pi}{3}k^3 \ln\left[1 + z\exp\left(-\frac{\beta\hbar^2 k^2}{2m}\right)\right]\Bigg|_0^\infty +$$

$$+\frac{2\beta}{3}\int\limits_0^\infty 4\pi k^2 dk \left(\frac{\hbar^2 k^2}{2m}\right)\left[z^{-1}\exp\left(\frac{\beta\hbar^2 k^2}{2m}\right) + 1\right]^{-1}\} \sim$$

$$\sim \frac{2\beta}{3}\sum_j \frac{\epsilon_j}{z^{-1}\exp\left(\beta\epsilon_j\right) + 1} = \frac{2\beta}{3}U,$$

from which we prove that $pV = 2U/3$. The same manipulations can be carried out for bosons, but we should pay special attention to the $k = 0$ state. For the classical gas, this result is trivial.

4. Consider a quantum ideal gas inside a cubic vessel of side L, and suppose that the orbitals of the particles are associated with wave functions that vanish at the surfaces of the cube. Find the density of states in $\vec{k}$ space. In the thermodynamic limit, show that we have the same expressions as calculated with periodic boundary conditions.

5. An ideal gas of N atoms of mass m is confined to a vessel of volume V, at a given temperature T. Calculate the classical limit of the chemical potential of this gas.

Now consider a "two-dimensional" gas of N_A free particles adsorbed on a surface of area A. The energy of an adsorbed particle is given by

$$\epsilon_A = \frac{1}{2m}\vec{p}^2 - \epsilon_o,$$

where $\vec{p}$ is the (two-dimensional) momentum, and $\epsilon_o > 0$ is the binding energy that keeps the particle stuck to the surface. In the classical limit, calculate the chemical potential μ_A of the adsorbed gas.

The condition of equilibrium between the adsorbed particles and the particles of the three-dimensional gas can be expressed in terms of the respective chemical potentials. Use this condition to find the surface density of adsorbed particles as a function of temperature and pressure p of the surrounding gas.

*** In the thermodynamic limit, the chemical potential of the three-dimensional gas is given by

$$\mu = k_B T \ln \left[\frac{8\pi^3}{\gamma} \frac{N}{V} \left(\frac{\beta\hbar^2}{2\pi m} \right)^{3/2} \right].$$

For the adsorbed gas, we have the classical limit

$$\ln \Xi = \sum_j z \exp\left(-\beta\epsilon_j\right) = z\frac{\gamma A}{(2\pi)^2}\int_0^\infty 2\pi k \exp\left[-\frac{\beta\hbar^2k^2}{2m}+\beta\epsilon_o\right],$$

which yields the chemical potential

$$\mu_A = k_BT\ln\left[\frac{4\pi^2}{\gamma}\frac{N_A}{A}\left(\frac{\beta\hbar^2}{2\pi m}\right)\right]-\epsilon_o.$$

From the physical requirement of equilibrium, $\mu=\mu_A$, we obtain N_A/A in terms of temperature and pressure.

6. Obtain an expression for the entropy per particle, in terms of temperature and density, for a classical ideal monatomic gas of N particles of spin S adsorbed on a surface of area A. Obtain the expected values of $\mathcal{H}$, $\mathcal{H}^2$, $\mathcal{H}^3$, where $\mathcal{H}$ is the Hamiltonian of the system. What are the expressions of the second and third moments of the Hamiltonian with respect to its average value?

7. Consider a homogeneous mixture of two ideal monatomic gases, at temperature T, inside a container of volume V. Suppose that there are N_A particles of gas A and N_B particles of gas B. Write an expression for the grand partition function associated with this system (it should depend on T, V, and the chemical potentials μ_A and μ_B). In the classical limit, obtain expressions for the canonical partition function, the Helmholtz free energy F, and the pressure p of the gas. Show that $p=p_A+p_B$ (Dalton's law), where p_A and p_B are the partial pressures of A and B, respectively.

8. Under some conditions, the amplitudes of vibration of a diatomic molecule may be very large, with a certain degree of anharmonicity. In this case, the vibrational energy levels are given by the approximate expression

$$\epsilon_n = \left(n+\frac{1}{2}\right)\hbar\omega - x\left(n+\frac{1}{2}\right)^2\hbar\omega,$$

where x is the parameter of anharmonicity. To first order in x, obtain an expression for the vibrational specific heat of this system.

*** Note that

$$\ln Z_v = \ln S(\alpha) + x \frac{\alpha}{S(\alpha)} \frac{d^2}{d\alpha^2} S(\alpha) + O\left(x^2\right),$$

where

$$S(\alpha) = \sum_{n=0}^{\infty} \exp\left[-\alpha\left(n+\frac{1}{2}\right)\right] = \left[2\sinh\frac{\alpha}{2}\right]^{-1},$$

with $\alpha = \beta\hbar\omega$. We then have

$$u = -\hbar\omega \frac{\partial}{\partial\alpha} \ln Z_v \quad \text{and} \quad c = k_B \left(\frac{\hbar\omega}{k_B T}\right)^2 \frac{\partial^2}{\partial\alpha^2} \ln Z_v,$$

from which we calculate the first-order correction to the specific heat,

$$\Delta c = k_B \left(\frac{\hbar\omega}{k_B T}\right)^2 x \frac{d^2}{d\alpha^2} \left[\frac{\alpha}{S(\alpha)} \frac{d^2}{d\alpha^2} S(\alpha)\right].$$

9. The potential energy between atoms of a hydrogen molecule may be described by the Morse potential,

$$V(r) = V_o \left\{ \exp\left[-\frac{2(r-r_o)}{a}\right] - 2\exp\left[-\frac{r-r_o}{a}\right] \right\},$$

where $V_o = 7 \times 10^{-19}\,\mathrm{J}$, $r_o = 8 \times 10^{-11}\,\mathrm{m}$, and $a = 5 \times 10^{-11}\,\mathrm{m}$. Sketch a graph of $V(r)$ versus r. Calculate the characteristic temperatures of vibration and rotation to compare with experimental data (see table on Section 8.4).

