

Problem 3.36. Consider an Einstein solid for which $N \gg 1$ and $q \gg 1$. Think of each oscillator as a separate particle.

(a) Show that the chemical potential is

$$\mu = -kT \ln \left(\frac{N+q}{N} \right).$$

(b) Discuss this result in the limits $N \gg q$ and $N \ll q$, concentrating on the question how much S increases when another particle carrying no energy is added to the system. Does the formula make intuitive sense?

(a) The chemical potential, μ , is given by Equation 3.55 to be

$$\mu = -T \left(\frac{\partial S}{\partial N} \right)_{U,V}.$$

The entropy, S , is given in terms of the multiplicity, Ω , by Equation 2.45 to be

$$S = k \ln(\Omega).$$

The multiplicity of an Einstein solid is given by Equation 2.9 to be

$$\Omega(N, q) = \frac{(q + N - 1)!}{q!(N - 1)!}.$$

The natural log of factorial terms would be unpleasant to work with so we will find an approximation for Ω in the $N \gg 1$ and $q \gg 1$ limit. We begin with Equation 2.9 by noting $(N - 1)! = N!/N$, and likewise $(q + N - 1)! = (q + N)!/(q + N)$. Then,

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

We then turn to Stirlings approximation of the factorial function given by Equation 2.14:

$$N! \approx N^N e^{-N} \sqrt{2\pi N},$$

where $N \gg 1$. Then,

$$\Omega(N, q) \approx \frac{N}{q + N} \left(\frac{(q + N)^{q+N} \sqrt{2\pi(q + N)} e^{-(q+N)}}{q^q \sqrt{2\pi q} e^{-q} N^N \sqrt{2\pi N} e^{-N}} \right).$$

This in turn simplifies to

$$\Omega(N, q) \approx \left(\frac{q+N}{q} \right)^q \left(\frac{q+N}{N} \right)^N \left(\frac{N}{2\pi q(q+N)} \right)^{1/2}.$$

Then, by Equation 2.45,

$$S = kq \ln \left(1 + \frac{N}{q} \right) + kN \ln \left(1 + \frac{q}{N} \right) + \frac{1}{2} k \ln \left(\frac{N}{2\pi q(q+N)} \right).$$

The final additive term is notably smaller than the first two additive terms. See that the first two terms are multiplied by the relatively large q and N . Thus, we may neglect the last term in the large q and N approximation. Finally, Equation 3.55 relates the entropy to the chemical potential by

$$\mu = -T \left(\frac{\partial S}{\partial N} \right)_{U,V}.$$

Then,

$$\mu = -kT \left(q \frac{\partial}{\partial N} \ln \left(1 + \frac{N}{q} \right) + \frac{\partial}{\partial N} N \ln \left(1 + \frac{q}{N} \right) \right).$$

The first term in the outer-parenthesis requires a chain rule:

$$\frac{\partial}{\partial N} \ln \left(1 + \frac{N}{q} \right) = \left(1 + \frac{N}{q} \right)^{-1} \frac{1}{q} = \frac{1}{q+N}.$$

The second term in the outer-parenthesis requires a product rule and a chain rule:

$$\frac{\partial}{\partial N} N \ln \left(1 + \frac{q}{N} \right) = \ln \left(1 + \frac{q}{N} \right) - N \left(1 + \frac{q}{N} \right)^{-1} N^{-2} = -\frac{q}{N+q} + \ln \left(1 + \frac{q}{N} \right).$$

Finally,

$$\mu = -kT \left(\frac{q}{q+N} - \frac{q}{N+q} + \ln \left(1 + \frac{q}{N} \right) \right) = \ln \left(1 + \frac{q}{N} \right),$$

where we notice

$$\ln \left(1 + \frac{q}{N} \right) = \ln \left(\frac{N+q}{N} \right)$$

as desired.

(b) Suppose $N \gg q$. Then,

$$\frac{1}{k} \left(\frac{\partial S}{\partial N} \right)_{U,V} \approx \ln \left(\frac{N}{N} \right) = 0.$$

Thus, the entropy of the system when $N \gg q$ is not altered significantly when a particle without energy is added.

Suppose $q \gg N$. Then,

$$\frac{1}{k} \left(\frac{\partial S}{\partial N} \right)_{U,V} \approx \ln \left(\frac{q}{N} \right).$$

Since $q \gg N$, the increase in entropy for a new particle without energy is greater than 1.

Problem 3.37. Consider a monoatomic ideal gas that lives at a height z above sea level, so each molecule has potential energy mgz in addition to its kinetic energy.

- (a) Show that the chemical potential is the same as if the gas were at sea level, plus an additional term mgz :

$$\mu(z) = -kT \ln \left(\frac{V}{N} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right) + mgz.$$

- (b) Consider two chunks of helium gas, one at sea level and one at height z , each having the same temperature and volume. Assuming that they are in diffusive equilibrium, show that the number of molecules in the higher chunk is

$$N(z) = N(0) \exp \left[-\frac{mgz}{kT} \right],$$

in agreement with the result of Problem 1.16.

