1.8 Problems for Chapter 1

1.1 Demonstrate that gravitational energy is not extensive: show that the gravitational energy of a sphere of radius r and uniform density varies with volume as V^n and find the exponent n.

1.2 Demonstrate that *entropy*, as given by the Boltzmann expression $S = k \ln \Omega$, is an *extensive* property. The best way to do this is to argue *clearly* that Ω is multiplicative.

1.3 In investigating the conditions for the establishment of equilibrium through the transfer of thermal energy the fundamental requirement is that the entropy of the equilibrium state should be a maximum. Equality of temperature was established from the vanishing of the first derivative of S. What follows from a consideration of the *second derivative*? (Hint: consider the heat capacity.)

1.4 Do particles flow from high μ to low μ or *vice versa*? Explain your reasoning.

1.5 In the derivation of the Boltzmann factor the entropy of the bath was expanded in powers of the energy of the "system of interest". The higher order terms of the expansion were neglected. Discuss the validity of this.

1.6 The Boltzmann factor might have been derived by expanding Ω rather than by expanding S. In that case, however, the expansion cannot be terminated. Why not?

1.7 Show that $\ln N! = \sum_{n=1}^{N} \ln n$. By approximating this sum by an integral obtain *Stirling's approximation*: $\ln N! \approx N \ln N - N = N \ln(N/e)$.

1.8 Show that the Gibbs expression for entropy: $S = -k \sum_j P_j \ln P_j$, reduces to the Boltzmann expression $S = k \ln \Omega$ in the case of an isolated system.

1.9 This problem considers the probability distribution for the energy fluctuations in the canonical ensemble. The *moments* of the energy fluctuations are defined by

$$\sigma_n = \frac{1}{Z} \sum_j \left(E_j - \varepsilon\right)^n \, e^{-\beta E_j}$$

where $\beta = 1/kT$ and ε is an arbitrary (at this stage) energy.

Show that

$$\sigma_n = (-1)^n \frac{1}{Ze^{\beta\varepsilon}} \frac{\partial^n\{Ze^{\beta\varepsilon}\}}{\partial\beta^n}$$

and use this to prove that the energy fluctuations in an ideal gas, in the thermodynamic limit, follow a *normal distribution*. It will prove to be convenient to take ε as the mean energy. (This is difficult. You really need to use a computer algebra system to do this problem.)

1.10 Starting from the expression for the Gibbs factor for a many-particle system, write down the grand partition function Ξ and show how it may be expressed as the product of Ξ_k, the grand partition function for the subsystem comprising particles in the kth single-particle state.

1.11 What is the condition for the geometric progression in the derivation of the Bose-Einstein distribution be convergent?

1.12 Why can't the evolutionary curve in phase space intersect? You need to demonstrate that the evolution from a point is unique.

1.13 Show that the trajectory of a 1d harmonic oscillator is an ellipse in phase space. What would the trajectory be if the oscillator were *weakly* damped.

1.14 The Fundamental Postulate of classical statistical mechanics states that for an isolated system all available regions of phase space on the constant energy hyper-surface are equally likely.

In terms of this discuss the properties of the phase space of a Boltzmann ensemble of simple harmonic oscillators of identical energy.

1.15 A *quartic* oscillator has a potential energy that varies with its displacement as $V(x) = gx^4$. What would be the equipartition thermal energy corresponding to the displacement degree of freedom?

1.16 Consider a particle subject to a hypothetical confining potential $V(x) = gx^n$ (where n is even and positive).

(a) Calculate the heat capacity of a collection of such particles as a function of n.

(b) Show that in the limit $n \to \infty$ the heat capacity tends to that for a free particle.

(c) Comment on this limit – in the context of a gas of free particles.

1.17 For a single-component system with a variable number of particles, the Gibbs free energy is a function of temperature, pressure and number of particles: $G = G(T, p, N)$. Since N is the only extensive variable upon which G depends, show that the chemical potential for this system is equal to the Gibbs free energy per particle: $G = N\mu$.

1.18 Use the definition of the Gibbs free energy together with the result of the previous question, Problem 1.17, to obtain the Euler relation of Appendix A.2:

$$E = TS - pV + \mu N.$$

1.19 The energy of a harmonic oscillator may be written as $m\omega^2 x^2/2 + p^2/2m$ so it is quadratic in both position and momentum – thus equipartition will give a classical internal energy of kT.

The energy levels of the quantum harmonic oscillator are given by $\varepsilon_n = (\frac{1}{2} + n)\hbar\omega$.

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

$$Z = \frac{1}{2}\mathrm{cosech}\frac{\hbar\omega}{2kT} \tag{1.8.1}$$

and that the internal energy is given by

$$E = \frac{1}{2}\hbar\omega \coth\frac{\hbar\omega}{2kT} = \frac{\hbar\omega}{e^{\hbar\omega/kT} - 1} + \frac{\hbar\omega}{2}. \tag{1.8.2}$$

(b) Show that at high temperatures E may be expanded as

$$E = kT + \frac{\hbar^2\omega^2}{12kT} + \cdots \tag{1.8.3}$$

(c) Identify the terms in this expansion.