*** Note that

$$\frac{dV}{dr} = 0 \quad \text{for} \quad r = r_o$$

and

$$\left(\frac{d^2V}{dr^2}\right)_{r_o} = \frac{2V_o}{a^2} > 0,$$

which shows the existence of a minimum at $r = r_o$.

The characteristic temperature of rotation is given by

$$\Theta_r = \frac{\hbar^2}{2k_B I} = \frac{\hbar^2}{2k_B M r_o^2},$$

where I is the moment of inertia and M is the reduced mass of the hydrogen molecule.

From the frequency of vibrations,

$$\omega = \left(\frac{2V_o}{a^2 M} \right)^{1/2},$$

we write the characteristic temperature of vibrations,

$$\Theta_v = \frac{\hbar}{k_B} \left(\frac{2V_o}{a^2 M} \right)^{1/2}.$$

Now it is easy to check the numerical predictions.

9

The Ideal Fermi Gas

1. What is the compressibility of a gas of free fermions at zero temperature? Obtain the numerical value for electrons with the density of conduction electrons in metallic sodium. Compare your results with experimental data for sodium at room temperature.

*** It is straightforward to show that pressure of a completely degenerate system of free fermions is given by

$$p = \frac{2}{5}\frac{N}{V}\epsilon_F = \frac{\hbar^2}{5m}\left(\frac{6\pi^2}{\gamma}\right)^{2/3}\left(\frac{N}{V}\right)^{5/3}.$$

The compressibility is given by

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right) = \frac{3m}{\hbar^2}\left(\frac{\gamma}{6\pi^2}\right)^{2/3}\left(\frac{V}{N}\right)^{5/3}.$$

Using the density of sodium (at room temperature), it is easy to show that $\kappa \sim 10^{-5}\ atm$, which is of the order of the experimental compressibility of sodium at room temperature. Also, it is interesting to see that fermions are associated with large values of pressure, of the order of $10^4 - 10^5\ atm$, at zero temperature (due to the restrictions of the Pauli principle, of course).

2. An ideal gas of fermions, with mass m and Fermi energy ϵ_F, is at rest at zero temperature. Find expressions for the expected values $\langle v_x \rangle$ and $\langle v_x^2 \rangle$, where $\vec{v}$ is the velocity of a fermion.

*** At zero temperature, the expected value of the (single-particle) energy is calculated in terms of the density of states $D(\epsilon)$. With $D(\epsilon) = C\epsilon^{1/2}$, we have

$$\langle \epsilon \rangle = \frac{\int_0^{\epsilon_F} \epsilon D(\epsilon)\, d\epsilon}{\int_0^{\epsilon_F} D(\epsilon)\, d\epsilon} = \frac{3}{5}\epsilon_F.$$

Note that

$$\langle \epsilon \rangle = \left\langle \frac{1}{2} m \overrightarrow{v}^2 \right\rangle \quad \rightarrow \quad \left\langle \overrightarrow{v}^2 \right\rangle = \frac{6}{5}\frac{\epsilon_F}{m} \quad \rightarrow \quad \left\langle \overrightarrow{v}_x^2 \right\rangle = \frac{2}{5}\frac{\epsilon_F}{m},$$

in contrast to the predictions of the classical equipartition theorem.

3. Consider a gas of free electrons, in a d-dimensional space, within a hypercubic container of side L. Sketch graphs of the density of states $D(\epsilon)$ versus energy ϵ for dimensions $d = 1$ and $d = 2$. What is the expression of the Fermi energy in terms of the particle density for $d = 1$ and $d = 2$?

*** Given the spectrum of energy

$$\epsilon_j = \epsilon_{\overrightarrow{k},\sigma} = \frac{\hbar^2 k^2}{2m},$$

we write the thermodynamic number of fermions in d dimensions,

$$N = \gamma \frac{L^d}{(2\pi)^d} \int d^d k \frac{1}{\exp\left(\beta \frac{\hbar^2 k^2}{2m} - \beta\mu\right) + 1}.$$

Due to the spherical symmetry of the integrand, we have

$$\int d^d k \, (...) \Longrightarrow \int_0^\infty C_d k^{d-1} dk \, (...),$$

where it can be shown (see Appendix 4) that

$$C_d = \frac{2\pi^{d/2}}{\Gamma\left(\frac{d}{2}\right)}.$$

Check that $C_2 = 2\pi$, $C_3 = 4\pi$, and so on. Introducing the change of variables

$$\epsilon = \frac{\hbar^2 k^2}{2m},$$

and the definition of the "Fermi-Dirac distribution",

$$f(\epsilon) = \frac{1}{\exp(\beta\epsilon - \beta\mu) + 1},$$

we have

$$N = \gamma \frac{L^d}{(2\pi)^d} \int_0^\infty C_d \frac{1}{2} \left(\frac{2m}{\hbar^2}\right)^{d/2} \epsilon^{d/2-1} f(\epsilon)\, d\epsilon =$$

$$= \gamma L^d \int_0^\infty D(\epsilon) f(\epsilon)\, d\epsilon,$$

with the "density of states"

$$D(\epsilon) = \frac{1}{2(2\pi)^d} C_d \left(\frac{2m}{\hbar^2}\right)^{d/2} \epsilon^{\frac{d}{2}-1}.$$

In two dimensions, note that $D(\epsilon)$ is just a constant.

