

Chemical potential of one-dimensional simple harmonic oscillators

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Abstract

Expressions for the chemical potential of an Einstein solid, and of ideal Fermi and Bose gases in an external one-dimensional oscillatory trap, are calculated by two different methods and are all found to share the same functional form. These derivations are easier than traditional textbook calculations for an ideal gas in an infinite three-dimensional square well. Furthermore, the results indicate some important features of chemical potential that could promote student learning in an introductory course in statistical mechanics at the undergraduate level.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The thermodynamic identity [1] describes differential changes in the internal energy U of a system as

$$dU = T dS + (-P dV + \mu dN + \dots), \quad (1)$$

where T , S , P , V , μ and N are the temperature, entropy, pressure, volume, chemical potential and number of particles (assumed to be of a single species as opposed to a mixture), respectively. This expression assumes that the system is close to equilibrium, as otherwise it will not have a single well-defined temperature, pressure and so on. If the process is reversible, one can identify TdS as the heat added to the system and the sum of the terms in parentheses in equation (1) as the work done on it¹. If a process is irreversible, one cannot always divide the energy change into a heat term and a work term; an example is kinetic friction in which the mechanical and thermal transfers are commingled at mesoscopic length scales [2].

¹ Specifically $-P dV$ is the expansion/compression work and μdN is the diffusive or chemical work. The ellipsis in equation (1) indicates that many other kinds of work can also occur, such as magnetizing a paramagnet or charging up a capacitor.

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Of the various terms in equation (1), probably μ is the least familiar to undergraduate students being introduced to thermodynamics for the first time [3, 4]. Part of the reason may be that there are few examples of analytic calculations of μ for a system of particles other than for a classical ideal gas in a three-dimensional box with rigid walls (typically computed by first deducing the Sackur–Tetrode equation by approximating the translational partition function as a Gaussian integral, not a trivial derivation for novices).

Given that μ is usually first introduced in thermodynamics to describe diffusion [5], i.e. variations in the number of particles, a student might reasonably ask why μ varies with T for fixed N ? In reply, one can discuss the analogous issue of why P varies with T for fixed V for a gas. Part of the difficulty may be one of language: textbooks state that pressure controls any *changes* in volume (and likewise chemical potential controls any *changes* in the number of particles) which can lead to the incorrect conclusion that if the number of particles does *not* change, then the chemical potential can be ignored.

In order to improve student understanding, in this paper two oscillator models (a solid and a fermionic or bosonic quantum gas) are analysed for which μ is readily calculable. Different methods are used to determine μ for these two models and the results are then compared to demonstrate the underlying unity of the ideas.

2. Chemical potential of an Einstein solid

Einstein’s model of a solid [1] consists of a set of N independent one-dimensional oscillators (corresponding to $N/3$ atoms in three dimensions) among which a total of $q = U/h\nu$ integer units of energy are distributed. (Here h is Planck’s constant and ν is the fundamental frequency of oscillation, assumed to be the same for all N oscillators.) That is, if one writes the energy of the i th oscillator (for $i = 1, \dots, N$) as $\varepsilon_i = n_i h\nu$ (after subtracting off the thermodynamically uninteresting zero-point energy), where n_i is the quantum number of that oscillator, then

$$q \equiv \sum_{i=1}^N n_i. \quad (2)$$

In the usual ‘sticks and dots’ representations of the possible microstates of this system, the units of energy are pictured as dots partitioned by $N - 1$ sticks into N groups representing the oscillators. The multiplicity Ω is then equal to the number of ways of choosing to distribute the q dots among the $q + N - 1$ total objects, which is given by a binomial coefficient

$$\Omega = \frac{(q + N - 1)!}{q!(N - 1)!}. \quad (3)$$

The Boltzmann entropy is $S = k \ln \Omega$, where k is Boltzmann’s constant. Assuming that both q and N are large, the factors of unity in equation (3) can be dropped and Stirling’s approximation, $\ln(n!) \approx n \ln n - n$ for sufficiently large integer n , can be invoked to obtain

$$S \approx k \ln \left[\left(\frac{q + N}{q} \right)^q \left(\frac{q + N}{N} \right)^N \right]. \quad (4)$$

