The Chemical Potential: Classical vs Quantum, Non-Relativistic vs Relativistic, Particle vs Oscillator

In everything below we are talking about a system of free (no-external potential energy), non-interacting, indistinguishable particles in a box of volume V.

Classical

particles

It is only in the classical limit that the ideal gas law, $pV = Nk_BT$, holds (and it holds no matter what is the internal structure of the particles). In the classical limit it does not make sense to speak of fermions vs bosons, since there are no quantum statistics. If we are talking about real particles, where it makes sense to say there are exactly N particles in the box, then we can compute the entropy whether particles are non-relativistic, with $\epsilon = p^2/2m$, or relativistic, with $\epsilon = pc$. See notes 2-7 and notes from discussion session on Feb. 9. We have for indistinguishable particles,

$$\text{non-relativistic:} \quad E = \frac{3}{2}Nk_BT \ \Rightarrow \ S(E,V,N) = \frac{5}{2}Nk_B + Nk_B \ln\left[\frac{V}{h^3N}\left(\frac{4\pi mE}{3N}\right)^{3/2}\right] \quad \text{(Sackur-Tetrode)}$$

$$(1)$$

$$\text{relativistic:} \quad E = 3Nk_BT \ \Rightarrow \ S(E,V,N) = 4Nk_B + Nk_B \ln\left[\frac{8\pi}{27c^3h^3}\left(\frac{V}{N}\right)\left(\frac{E}{N}\right)^3\right] \quad (2)$$

In both cases we have $\dfrac{\mu}{T} = -\left(\dfrac{\partial S}{\partial N}\right)_{E,V}$ and we then get,

$$\text{non-relativistic:} \quad \mu = -k_BT \ln\left[\frac{V}{N\lambda^3}\right] \qquad \text{with the thermal wavelength } \lambda = \sqrt{\frac{h^2}{2\pi mk_BT}} \quad (3)$$

$$\text{relativistic:} \quad \mu = -k_BT \ln\left[\frac{8\pi V}{3N\lambda^3}\right] \qquad \text{with the relativistic thermal wavelength defined by } k_BT = \frac{hc}{\lambda} \ (4)$$

In both cases, if V is sufficiently large so that $V/N > \lambda^3$, i.e. particles are separated from each other by more than one thermal wavelength, which is just the condition that the system is in the classical limit, then $\mu < 0$. So for the classical ideal gas one cannot have $\mu = 0$ or $\mu > 0$, no matter whether the particles are non-relativistic or relativistic.

The above calculations were done in the microcanonical ensemble. We could do the same calculations in the canonical ensemble and would get the same results. We could also do them in the grand canonical ensemble where N is not fixed, but we will get the same result since the relative fluctuations in N, $\sqrt{\langle N^2 \rangle - \langle N \rangle^2}/\langle N \rangle \sim 1/\sqrt{N}$ vanish in the thermodynamic limit.

It might be surprising that $\mu < 0$, since one is used to thinking of μ as the change in energy when one adds a particle to the system, and so one might expect that to be positive. But $\mu = (\partial E/\partial N)_{S,V}$ is the energy change *when the entropy is kept constant*, and most people don't really have a good feeling for what it means to keep S constant. A better way to think about it is in the canonical ensemble at fixed T, where μ is related to the change in *free energy*, $\mu = (\partial A/\partial N)_{T,V}$, with $A = E - TS$. So even if E increases when we add a particle, so will TS increase. If the increase in TS is greater than the increase in E, then A will decrease and $\mu < 0$. This is the case for both the non-relativistic and relativistic classical ideal gas.

oscillators

For a single harmonic oscillator of frequency ω_0 in the classical limit, the equipartition theorem will hold and $E = k_BT$. For the classical oscillator, there are no "particles" and so no variable N to take derivatives with respect to. The chemical potential is thus not defined.