4. Show that the chemical potential of an ideal classical gas of N monatomic particles, in a container of volume V, at temperature T, may be written as

$$\mu = k_B T \ln\left(\frac{\lambda^3}{v}\right),$$

where $v = V/N$ is the volume per particle, and $\lambda = h/\sqrt{2\pi m k_B T}$ is the thermal wavelength. Sketch a graph of $\mu/k_B T$ versus T. Obtain the first quantum correction to this result. That is, show that the chemical potential of the ideal quantum gas may be written as the expansion

$$\frac{\mu}{k_B T} - \ln\left(\frac{\lambda^3}{v}\right) = A \ln\left(\frac{\lambda^3}{v}\right) + B \ln\left(\frac{\lambda^3}{v}\right)^2 + \dots,$$

and obtain explicit expressions for the prefactor A for fermions and bosons. Sketch a graph of μ/k_BT versus λ^{-2} (that is, versus the temperature in convenient units) for fermions, bosons, and classical particles.

*** The grand partition function of the ideal quantum gas is given by

$$\ln \Xi = \pm \sum_j \ln\left[1 \pm z \exp\left(-\beta\epsilon_j\right)\right].$$

We now write an expansion in terms of powers of z,

$$\ln \Xi = \pm \sum_j \left\{ \pm z \exp\left(-\beta\epsilon_j\right) - \frac{1}{2} z^2 \exp\left(-2\beta\epsilon_j\right) \pm \cdots \right\} =$$

$$= z \sum_j \exp\left(-\beta\epsilon_j\right) \mp \frac{1}{2} z^2 \sum_j \exp\left(-2\beta\epsilon_j\right) + \cdots.$$

The first term corresponds to the classical limit (there is no difference between fermions and bosons). The second term gives the first quantum correction. In the thermodynamic limit, we have

$$\sum_j \exp\left(-n\beta\epsilon_j\right) = \gamma \frac{V}{(2\pi)^3} \int_0^\infty 4\pi k^2 \exp\left(-n\beta \frac{\hbar^2 k^2}{2m}\right) dk =$$

$$= \gamma V \left(\frac{m k_B T}{2\pi n \hbar^2}\right)^{3/2}.$$

The classical limit is given by

$$\ln \Xi_{cl} = z \gamma V \left(\frac{m k_B T}{2\pi \hbar^2}\right)^{3/2},$$

from which we have

$$N = z \frac{\partial}{\partial z} \ln \Xi_{cl} = z \gamma V \left(\frac{m k_B T}{2\pi \hbar^2}\right)^{3/2}.$$

Thus,

$$z = \exp\left(\beta\mu\right) = \frac{N}{\gamma V} \left(\frac{2\pi \hbar^2}{m k_B T}\right)^{3/2},$$

which leads to the well-known result

$$\mu = k_B T \ln\left(\frac{\lambda^3}{v}\right),$$

with

$$v = \gamma\frac{V}{N} \quad \text{and} \quad \lambda = \left(\frac{2\pi\hbar^2}{mk_BT}\right)^{1/2} = \frac{h}{\sqrt{2\pi mk_BT}}.$$

Check that the same result can be obtained in the classical formalism of the grand ensemble, with the introduction of the "correct Boltzmann counting", $N!$, and of the "quantum dimensional correction" of the classical phase space, h^{3N}.

The first quantum correction of this result is given by

$$\ln\Xi = z\gamma V\left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2} \mp \frac{1}{2}z^2\gamma V\left(\frac{mk_BT}{4\pi\hbar^2}\right)^{3/2} + O\left(z^3\right).$$

Thus,

$$N = z\gamma V\left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2} \mp z^2\gamma V\left(\frac{mk_BT}{4\pi\hbar^2}\right)^{3/2} + O\left(z^3\right),$$

which can be written as

$$\frac{N}{V}\lambda^3\frac{1}{\gamma} = z \mp \frac{1}{2^{3/2}}z^2 + O\left(z^3\right).$$

Taking into account that $z << 1$, which means that $\lambda^3 v << 1$, we can write

$$z = \frac{\lambda^3}{v} + A\left(\frac{\lambda^3}{v}\right)^2 + \cdots,$$

and

$$\frac{\lambda^3}{v} = \frac{\lambda^3}{v} + A\left(\frac{\lambda^3}{v}\right)^2 + ... \mp \frac{1}{2^{3/2}}\left[\frac{\lambda^3}{v} + A\left(\frac{\lambda^3}{v}\right)^2 + \cdots\right]^2 + \cdots,$$

from which we have

$$A = \pm\frac{1}{2^{3/2}}.$$

Therefore,

$$\ln z = \ln\left[\frac{\lambda^3}{v} + A\left(\frac{\lambda^3}{v}\right)^2 + \cdots\right] = \ln\left(\frac{\lambda^3}{v}\right) \pm \frac{1}{2^{3/2}}\frac{\lambda^3}{v} + \cdots,$$

which leads to the expression

$$\frac{\mu}{k_BT} - \ln\left(\frac{\lambda^3}{v}\right) = \pm\frac{1}{2^{3/2}}\frac{\lambda^3}{v} + \cdots.$$

Try to use the same scheme to show that $B = -1/16$ (check that B assumes the same value for either fermions or bosons).

5. Obtain an asymptotic form, in the limit $T << T_F$, for the specific heat of a gas of N free fermions adsorbed on a surface of area A, at a given temperature T.