Next, by rearranging equation (1), the standard statistical mechanics definitions of temperature and chemical potential are deduced,

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_{N,V} \quad (5a)$$

and

$$\mu = -T \left(\frac{\partial S}{\partial N} \right)_{U,V}, \quad (5b)$$

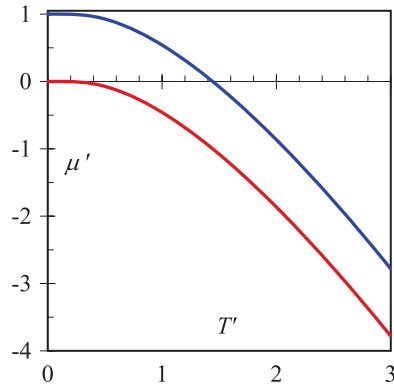


Figure 1. Plots of the dimensionless chemical potential as a function of the dimensionless temperature. The upper curve is for the ideal Fermi gas, while the lower curve is for either the Einstein solid or the ideal Bose gas.

where the subscripts indicate variables that are held fixed during the partial differentiation. Volume is not an independent variable in the Einstein model, so the V subscripts can be dropped in equations (5a) and (5b). Substituting $U = qh\nu$ and equation (4) into equation (5a) leads to

$$\frac{q}{N} = \frac{1}{e^{h\nu/kT} - 1}, \quad (6)$$

which, according to equation (2), equals the average quantum number $\langle n \rangle$ per oscillator as a function of temperature. As $T \rightarrow 0$, this expression correctly predicts that $\langle n \rangle \rightarrow 0$ because every oscillator is near its ground state². At the opposite limit, as T gets large (compared to the characteristic Einstein temperature $T_E \equiv h\nu/k$), equation (6) predicts that $U \equiv qh\nu \approx NkT$, consistent with the equipartition theorem (remembering that each one-dimensional oscillator has one kinetic and one potential degree of freedom at high temperatures). Finally, substituting equation (4) into (5b), performing the derivative and then substituting equation (6) into the result to eliminate q in favour of T lead to a compact expression for the temperature dependence of the chemical potential for an Einstein solid,

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

Defining the dimensionless chemical potential $\mu' \equiv \mu/h\nu$ and temperature $T' \equiv T/T_E$, then equation (7) becomes

$$\mu' = T' \ln(1 - e^{-1/T'}) \quad (8)$$

as plotted in figure 1.

3. Chemical potential of a quantum gas in an external parabolic trap

Consider a set of N noninteracting particles confined in one dimension by an applied harmonic potential so that they translationally oscillate at fundamental frequency ν . Their energy levels

² Technically T cannot be set to zero because Stirling's approximation for $q!$ was used in the derivation. In practice, that restriction can be ignored because if N is of the order of say Avogadro's number, then there is a large range of values of q for which $q/N \ll 1$ while simultaneously maintaining $q \gg 1$.

are nondegenerate (ignoring spin degeneracy) and uniformly spaced by $h\nu$, so that the density of states g is constant,

$$g = \frac{1}{h\nu}, \quad (9)$$

where, as in section 2, the particle energies ε are measured relative to the ground state, $\varepsilon_{\text{ground state}} \equiv 0$. The total number of oscillators must be equal to

$$N = \int_0^\infty g(\varepsilon)f(\varepsilon) d\varepsilon = \frac{1}{h\nu} \int_0^\infty f(\varepsilon) d\varepsilon, \quad (10)$$

where f is the occupancy or distribution function. In writing this as an integral rather than as a sum over states, it is assumed that the spacing between levels (compared to typical thermal energies) is small enough that they form a quasi-continuum, i.e. $h\nu \ll kT$.