- (a) Suppose the molecules in an ideal gas are at approximately the same height z . Then, the total energy, U , of the gas can be expressed in terms of the kinetic energy, U_k , and the gravitational potential energy of N particles; that is,

$$U_t = U + Nmgz.$$

Equation 3.62, the Sackur-Tetrode equation, gives the entropy of an ideal monoatomic gas to be

$$S = Nk \left(\ln \left[V \left(\frac{4\pi mU}{2h^2} \right)^{3/2} \right] - \ln [N^{5/2}] + \frac{5}{2} \right),$$

where U is the kinetic energy of the gas, U_k . Expressing Equation 3.62 in terms of U_k yields

$$S = Nk \left(\ln \left[V \left(\frac{4\pi m(U - Nmgz)}{2h^2} \right)^{3/2} \right] - \frac{5}{2} \ln [N] + \frac{5}{2} \right).$$

The chemical potential, μ , is then obtained by Equation 3.55,

$$\mu = -T \left(\frac{\partial S}{\partial N} \right)_{U,V}.$$

Problem 3.39. In Problem 2.32, the entropy of an ideal monoatomic gas that lives in a two-dimensional universe was found. Take the partial derivative with respect to U , A , and N to determine the temperature, pressure, and chemical potential of this gas. Simplify the result and discuss.

The multiplicity of the two-dimensional gas was found in Problem 2.26 to be

$$\Omega_N \approx \frac{\pi^N}{(N!)^2} \frac{A^N}{h^{2N}} (2mU)^N = \frac{1}{(N!)^2} \left(\frac{2\pi AmU}{h^2} \right)^N.$$

The entropy of a system with multiplicity Ω can be found by

$$S = k \ln(\Omega).$$

Substituting the entropy of the two-dimensional gas for $N \gg 1$ yields

$$S = k \ln \left(\frac{1}{(N!)^2} \left(\frac{2\pi AmU}{h^2} \right)^N \right).$$

Then,

$$S = k \left(N \ln \left(\frac{2\pi mUA}{h^2} \right) - 2 \ln(N!) \right).$$

Applying Stirlings approximation in the form of Equation 2.16,

$$\ln(N!) = N \ln(N) - N,$$

yields

$$S = Nk \left(\ln \left[\frac{2\pi mUA}{N^2 h^2} \right] + 2 \right).$$

The partial derivative with respect to U is then,

$$\begin{aligned} \frac{\partial S}{\partial U} &= Nk \left(\frac{\partial}{\partial U} \ln \left[\frac{2\pi mUA}{N^2 h^2} \right] \right) \\ &= Nk \left(\frac{N^2 h^2}{2\pi mUA} \frac{2\pi mA}{N^2 h^2} \right) \\ &= \frac{Nk}{U}. \end{aligned}$$

The partial derivative with respect to A is then,

$$\begin{aligned} \frac{\partial S}{\partial A} &= Nk \left(\frac{\partial}{\partial A} \ln \left[\frac{2\pi mUA}{N^2 h^2} \right] \right) \\ &= Nk \left(\frac{N^2 h^2}{2\pi mUA} \frac{2\pi mU}{N^2 h^2} \right) \\ &= \frac{Nk}{A}. \end{aligned}$$

The partial derivative with respect to N is then,

$$\begin{aligned}
\frac{\partial S}{\partial N} &= k \left(\ln \left[\frac{2\pi m U A}{N^2 h^2} \right] + 2 \right) + Nk \left(\frac{\partial}{\partial N} \ln \left[\frac{2\pi m U A}{N^2 h^2} \right] \right) \\
&= \frac{S}{N} + Nk \left(\frac{N^2 h^2}{2\pi m U A} \frac{2\pi m U A}{h^2} (-2) N^{-3} \right) \\
&= \frac{S}{N} - 2k \\
&= k \ln \left(\frac{2\pi m U A}{N^2 h^2} \right).
\end{aligned}$$

The temperature of the two-dimensional gas is given by

$$T = \left(\frac{\partial S}{\partial U} \right)^{-1} = \frac{U}{Nk}.$$

The pressure of the two-dimensional gas is given by

$$P = T \frac{\partial S}{\partial A} = \frac{NkT}{A},$$

which we notice is a two-dimensional form of the Ideal Gas Law. The chemical potential of the two-dimensional gas is given by

$$\mu = -T \frac{\partial S}{\partial N} = -kT \ln \left(\frac{2\pi m U A}{N^2 h^2} \right),$$

where we may substitute our expression for temperature to obtain a more familiar form:

$$\mu = -kT \ln \left(\frac{A}{N} \frac{2\pi m kT}{h^2} \right).$$

The two-dimensional system is not so different from the three-dimensional system.