*** For the two-dimensional gas of free fermions, we write

$$N = \gamma A\frac{m}{2\pi\hbar^2}\int_0^\infty f(\epsilon)\, d\epsilon,$$

and

$$U = \gamma A\frac{m}{2\pi\hbar^2}\int_0^\infty \epsilon f(\epsilon)\, d\epsilon,$$

with the Fermi-Dirac distribution,

$$f(\epsilon) = \frac{1}{\exp\left[\beta(\epsilon-\mu)\right]+1}.$$

Discarding exponentially small corrections (in the limit $\beta\epsilon_F \to \infty$), we have

$$\int_0^\infty f(\epsilon)\, d\epsilon = \int_{-\beta\mu}^\infty \left(\frac{x}{\beta}+\mu\right)\frac{\exp(x)\, dx}{\left[\exp(x)+1\right]^2}dx \to$$

$$\to \mu\int_{-\infty}^\infty \left(\frac{x}{\beta\mu}+1\right)\frac{\exp(x)\, dx}{\left[\exp(x)+1\right]^2}dx = \mu.$$

Note that $\exp(x)/\left[\exp(x)+1\right]^2$ is an even function of x, and that

$$\int_{-\infty}^\infty \frac{\exp(x)\, dx}{\left[\exp(x)+1\right]^2}dx = -\frac{d}{dx}\frac{1}{\exp(x)+1} = 1.$$

Also, we have

$$\int_0^\infty \epsilon f(\epsilon)\, d\epsilon \to \frac{1}{2}\mu^2 \{ \int_{-\infty}^{\infty} \frac{\exp(x)}{[\exp(x)+1]^2} +$$

$$+ \frac{1}{(\beta\mu)^2} \int_{-\infty}^{\infty} \frac{x^2 \exp(x)\, dx}{[\exp(x)+1]^2} \} = \frac{1}{2}\mu^2 \left\{ 1 + \frac{1}{(\beta\mu)^2}\frac{\pi^2}{3} \right\}.$$

From these results, we write a low-temperature expression for the internal energy (except for vanishingly exponential corrections),

$$U = \frac{1}{2} N \epsilon_F \left[1 + \frac{\pi^2}{3} \left(\frac{T}{T_F} \right)^2 \right],$$

where

$$\epsilon_F = \frac{2\pi\hbar^2}{\gamma m} \left(\frac{N}{A} \right),$$

which leads to a linear dependence of the specific heat with temperature as in the three-dimensional case.

6. Consider a gas of N free electrons, in a region of volume V, in the ultrarelativistic regime. The energy spectrum is given by

$$\epsilon = \left[p^2 c^2 + m^2 c^4 \right]^{1/2} \approx pc,$$

where $\vec{p}$ is the linear momentum.

(a) Calculate the Fermi energy of this system.

(b) What is the total energy in the ground state?

(c) Obtain an asymptotic form for the specific heat at constant volume in the limit $T << T_F$.

*** Using the energy spectrum $\epsilon_{\vec{k}} = \hbar k c$, the number of particles and the internal energy of this fermion gas are given by

$$N = \gamma V \frac{1}{2\pi^2 \hbar^3 c^3} \int_0^\infty \epsilon^2 f(\epsilon)\, d\epsilon$$

and

$$U = \gamma V \frac{1}{2\pi^2 \hbar^3 c^3} \int_0^\infty \epsilon^3 f(\epsilon)\, d\epsilon,$$

where $f(\epsilon)$ is the Fermi-Dirac distribution.

At $T=0$, we have

$$\epsilon_F = \hbar c \left(\frac{6\pi^2}{\gamma}\right)^{1/3} \left(\frac{N}{V}\right)^{1/3},$$

and

$$U = \frac{3}{4} N \epsilon_F.$$

The asymptotic form of the specific heat at low temperatures comes from a straightforward application of Sommerfeld´s method. We should note that

$$\int_0^\infty \epsilon^2 f(\epsilon)\, d\epsilon = \frac{1}{3}\mu^3 \int_{-\beta\mu}^{\infty} \left(1+\frac{x}{\beta\mu}\right)^3 \frac{\exp(x)\, dx}{\left[\exp(x)+1\right]^2} dx \to$$

$$\to \frac{1}{3}\mu^3 \left[1+\pi^2 \frac{1}{(\beta\mu)^2}\right],$$

and

$$\int_0^\infty \epsilon^3 f(\epsilon)\, d\epsilon = \frac{1}{4}\mu^4 \int_{-\beta\mu}^{\infty} \left(1+\frac{x}{\beta\mu}\right)^4 \frac{\exp(x)\, dx}{\left[\exp(x)+1\right]^2} dx \to$$

$$\to \frac{1}{4}\mu^4 \left[1+6\frac{\pi^2}{3}\frac{1}{(\beta\mu)^2} + \frac{7\pi^4}{15}\frac{1}{(\beta\mu)^4}\right],$$

where

$$\int_{-\infty}^{\infty} \frac{\exp(x)\, dx}{\left[\exp(x)+1\right]^2} dx = \frac{7\pi^4}{15}.$$

as can be checked in a good integral table (in Gradshteyn and Ryzhik, for example).

We then write

$$\epsilon_F^3 = \mu^3 \left[1+\pi^2 \frac{1}{(\beta\mu)^2}\right],$$

and

$$U = \frac{3}{4} N \frac{1}{\epsilon_F^3} \mu^4 \left[1+6\frac{\pi^2}{3}\frac{1}{(\beta\mu)^2} + \frac{7\pi^4}{15}\frac{1}{(\beta\mu)^4}\right].$$

From the first equation, we write an expansion for the chemical potential potential μ in terms of $1/\left[\beta\epsilon_F\right] = (T/T_F)$,

$$\mu = \epsilon_F \left[1 - \frac{\pi^2}{3}\left(\frac{T}{T_F}\right)^2 + ...\right].$$

Inserting this expansion of μ into the expression for the internal energy, we finally have

$$U = \frac{3}{4}N\epsilon_F \left[1 + \frac{2\pi^2}{3}\left(\frac{T}{T_F}\right)^2 + ...\right].$$

Note that there is no linear power of (T/T_F).

7. At low temperatures, the internal energy of a system of free electrons may be written as an expansion,

$$U = \frac{3}{5}N\epsilon_F \left\{1 + \frac{5\pi^2}{12}\left(\frac{T}{T_F}\right)^2 - A\left(\frac{T}{T_F}\right)^4 + \ldots\right\}.$$

Obtain the value of the constant A, and indicate the order of magnitude of the terms that have been discarded.

*** This is again a straightforward (although somewhat laborious) application of the method of Sommerfeld to obtain asymptotic low-temperature results.

