

Temperature Dependence of the Chemical Potential—C.E. Mungan, Spring 2000

Consider a set of one-dimensional simple harmonic oscillators of frequency ν . Their energy levels are nondegenerate and uniformly spaced by $h\nu$, so that the density of states is constant,

$$g = \frac{1}{h\nu} \quad (1)$$

where I choose to measure energies relative to the ground state, $\epsilon_{\text{groundstate}} = 0$. The total number N of oscillators is given by

$$N = \int_0^{\infty} g(\epsilon) f(\epsilon) d\epsilon = \frac{1}{h\nu} \int_0^{\infty} f(\epsilon) d\epsilon \quad (2)$$

where f is the average occupation number. In writing this as an integral rather than as a sum over states, I have implicitly assumed that the spacing between levels is small enough that they form a quasi-continuum; see the Appendix for a discussion of this point.

Let's first apply this to a set of fermions. The Fermi-Dirac distribution function is

$$f(\epsilon) = \frac{1}{e^{(\epsilon-\mu)/kT} + 1} \quad (3)$$

where μ is the chemical potential. Substituting this into Eq. (2) and changing variables to $x \equiv (\epsilon - \mu)/kT$ gives

$$N = \frac{kT}{h\nu} \int_{-\mu/kT}^{\infty} \frac{dx}{e^x + 1} = \frac{kT}{h\nu} \left[x - \ln(1 + e^x) \right]_{-\mu/kT}^{\infty} \quad (4)$$

As $x \rightarrow \infty$ note that $\ln(1 + e^x) \rightarrow \ln(e^x) = x$, and hence the integral evaluated at the upper limit is equal to zero. Therefore Eq. (4) becomes

$$N = \frac{\mu}{h\nu} + \frac{kT}{h\nu} \ln(1 + e^{-\mu/kT}). \quad (5)$$

Now evaluate this at $T = 0$, for which $\mu \equiv \epsilon_F$, the Fermi energy. The Fermi energy is equal to the energy of the highest occupied level at absolute zero and is therefore necessarily positive for our choice of the zero of energy. We get

$$N = \frac{\epsilon_F}{h\nu} \Rightarrow \epsilon_F = N h\nu \quad (6)$$

and hence Eq. (5) becomes

$$\epsilon_F = \mu + kT \ln(1 + e^{-\mu/kT}). \quad (7)$$

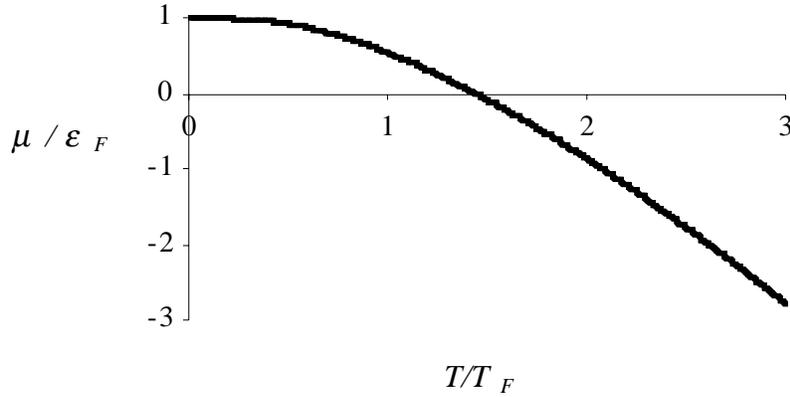
This can be rearranged to give

$$\boxed{\mu = kT \ln(e^{\epsilon_F/kT} - 1)}. \quad (8)$$

Defining the Fermi temperature as $T_F \equiv \varepsilon_F / k$, Eq. (8) becomes

$$\frac{\mu}{\varepsilon_F} = \frac{T}{T_F} \ln(e^{T_F/T} - 1). \quad (9)$$

Notice that $\mu = 0$ when $T = T_F / \ln 2$, and at higher temperatures the chemical potential becomes negative and arbitrarily large in magnitude, as we can see from the following plot of Eq. (9).