First apply this formula to a set of fermions. The Fermi–Dirac distribution function is

$$f(\varepsilon) = \frac{1}{e^{(\varepsilon-\mu)/kT} + 1}, \quad (11)$$

where μ is the chemical potential. Substituting this function into equation (10) and changing variables to $x \equiv (\varepsilon - \mu)/kT$ give

$$N = \frac{kT}{h\nu} \int_{-\mu/kT}^\infty \frac{dx}{e^x + 1} = \frac{kT}{h\nu} [x - \ln(1 + e^x)]_{-\mu/kT}^\infty. \quad (12)$$

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 equation (12) becomes

$$N = \frac{\mu}{h\nu} + \frac{kT}{h\nu} \ln(1 + e^{-\mu/kT}). \quad (13)$$

Now evaluate this at $T = 0$, for which $\mu \equiv \varepsilon_F$, 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, so that equation (13) becomes

$$N = \frac{\varepsilon_F}{h\nu} \Rightarrow \varepsilon_F = N h\nu \quad (14)$$

as expected because the levels are nondegenerate. Substituting this result into equation (13) leads to

$$\varepsilon_F = \mu + kT \ln(1 + e^{-\mu/kT}), \quad (15)$$

which rearranges into

$$\mu = kT \ln(e^{T_F/T} - 1), \quad (16)$$

where the Fermi temperature is $T_F \equiv \varepsilon_F/k$. Note that equation (16) correctly reduces to $\mu = \varepsilon_F$ in the limit³ as $T \rightarrow 0$. On the other hand, $\mu = 0$ when $T = T_F/\ln 2$, in contrast to an ideal Fermi gas in a three-dimensional box with rigid walls for which $\mu = 0$ when $T \approx T_F$ (cf figure 7.16 in Schroeder [1], obtained by a nontrivial numerical calculation).

The dimensionless chemical potential and temperature can be defined as $\mu' \equiv \mu/\varepsilon_F = \mu/Nh\nu$ and $T' \equiv T/T_F = kT/Nh\nu$, respectively, so that equation (16) becomes

$$\mu' = T' \ln(e^{1/T'} - 1) \quad (17)$$

as is plotted in figure 1. Defining μ'_E to be the right-hand side of equation (8) and μ'_F to be the right-hand side of equation (17), it can be shown that $\mu'_F = \mu'_E + 1$. In other words, a

³ Technically T again cannot actually equal zero because the integral approximation in equation (10) requires that $T > h\nu/k$. Nevertheless if N is large enough, this requirement can be maintained even when $T \ll T_F = Nh\nu/k$.

dimensionless graph of chemical potential for an ideal gas of fermions in one overall harmonic oscillator potential has the same shape as that for a collection of individual Einstein oscillators each in their own potentials. The upward shift in the vertical intercept for the fermion case is required by the Pauli exclusion principle. If one is only interested in *changes* in the value of the chemical potential with temperature, as in many chemistry problems, then this vertical shift is irrelevant.

Next, consider a set of N bosons in the same external one-dimensional simple harmonic potential so that they again oscillate at fundamental frequency ν . The Bose–Einstein distribution function is

$$f(\varepsilon) = \frac{1}{e^{(\varepsilon-\mu)/kT} - 1}, \quad (18)$$

where $\mu < \varepsilon_{\text{ground state}} \equiv 0$ is a necessary requirement. That is, the chemical potential must be negative at all nonzero temperatures, unlike for fermions, as otherwise f would diverge to infinity at some (positive) energy. However, it must be true that $\mu \rightarrow 0$ as $T \rightarrow 0$ because otherwise the occupancy of all levels would be zero at absolute zero; in contrast, $\mu \approx \varepsilon_{\text{ground state}}$ permits all N bosons to occupy the ground state at sufficiently low temperatures. (Note, however, that Bose–Einstein condensation *cannot* occur in a one-dimensional gas [6].) Substituting equation (18) into equation (10) and again changing variables to $x \equiv (\varepsilon - \mu)/kT$ gives