In the grand-canonical ensemble, the number of particles and the internal energy of the gas of free fermions are give by

$$N = \gamma V C \int_0^\infty \epsilon^{1/2} f(\epsilon)\, d\epsilon,$$

and

$$U = \gamma V C \int_0^\infty \epsilon^{3/2} f(\epsilon)\, d\epsilon,$$

where

$$f(\epsilon) = \frac{1}{\exp\left[\beta(\epsilon - \mu)\right] + 1}.$$

At low temperatures, $f(\epsilon)$ is almost a step function, so the derivative $df/d\epsilon$ has a pronounced peak at $\epsilon = \mu$, which provides the basis for the development of a low-temperature expansion. Let us write

$$\int_0^\infty \epsilon^{1/2} \frac{1}{\exp\left[\beta\left(\epsilon-\mu\right)\right]+1} d\epsilon =$$

$$= \frac{2\beta}{3} \int_0^\infty \epsilon^{3/2} \frac{\exp\left[\beta\left(\epsilon-\mu\right)\right]}{\left\{\exp\left[\beta\left(\epsilon-\mu\right)\right]+1\right\}^2} d\epsilon =$$

$$= \frac{2}{3}\mu^{3/2} \int_{-\beta\mu}^\infty \left(1+\frac{x}{\beta\mu}\right)^{3/2} \frac{\exp\left(x\right)}{\left[\exp\left(x\right)+1\right]^2} dx.$$

At low temperatures, $\beta\mu \sim \beta\epsilon_F \to \infty$, so that we may discard exponential corrections, of order $\exp\left(-\beta\epsilon_F\right)$, and write

$$\int_0^\infty \epsilon^{1/2} f\left(\epsilon\right) d\epsilon \to \frac{2}{3}\mu^{3/2} \int_{-\infty}^{+\infty} \left(1+\frac{x}{\beta\mu}\right)^{3/2} \frac{\exp\left(x\right)}{\left[\exp\left(x\right)+1\right]^2} dx,$$

which is the main idea of Sommerfeld´s scheme. Except for these exponential corrections, we have the series expansion

$$\int_0^\infty \epsilon^{1/2} f\left(\epsilon\right) d\epsilon = \frac{2}{3}\mu^{3/2} \{ I_0 + \frac{3}{8} I_2 \frac{1}{\left(\beta\mu\right)^2} +$$

$$+ \frac{3}{128} I_4 \frac{1}{\left(\beta\mu\right)^4} + O\left(\frac{1}{\left(\beta\mu\right)^6}\right) \},$$

where

$$I_0 = \int_{-\infty}^{+\infty} \frac{\exp\left(x\right)}{\left[\exp\left(x\right)+1\right]^2} dx = 1,$$

$$I_2 = \int_{-\infty}^{+\infty} \frac{x^2\exp\left(x\right)}{\left[\exp\left(x\right)+1\right]^2} dx = \frac{\pi^2}{3},$$

$$I_4 = \frac{x^4\exp\left(x\right)}{\left[\exp\left(x\right)+1\right]^2} d \int_{-\infty}^{+\infty} x = \frac{7\pi^2}{15},$$

and so on (as you can check in the integral table of Gradshteyn and Ryzhik, for example). We then have the expansion

$$\frac{3N}{2\gamma VC} = \epsilon_F^{3/2} = \mu^{3/2} \left\{ 1 + \frac{3\pi^2}{24} \frac{1}{\left(\beta\mu\right)^2} + \frac{7\pi^2}{640} \frac{1}{\left(\beta\mu\right)^4} + O(\frac{1}{\left(\beta\mu\right)^6}) \right\},$$

from which we write

$$\mu = \epsilon_F \left\{ 1 + M_2 \left(\frac{T}{T_F} \right)^2 + M_4 \left(\frac{T}{T_F} \right)^4 + O \left[\left(\frac{T}{T_F} \right)^6 \right] \right\}.$$

We left for the reader the task of obtaining the numerical coefficients (M_2 and M_4). It is then easy to write an expansion of the internal energy in terms of (even) powers of (T/T_F).

8. Consider a system of free fermions in d dimensions, with the energy spectrum

$$\epsilon_{\vec{k},\sigma} = c \left| \vec{k} \right|^a ,$$

where $c > 0$ and $a > 1$.

(a) Calculate the prefactor A of the relation $pV = AU$.

(b) Calculate the Fermi energy as a function of volume V and number of particles N.

(c) Calculate an asymptotic expression, in the limit $T << T_F$, for the specific heat at constant volume.

*** In the thermodynamic limit, we have

$$\beta p V = \ln \Xi = \gamma \frac{L^d}{(2\pi)^d} \int_0^\infty C_d k^{d-1} \ln \left[1 + z \exp \left(-\beta c k^a \right) \right] dk =$$

$$= \gamma \frac{L^d}{(2\pi)^d} C_d \frac{\beta c a}{d} \int_0^\infty \frac{k^{d-1+a}}{z^{-1} \exp \left(\beta c k^a \right) + 1} dk.$$

Also, we have

$$U = -\frac{\partial}{\partial \beta} \ln \Xi \left(\beta, z, V \right) = \gamma \frac{L^d}{(2\pi)^d} C_d c \int_0^\infty \frac{k^{d-1+a}}{z^{-1} \exp \left(\beta c k^a \right) + 1} dk.$$

Thus,

$$pV = \frac{a}{d} U.$$

In order to derive the Fermi energy, we write

$$N = z \frac{\partial}{\partial z} \ln \Xi \left(\beta, z, V \right) = \gamma \frac{L^d}{(2\pi)^d} C_d \int_0^\infty \frac{k^{d-1}}{z^{-1} \exp \left(\beta c k^a \right) + 1} dk,$$

and note that

$$N = \gamma \frac{L^d}{(2\pi)^d} C_d \int_0^{\epsilon_F} \frac{1}{ac^{d/a}} \epsilon^{\frac{d}{a}-1} d\epsilon.$$

9. Consider again the gas of N ultrarelativistic free electrons, within a container of volume V, at temperature T, in the presence of a magnetic field $\vec{H}$. If we neglect the effects of orbital magnetism, the energy spectrum is given by

$$\epsilon_{\vec{p},\sigma} = cp - \mu_B H \sigma,$$

where μ_B is the Bohr magneton and $\sigma = \pm 1$.