One could argue from quantum mechanics that the oscillator is, on average, excited up to an energy level n such that $k_BT \approx n\hbar\omega_0$, and the classical limit is then $k_BT \gg \hbar\omega_0$, and so n is very large. But recall from problem 1 on Problem

Set 8 that the relative fluctuation in the excitation level is $\sqrt{\langle n^2 \rangle - \langle n \rangle^2}/\langle n \rangle = e^{\hbar\omega_0/2k_B T} \approx 1$ is large in the classical limit $\hbar\omega_0/k_B T \ll 1$. The fluctuation in n is the same order of magnitude as $\langle n \rangle$ itself. Unlike for classical particles in the grand canonical ensemble, there is no thermodynamic limit in which we can make the relative fluctuations in n negligible. Thus we cannot think of this as being a system in which n is a controllable parameter that can be fixed to a particular value, and hence a chemical potential for the oscillator level is not really defined.

Quantum non-degenerate limit

particles

This is the limit where quantum effects are noticeable but small. It makes sense to speak of the difference between fermions and bosons, and each case gives a small correction to the ideal gas law as in the notes Eq. (3.8.31). We would therefore expect small corrections to the entropy and to the free energy, hence small corrections to the chemical potential, but still we expect $\mu < 0$ for both fermions and bosons. Recall the non-degenerate limit is the $z \ll 1$ limit. Since $z = e^{\mu/k_B T}$, small $z \ll 1$ necessarily means $\mu < 0$.

oscillators

Nothing new!

Quantum degenerate limit

Here quantum effects dominate, and we are not anywhere close to classical behavior. The ideal gas law $pV = Nk_B T$ does *not* hold, even approximately. So the expressions given above for the entropy S in the classical limit are not valid.

fermionic particles

The degenerate gas of fermions is dealt with in Notes 3-9.

At $T = 0$ the N-particle ground state is constructed by filling up single particle energy levels consistent with the Pauli exclusion principle. We add a particle first to the lowest energy level, then to the next lowest, then to the next lowest, until we use up all the N particles. The energy of the last particle added is the Fermi energy ϵ_F. All single particle states with $\epsilon < \epsilon_F$ are filled, and all single particle states with $\epsilon > \epsilon_F$ are empty. At $T = 0$, the Fermi energy is the same as the chemical potential, $\mu(T = 0) = \epsilon_F$. For free particles, the single particle energy levels are all $\epsilon_i > 0$, and so $\epsilon_F > 0$, and so the chemical potential is now positive, $\mu > 0$. To be in the degenerate limit, one have $\epsilon_F \gg k_B T$, or $T_F \gg T$. In this case, finite T is a small correction to the $T = 0$ limit, and we continue to expect that $\mu(T) > 0$. For none of these conclusions does it matter if the particles are non-relativistic with $\epsilon_\mathbf{k} = \hbar^2 k^2/2m$, or relativistic with $\epsilon_\mathbf{k} = \hbar k c$. The only difference between non-relativistic and relativistic particles will be a different density of states $g(\epsilon)$, and all the things that follow from that. So, for example, ϵ_F is different for non-relativistic and relativistic particles, but in both cases $\epsilon_F \gg k_B T > 0$, and so $\mu > 0$.

bosonic particles

The degenerate gas of bosons is dealt with in Notes 3-11.

The boson occupation function is,

$$\langle n(\epsilon) \rangle = \frac{1}{e^{\beta(\epsilon - \mu)} - 1} \tag{5}$$

For free particles, the lowest energy single particle state has $\epsilon = 0$, and so $\langle n(0) \rangle = 1/(e^{-\beta\mu} - 1)$. We therefore must have $\mu < 0$ or else we would have $\langle n(0) \rangle < 0$, which is unphysical. It does not matter if the bosons are non-relativistic or relativistic. The value of μ is determined so that $N/V = \int_0^\infty d\epsilon\, g(\epsilon)\langle n(\epsilon) \rangle$.