$$N = \frac{kT}{h\nu} \int_{-\mu/kT}^{\infty} \frac{dx}{e^x - 1} = \frac{kT}{h\nu} [-x + \ln(e^x - 1)]_{-\mu/kT}^{\infty} \quad (19)$$

and the integral evaluated at the upper limit is again zero⁴. Equation (19) therefore becomes

$$N = -\frac{\mu}{h\nu} - \frac{kT}{h\nu} \ln(e^{-\mu/kT} - 1), \quad (20)$$

which rearranges to

$$\mu = kT \ln(1 - e^{-Nh\nu/kT}). \quad (21)$$

Introducing $\mu' \equiv \mu/Nh\nu$ and $T' \equiv kT/Nh\nu$ as for the fermion case, equation (21) becomes

$$\mu' = T' \ln(1 - e^{-1/T'}), \quad (22)$$

which is identical to equation (8). In fact, the similarity extends beyond the normalized version of this expression to the fully dimensional forms. Equations (7) and (21) are the same if the Einstein frequency ν_E is related to the frequency of oscillation of the harmonically trapped bosons ν_B according to $\nu_E = N\nu_B$. Now consider typical experimental values. The Einstein temperature of copper [7] is 240 K so that $h\nu_E = 21$ meV. On the other hand, the average energy of a particle in an oscillatory trap of effective spring constant κ is $\langle \varepsilon \rangle = \frac{1}{2}\kappa L^2$ where L is the mean amplitude of the motion and thus represents the one-dimensional volume of the system of noninteracting particles. In particular, for the harmonic axis of a magnetic trap designed by Hess [8] for $N = 10^{12}$ hydrogen atoms (having a mass of $m = 1.67 \times 10^{-27}$ kg), $\langle \varepsilon \rangle = 2 \times 10^{-27}$ J and $L = 5$ cm so that

$$Nh\nu_B = \frac{N}{L} \hbar \sqrt{\frac{2\langle \varepsilon \rangle}{m}} = 20 \text{ meV} \quad (23)$$

which is comparable to 21 meV. Thus the chemical potential of an Einstein solid is equivalent to that of an ideal gas of bosons in an external harmonic potential both in theory and in practice⁵.

⁴ Note that, since the chemical potential is negative, the range of integration does not encompass $x = 0$ where the integral diverges.

⁵ Notice from equation (23) that $N\nu$ is proportional to the number density N/L of particles in the trap, so that μ in equations (16) and (21) properly scales intensively with the temperature and density. In accordance with equipartition, $\langle \varepsilon \rangle = kT$ at temperatures high enough that the integral approximation in equation (10) holds.

4. Conclusions

For either an Einstein solid or a quantum gas in a one-dimensional oscillatory trap, the dimensionless chemical potential μ' has the same functional dependence on temperature, decreasing monotonically with an asymptotic $-T' \ln T'$ dependence for large values of the dimensionless temperature T' . The calculations of μ presented in this paper are more straightforward than those for a quantum (or even a classical) gas in a three-dimensional rigid box and thus could be instructively presented in an introductory statistical mechanics course as a prelude. Notably, the vertical intercepts and general shapes of the graphs of $\mu(T)$ are the same for gases in either a one-dimensional harmonic potential or a three-dimensional infinite square well and have been neatly explained by Cook and Dickerson [3]. Furthermore, the fact that the Einstein solid and ideal Bose gas give the same result when computed by different methods (by differentiating the entropy in section 2 and by normalizing the distribution function in section 3) harmonizes different concepts about chemical potential and different models of oscillators. Finally, presentation of the one-dimensional Bose gas in a simple harmonic potential can serve as a springboard for treatment of the three-dimensional case that corresponds to actual Bose–Einstein condensation experiments for dilute atomic gases [9, 10].

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