(a) Show that the Fermi energy of this system may be written as

$$\epsilon_F = A + BH^2 + O\left(H^4\right).$$

Obtain expressions for the prefactors A and B.

(b) Show that the magnetization in the ground state can be written in the form

$$M = CH + O\left(H^3\right).$$

Obtain an expression for the constant C.

(c) Calculate the susceptibility of the ground state in zero field.

*** The grand partition functions may be written as

$$\ln \Xi = \ln \Xi_+ + \ln \Xi_-,$$

with

$$\ln \Xi_\pm = \sum_{\vec{k}} \ln \left\{1 + z \exp\left[-\beta \left(c\hbar k \pm \mu_B H\right)\right]\right\}.$$

We then write

$$N = z \frac{\partial}{\partial z} \ln \Xi = N_+ + N_-,$$

with

$$N_{\pm} = \frac{V}{2\pi^2}\left(\frac{1}{\hbar c}\right)^3 \int\limits_0^{\infty} \epsilon^2 f_{\pm}(\epsilon)\, d\epsilon,$$

where

$$f_{\pm}(\epsilon) = \frac{1}{\exp\left[\beta\left(\epsilon \pm \mu_B H - \mu\right) + 1\right]}.$$

As the Fermi energy is the chemical potential at zero temperature, we have

$$N = \frac{V}{2\pi^2}\left(\frac{1}{\hbar c}\right)^3 \left\{\int_0^{\epsilon_F - \mu_B H} \epsilon^2 d\epsilon + \int_0^{\epsilon_F + \mu_B H} \epsilon^2 d\epsilon\right\},$$

from which we obtain

$$\epsilon_F^3 + 3\epsilon_F\left(\mu_B H\right)^2 = 3\pi^2\left(\hbar c\right)^3 \frac{N}{V}.$$

For $\mu_B H << \epsilon_F\,(H=0)$, we have

$$\epsilon_F = \left(3\pi^2\right)^{1/3} \hbar c \left(\frac{N}{V}\right)^{1/3} - \frac{\mu_B^2}{3\left(3\pi^2\right)^{5/3} \hbar c \left(\frac{N}{V}\right)^{1/3}} H^2 + O\left(H^4\right).$$

The magnetization is given by

$$M = \mu_B\left(N_+ - N_-\right),$$

which leads to

$$M = \frac{3\mu_B^2 N}{\left(3\pi^2\right)^{1/3} \hbar c \left(\frac{N}{V}\right)^{1/3}} H + O\left(H^3\right),$$

so that we have the zero-field susceptibility

$$\chi_0 = \frac{1}{N}\left(\frac{\partial M}{\partial H}\right)_{H=0} = \frac{3\mu_B^2}{\left(3\pi^2\right)^{1/3} \hbar c \left(\frac{N}{V}\right)^{1/3}}.$$

10. In the classical paramagnetic theory of Langevin, proposed before the advent of quantum statistics, we assume a classical Hamiltonian, given by

$$\mathcal{H} = -\sum_{i=1}^{N} \vec{\mu}_i \cdot \vec{H} = -\sum_{i=1}^{N} \mu H \cos\theta_i,$$

where $\vec{\mu}_i$ is the magnetic moment of a localized ion.

(a) Show that the canonical partition function of this system is given by

$$Z = Z_1^N = \left\{ \int d\Omega \exp\left(\beta\mu H \cos\theta\right) \right\}^N ,$$

where $d\Omega$ is the elementary solid angle of integration.

(b) Show that the magnetization (along the direction of the field) is given by

$$M = N \left\langle \mu \cos\theta \right\rangle = N\mu \mathcal{L}\left(\beta\mu H\right),$$

where

$$\mathcal{L}\left(x\right) = \coth\left(x\right) - \frac{1}{x}$$

is the Langevin function.

(c) Show that the susceptibility in zero field is given by the Curie law,

$$\chi_o = \frac{N\mu^2}{3kT}.$$

*** The magnetization is given by

$$M = \left\langle \sum_{i=1}^{N} \mu_i \cos\theta_i \right\rangle = \frac{1}{\beta}\frac{\partial}{\partial H}\ln Z = \frac{N}{\beta}\frac{\partial}{\partial H}\ln Z_1,$$

where

$$Z_1 = \int d\Omega \exp\left(\beta\mu H \cos\theta\right) = 2\pi \int_0^{\pi} \sin\theta \exp\left(\beta\mu H \cos\theta\right) d\theta =$$

$$= \frac{4\pi}{\beta\mu H} \sinh\left(\beta\mu H\right).$$

Thus,

$$M = N\mu \left[-\frac{1}{\beta\mu H} + \coth\left(\beta\mu H\right) \right] = N\mu\mathcal{L}\left(\beta\mu H\right),$$

where $\mathcal{L}$ is the Langevin function.