For certain dispersion relations, i.e. how $\epsilon_\mathbf{k}$ varies with $|\mathbf{k}|$, in systems with a certain number of dimensions d (see problem 1 on Problem Set 11), one finds that below a certain temperature T_c, the above integral has a maximal value

as $\mu \to 0$. For a particle density larger than that maximal value, one can never get the desired N/V, no matter what one choses for μ. This leads to what is known as *Bose-Einstein condensation*. To get the desired density N/V, we take $\mu = 0$ and put all the missing particles in the ground state with $\epsilon = 0$. So for $T > T_c$ one has $\mu < 0$, but for $T \le T_c$ one has $\mu = 0$ and a finite fraction of the particles are in the ground state; when $\mu = 0$, the number of particles in the ground state is $1/(1-1)$, which is indeterminate – one gets the number needed by a careful choice of how one takes the limits $V \to \infty$ and $\mu \to 0$. The number of particles excited out of the ground state is controlled just by the temperature T (because $\mu = 0$). The particles in excited states are called the "normal fluid", while the particles in the ground state are called the "condensate" or the "superfluid." For $T \le T_c$, the particles in the normal fluid behave like quantum excitations of a harmonic oscillator (see more below): they have $\mu = 0$, the average number is controlled solely by the temperature T, and the number of particles is not conserved – one can always "create" a normal particle by exciting an additional particle out of the condensate, and one can always "destroy" a normal particle by adding it into the condensate. For $T \le T_c$ the pressure in the system goes as $p \propto T^{5/2}$; it is independent of the particle density N/V and is nothing like the ideal gas law. For $T \le T_c$, the entropy S is independent of the number of particles N (see Eq. (3.11.50) for non-relativistic particles), consistent with $\mu = 0$.

oscillators

Treating harmonic oscillators quantum mechanically, the energy levels are $\epsilon_n = \hbar\omega_0(n + 1/2)$. One finds that the average $\langle n \rangle$ to which the oscillator is excited is exactly the same as the boson occupation function for a boson single particle energy level $\epsilon = \hbar\omega_0$, except with $\mu = 0$,

$$\langle n \rangle = \frac{1}{e^{\beta\hbar\omega_0} - 1} \tag{6}$$

and the probability to be excited to level n is similarly the same as the probability to have n bosons, but with $\mu = 0$,

$$p(n) = \frac{e^{-\beta\hbar\omega_0 n}}{\sum\limits_{m=0}^{\infty} e^{-\beta\hbar\omega_0 m}} = e^{-\beta\hbar\omega_0 n}\left[1 - e^{-\beta\hbar\omega_0}\right] \tag{7}$$

We therefore regard an harmonic oscillator excited to level n as if it had n quanta, or bosonic "particles", each with energy $\hbar\omega_0$, and that the chemical potential $\mu = 0$ for such particles. That $\mu = 0$ implies that such bosons do not obey number conservation; we can create a boson by exciting the oscillator to the next level, and we can destroy a boson by having the oscillator go to the next lower level.

For systems in which oscillations are extended through space, such as electromagnetic field oscillations, or sound modes in a solid, the oscillation mode is (for a spatially uniform system) usually characterized by a wavevector $\mathbf{k}$, and the mode has a frequency given by a dispersion relation $\omega(\mathbf{k})$. We thus say that a quantum of excitation of such oscillation acts like a boson with energy $\hbar\omega(\mathbf{k})$ and momentum $\hbar\mathbf{k}$, and that exciting the oscillator to level n is like having n such bosons. In interactions of the oscillator with other degrees of freedom (such as particles), one usually has it that energy and momentum must be conserved, so it is really quite accurate to think of these quanta of oscillation as if they are bosonic particles, only with $\mu = 0$.

It does not matter to this picture just what the dispersion relation $\omega(\mathbf{k})$ is. For many wave phenomena, such as electromagnetic waves in the vacuum, or sound waves in a solid, at small $|\mathbf{k}|$ one usually has a linear dispersion relation, $\omega = ck$. But in other situations, such as the longitudinal plasma oscillation in a metal, or for *optical phonons* in a solid, this need not be the case, and one has $\lim_{|\mathbf{k}| \to 0} \omega(\mathbf{k}) = \omega_0$, a constant. It might even be that the dispersion relation could be quadratic, $\omega \propto k^2$. None of that is relevant for the analogy between the excitation level n of the oscillator and the description of that as n bosonic particles with $\mu = 0$.