Let's repeat this analysis for a set of (massive) bosons. The Bose-Einstein distribution function is

$$f(\varepsilon) = \frac{1}{e^{(\varepsilon - \mu)/kT} - 1}, \quad (10)$$

where $\mu < \varepsilon_{\text{groundstate}} \equiv 0$ is a necessary condition in its derivation (cf. Stowe Eq. 24.5). That is, the chemical potential is negative at all nonzero temperatures, unlike what we found for fermions above, as otherwise f would blow up at some (positive) energy. Note however that we must have $\mu \rightarrow 0$ as $T \rightarrow 0$ because otherwise the occupancy of all levels would be zero; in contrast $\mu = \varepsilon_{\text{groundstate}}$ permits all N bosons to condense into the groundstate at absolute zero. Substituting Eq. (10) into Eq. (2) and again changing variables to $x \equiv (\varepsilon - \mu)/kT$ gives

$$N = \frac{kT}{h\nu} \int_{-\mu/kT}^{\infty} \frac{dx}{e^x - 1} = \frac{kT}{h\nu} \left[-x + \ln(e^x - 1) \right]_{-\mu/kT}^{\infty} \quad (11)$$

and the integral evaluated at the upper limit is again zero. Note that the range of integration does not encompass $x = 0$ where the integral diverges, since the chemical potential is negative! Equation (11) therefore becomes

$$N = -\frac{\mu}{h\nu} - \frac{kT}{h\nu} \ln(e^{-\mu/kT} - 1) \quad (12)$$

which can be rearranged to give

$$\boxed{\mu = kT \ln(1 - e^{-Nh\nu/kT})}. \quad (13)$$

Introducing the Fermi energy and temperature as before, Eq. (13) becomes

$$\frac{\mu}{\varepsilon_F} = \frac{T}{T_F} \ln(1 - e^{-T_F/T}) = \frac{T}{T_F} \ln(e^{T_F/T} - 1) - 1. \quad (14)$$

Writing the chemical potential for fermions as μ_F and that for bosons as μ_B , this intriguing result is

$$\mu_B(T) = \mu_F(T) - \varepsilon_F \quad (15)$$

using Eq. (9), assuming that the product Nv (and hence ε_F and T_F) has the same value for both sets of particles. We thus get the same graph as above, except that we need to shift the horizontal axis up by one unit so that μ_B begins at the origin. That is, the ‘‘Bose energy’’ is zero.

To summarize, for both fermionic and bosonic 1D simple harmonic oscillators, the chemical potential decreases monotonically with temperature, becoming negative with an arbitrarily large magnitude at high temperatures. At absolute zero, however, $\mu_B = 0$ while $\mu_F = \varepsilon_F$ where the Fermi energy is necessarily positive; $\mu_F = 0$ only when $T = T_F / \ln 2$, which is typically of the order of many thousands of degrees.

Appendix: Chemical Potential at Low Temperatures

When kT becomes comparable to the spacing $h\nu$ between levels, then Eq. (2) should be replaced by

$$N = \sum_{n=0}^{\infty} \frac{1}{e^{(nh\nu - \mu)/kT} \pm 1}. \quad (16)$$

For temperatures which are low compared to the excitation temperature, $T_e \equiv h\nu/k$, only the groundstate is occupied for the case of bosons, so that

$$N \approx \frac{1}{e^{-\mu/kT} - 1} \Rightarrow \mu = -kT \ln(1 + 1/N) \approx -\frac{kT}{N} \quad (17)$$

assuming we have a large number of particles ($N \gg 1$). The case of fermions is considerably more complicated, since we are looking for small deviations in the occupation number from a step function; the result is given for example by Pathria as

$$\mu \approx \varepsilon_F \left[1 - \frac{\pi^2}{12} \left(\frac{kT}{\varepsilon_F} \right)^2 \right], \quad (18)$$

so that

$$\mu - \varepsilon_F \approx -\frac{0.82(kT)^2}{Nh\nu}. \quad (19)$$

On the other hand, Eqs. (13) and (15) imply that

$$\mu_B = \mu_F - \varepsilon_F \approx -\frac{kT}{\exp(Nh\nu/kT)} \quad (20)$$

in the limit of low temperatures. However, the difference between the right-hand side of this and that of Eq. (17) or (19) is negligible in the limit of very large N , and hence there will be no noticeable error in the preceding graph.