11. Obtain an expression for the magnetic susceptibility associated with the orbital motion of free electrons in the presence of a uniform magnetic field H, under conditions of strong degeneracy, $T << T_F$, and very weak fields, $\mu_B H << k_B T$. To simplify the expression of Ξ, you may use Euler's sum rule,

$$\sum_{n=0}^{\infty} f\left(n+\frac{1}{2}\right) \approx \int_0^{\infty} f\left(x\right) dx + \frac{1}{24} f'\left(0\right).$$

*** The grand partition function for this system was written as

$$\ln \Xi = 2\frac{eHL^2}{hc} \sum_{n=0}^{\infty} \frac{L}{2\pi} \int_{-\infty}^{+\infty} dk_z \times$$

$$\times \ln\left\{ 1 + z\exp\left[-\frac{\beta\hbar^2 k_z^2}{2m} - \frac{\beta He}{mc}\left(n+\frac{1}{2}\right)\right]\right\}.$$

Since $\beta\mu H/mc << 1$, we can use Euler´s formula to rewrite this expression,

$$\ln \Xi = 2\frac{eHL^2}{hc}\frac{L}{2\pi} \int_{-\infty}^{+\infty} dk_z \int_0^{\infty} dx \ln\left[1 + z\exp\left(-\frac{\beta\hbar^2 k_z^2}{2m} - \frac{\beta He}{mc}x\right)\right] -$$

$$-2\frac{eHL^2}{hc}\frac{L}{2\pi}\int_{-\infty}^{+\infty} dk_z \frac{\beta He}{mc} \frac{1}{z^{-1}\exp\left(\frac{\beta\hbar^2 k_z^2}{2m}\right) + 1}.$$

In the first integral, it is convenient to introduce the new variable

$$\epsilon = \frac{\hbar^2 k_z^2}{2m} + \frac{He}{mc}x,$$

so that it becomes easy to integrate over k_z. In the second integral, we just call $\epsilon = \hbar^2 k_z^2/2m$. It is now straightforward to obtain an expression for the zero-field susceptibility [check the excellent article by R. B. Dingle, "Some magnetic properties of metals. I. General introduction and properties of large systems of electrons", Proc. Roy. Soc. A**211**, 500 (1952)].

10

Free Bosons: Bose-Einstein Condensation; Photon Gas

1. Consider a system of ideal bosons of zero spin ($\gamma = 1$), within a container of volume V.

(a) Show that the entropy above the condensation temperature T_o is given by

$$S = k_B \frac{V}{\lambda^3} \left[\frac{5}{2} g_{5/2}\left(z\right) - \frac{\mu}{k_B T} g_{3/2}\left(z\right) \right],$$

where

$$\lambda = \frac{h}{\sqrt{2\pi m k_B T}}$$

and

$$g_\alpha\left(z\right) = \sum_{n=1}^{\infty} \frac{z^n}{n^\alpha}.$$

(b) Given N and V, what is the expression of the entropy below T_o? What is the entropy associated with the particles of the condensate?

(c) From the expression for the entropy, show that the specific heat at constant volume above T_o is given by

$$c_V = \frac{3}{4} k_B \left[5 \frac{g_{5/2}\left(z\right)}{g_{3/2}\left(z\right)} - 3 \frac{g_{3/2}\left(z\right)}{g_{1/2}\left(z\right)} \right].$$

(d) Below T_o, show that the specific heat at constant volume is given by

$$c_V = \frac{15}{4} k_B \frac{v}{\lambda^3} g_{5/2}(1) .$$

(e) Given the specific volume v, sketch a graph of c_V/k_B versus λ^{-2} (that is, in terms of the temperature in convenient units). Obtain the asymptotic expressions of the specific heat for $T \to 0$ and $T \to \infty$. Obtain the value of the specific heat at $T = T_o$.

*** Note the asymptotic limits of the specific heat,

$$c_V = \frac{15}{4} k_B \frac{v}{\lambda^3} g_{5/2}(1) \sim T^{3/2},$$

for $T \to 0$, in agreement with Nernst´s third law of thermodynamics, and

$$c_V \to \frac{3}{2} k_B,$$

for $T \to \infty$ ($z \to 0$), according to the classical theorem of equipartition of energy. Also, note the value of the specific heat at the temperature of the Bose-Einstein condensation,

$$c_V(T = T_0) = \frac{15}{4} k_B \frac{g_{5/2}(1)}{g_{3/2}(1)} > \frac{3}{2} k_B .$$

Sketch a graph of c_V versus T.

2. Consider again the same problem for an ideal gas of two-dimensional bosons confined to a surface of area A. What are the changes in the expressions of item (a)? Show that there is no Bose–Einstein condensation in two dimensions (that is, show that in this case the Bose–Einstein temperature vanishes).

*** Consider a system of N free bosons in d dimensions (in a hypercubic box of volume L^d). The temperature of the Bose-Einstein condensation comes from the expression

$$N = \gamma \frac{L^d}{(2\pi)^d} \int_0^\infty \frac{C_d k^{d-1} dk}{\exp\left(\frac{\beta_0 \hbar^2 k^2}{2m}\right) - 1},$$

where $C_d = 2\pi^{d/2}/\Gamma\left(d/2\right)$. With a suitable change of variables, we have

$$k_B T_0 = \frac{\left(2\pi\right)^{1/2}\hbar^2}{2m}\left[\frac{N}{L^d}\frac{2}{\gamma C_d}\frac{1}{I}\right]^{2/d},$$

where

$$I = \int\limits_0^\infty \frac{x^{d/2}dx}{\exp\left(x\right)-1}.$$

It is easy to see that the integral I diverges ($I \rightarrow \infty$) for $d \leq 2$, which means that there is no Bose-Einstein condensation below three dimensions.

3. Consider an ideal gas of bosons with internal degrees of freedom. Suppose that, besides the ground state with zero energy ($\epsilon_o = 0$), we have to take into account the first excited state, with internal energy $\epsilon_1 > 0$. In other words, assume that the energy spectrum is given by

$$\epsilon_j = \epsilon_{\vec{k},\sigma} = \frac{\hbar^2 k^2}{2m} + \epsilon_1 \sigma,$$

where $\sigma = 0, 1$. Obtain an expression for the Bose–Einstein condensation temperature as a function of the parameter ϵ_1.

*** In the grand-canonical formalism, above the temperature of condensation, the number of bosons is given by

$$N = \sum_j \frac{1}{\exp\left(\beta\epsilon_j - \beta\mu\right) - 1} = \sum_{\vec{k},\sigma} \frac{1}{\exp\left(\frac{\beta\hbar^2k^2}{2m} + \beta\epsilon_1 - \beta\mu\right) - 1}.$$

In the thermodynamic limit, we write

$$\frac{N}{V} = \frac{1}{8\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\{\int_0^\infty \frac{\epsilon^{1/2}d\epsilon}{\exp\left(\beta\epsilon - \beta\mu\right) - 1} +$$

$$+ \int_0^\infty \frac{\epsilon^{1/2}d\epsilon}{\exp\left(\beta\epsilon + \beta\epsilon_1 - \beta\mu\right) - 1}\} =$$

$$= \frac{\left(2\pi m k_B T\right)^{3/2}}{h^3}\left[g_{3/2}\left(z\right) + g_{3/2}\left(ze^{-\beta\epsilon_1}\right)\right].$$

At the temperature of the Bose-Einstein condensation ($z \rightarrow 1$), we have

$$\frac{N}{V} = \frac{\left(2\pi m k_B T_0\right)^{3/2}}{h^3} \left[g_{3/2}\left(1\right) + g_{3/2}\left(\exp \frac{-\epsilon_1}{k_B T_0} \right) \right],$$

from which we may (numerically) obtain T_0 (which is smaller than the corresponding value with $\epsilon_1 = 0$).

4. Consider a gas of non-interacting bosons associated with the energy spectrum

$$\epsilon = \hbar c \left| \vec{k} \right|,$$

where $\hbar$ and c are constants, and $\vec{k}$ is a wave vector. Calculate the pressure of this gas at zero chemical potential. What is the pressure of radiation of a gas of photons?

*** In the thermodynamic limit we have

$$\beta p V = \ln \Xi = \frac{\gamma}{2\pi^2} V \int_0^\infty k^2 dk \ln \left[1 - z \exp\left(-\beta c \hbar k \right) \right].$$

In zero chemical potential, it is easy to show that

$$p = \frac{\gamma}{6\pi^2} \frac{\left(k_B T\right)^4}{\left(\hbar c\right)^3} \int_0^\infty \frac{x^3 dx}{\exp\left(x\right) - 1}.$$

Note that the pressure of radiation is given by the equation of state

$$pV = \frac{1}{3} U.$$

Taking into account the law of Stefan-Boltzmann, $U = \sigma V T^4$, we obtain an expression for the constant σ.

***5.** The Hamiltonian of a gas of photons within an empty cavity of volume V is given by the expression

$$\mathcal{H} = \sum_{\vec{k},j} \hbar \omega_{\vec{k},j} \left(a^\dagger_{\vec{k},j} a_{\vec{k},j} + \frac{1}{2} \right),$$

where $j = 1, 2$ indicates the polarization, $\vec{k}$ is the wave vector,

$$\omega_{\vec{k},j} = ck,$$

c is the velocity of light, and $k = \left|\vec{k}\right|$.

(a) Use the formalism of the occupation numbers (second quantization) to obtain the canonical partition function associated with this system.

(b) Show that the internal energy is given by

$$U = \sigma V T^n.$$

Obtain the value of the constants n and σ.

(c) Consider the Sun as a black body at temperature $T \approx 5800\,\mathrm{K}$. The solar diameter and the distance between the Sun and the Earth are of the order of $10^9\,\mathrm{m}$ and $10^{11}\,\mathrm{m}$, respectively. Obtain the intensity of the total radiation that reaches the surface of Earth. What is the value of the pressure of this radiation?

*** The canonical partition function is given by

$$Z = \mathbf{Tr}\exp\left(-\beta\mathcal{H}\right) = \sum_{\left\{n_{\vec{k},j}\right\}} \left\langle \left\{n_{\vec{k},j}\right\} \right| \exp\left(-\beta\mathcal{H}\right) \left| \left\{n_{\vec{k},j}\right\} \right\rangle =$$

$$= \sum_{\left\{n_{\vec{k},j}\right\}} \exp\left[-\beta \sum_{\vec{k},j} \hbar\omega_{\vec{k},j} \left(a^{\dagger}_{\vec{k},j} a_{\vec{k},j} + \frac{1}{2}\right)\right] =$$

$$= \prod_{\vec{k},j} \left\{ \sum_{n=0}^{\infty} \exp\left[-\beta\hbar\omega_{\vec{k},j}\left(n + \frac{1}{2}\right)\right] \right\} = \prod_{\vec{k},j} \frac{\exp\left(-\frac{1}{2}\beta\hbar ck\right)}{1 - \exp\left(-\beta\hbar ck\right)}.$$

In order to calculate the internal energy we write

$$\ln Z = -\frac{1}{2} \sum_{\vec{k},j} \beta\hbar ck - \sum_{\vec{k},j} \ln\left[1 - \exp\left(-\beta\hbar ck\right)\right],$$

where the first term in the right-hand-side leads to well-known (divergent) energy of the quantum vacuum. If we measure the internal energy with respect to the vacuum, we have

$$u = -\frac{1}{N}\frac{\partial}{\partial\beta}\ln Z = \frac{1}{N}\sum_{\vec{k},j}\frac{\hbar\omega_{\vec{k},j}}{\exp\left(\beta\hbar\omega_{\vec{k},j}\right)-1}.$$

In d dimensions, it is easy to check that this internal energy with respect to the quantum vacuum is given by

$$U = \sigma V T^{n},$$

where $n = d+1$ ($n = 4$ in three dimension, according to the Stefan-Boltzmann law) and

$$\sigma = \frac{4k_B^{d+1}}{\left(4\pi\hbar^2c^2\right)^{d/2}}\frac{\Gamma\left(d+1\right)\xi\left(d+1\right)}{\Gamma\left(\frac{d}{2}\right)}.$$