

- Chemical Potential $\mu = (\partial F / \partial N)_{\tau, V}$

Chemical potential of the ideal gas.

Recall that the free energy of a classical monatomic ideal gas is

$$F = N\tau \left[\ln(n\lambda_\tau^3) - 1 \right]$$

where $\lambda_\tau = h/\sqrt{2\pi m\tau}$ and $n \equiv N/V$ is the number density.

a)

Calculate the chemical potential of the ideal gas as a function of the number density n .

$$\begin{aligned} \mu &= \left(\frac{\partial F}{\partial N} \right)_{\tau, V} \\ &= \tau \left[\ln \left(\frac{N\lambda_\tau^3}{V} \right) - 1 \right] + N\tau \frac{\partial}{\partial N} \ln(N) \\ &= \tau \ln(n\lambda_\tau^3) - \tau + \tau \\ &= \tau \ln(n\lambda_\tau^3) \end{aligned}$$

b)

Does the chemical potential increase or decrease with density? Explain.

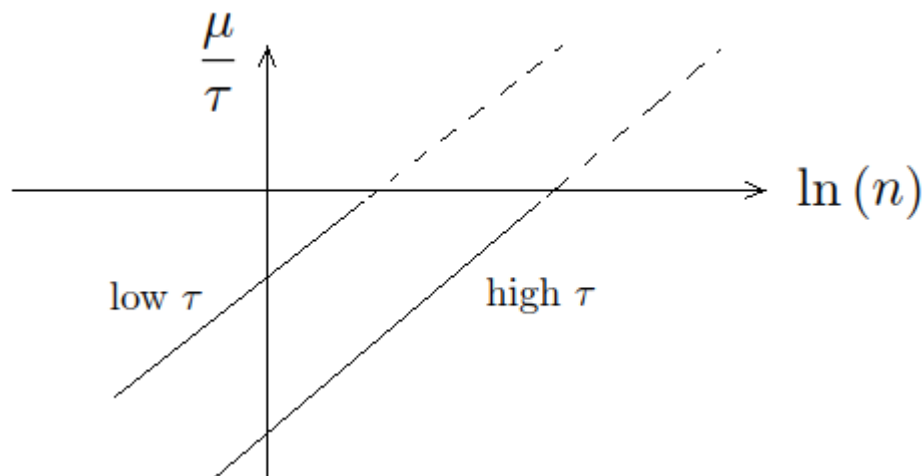
The chemical potential increases (a.k.a. becomes less negative) with increasing n . This is an entropic effect as the energies of the atoms are assumed to be independent. It is an entropic effect not unlike the urn problem. The increase in chemical potential is necessary for stability of the system; if it were negative two such systems in contact would tend toward one system with all the particles and the other with none.

c)

Sketch μ/τ vs. $\ln(n)$ for the ideal gas at two different temperatures $\tau_1 < \tau_2$. Indicate within which region of your plot the ideal gas model is valid.

This is the equation of a line

$$\frac{\mu}{\tau} = \ln(n\lambda_\tau^3)$$



d)

How do you interpret the sign of the chemical potential of the ideal gas?

$\mu < 0$ Because at fixed τ and V there are many possible states to put the new particle and all of its energy is supplied by the thermal bath as there is no penalty of putting two ideal gas particles in the same box. That is, the box is under-full.

e)

Suppose gas particles are in equilibrium with a dilute solution. There is a energy of solvation ΔE for each particle going into solution. What is the chemical potential of the particles in the solution?

The change in energy of salvation ΔE simply adds to the chemical potential. This will make it so that a particular particle will spend some fraction of the time in the gas phase and some time in the solution. Because the particles are dilute enough not to interact in either the gas or the solution this fraction will be the same for all gas particles independent of the concentration (as long as it is small). Therefor the chemical potential scales the same way with n in the gas as it does in the solution.

$$\mu_{\text{solution}} = \Delta E + \tau \ln (\lambda_{\tau}^3 n)$$

In general ΔE could be a function of τ .

Chemical potential due to an applied field

a)

What is the chemical potential of an ideal gas of atoms of mass m in a gravitational field? Express your answer in terms of the height z , the gravitational acceleration g , and the temperature τ (assumed to be uniform).

$$\mu = \tau \ln (n \lambda_{\tau}^3) + mgz$$

b)

Find the equilibrium ratio $n(z_2)/n(z_1)$ of densities at two different heights.

At equilibrium

$$\mu_1 = \mu_2$$

$$\tau \ln (n_2 \lambda_{\tau}^3) + mgz_2 = \tau \ln (n_1 \lambda_{\tau}^3) + mgz_1$$

$$\tau \ln (n_2/n_1) = e^{-mg(z_2-z_1)/\tau}$$

c)

What other method could you have used to obtain the result above?

d)

Suppose there is an ion of charge ez_1 that is in a gas around a ball of charge Q and radius a . What is the probability distribution for the location of that ion in terms of the electrical potential $\phi(\vec{r})$. Don't worry about normalizing the distribution.

$$P(\vec{v}) \propto e^{-\beta U(\vec{r})} = e^{-\beta ez\phi(\vec{r})}$$

e)

If there are many such ions they will affect the electrical potential as described by Poisson's equation

$$\epsilon \nabla^2 \phi = -\rho$$

where ρ is the charge density of the ions. Write Poisson's equation with the Boltzmann distribution for ρ in terms of ϕ and the number density of particles far away from ball n_0 .

$$\rho = zen$$

$$\frac{n(\vec{r})}{n_0} = \exp(-\beta ze\phi)$$

$$\rho(\vec{r}) = zqn_0 \exp(-\beta ze\phi(\vec{r}))$$

$$\epsilon \nabla^2 \phi = -zqn_0 \exp(-\beta ze\phi(\vec{r}))$$

f)

Now expand the exponential in right hand side for a small charge density.

$$\epsilon \nabla^2 \phi = -zen_0 (1 - \beta ze\phi)$$

g)

Suppose there are two types of ions, one with $z_+ = +1$ and one with $z_- = -1$ which each have a density n_0 at large distances. Write the differential equation for ϕ in the form

$$\nabla^2 \phi \approx \kappa^2 \phi$$

That is, what is κ ?

$$\epsilon \nabla^2 \phi = -(+1)en_0(1 - \beta(+1)e\phi) - (-1)en_0(1 - \beta(-1)e\phi)$$

$$\epsilon \nabla^2 \phi = 2qen_0\beta\phi$$

$$\kappa = \sqrt{\frac{2e^2n_0\beta}{\epsilon}}$$

Or more generally

$$\kappa^2 = \sum_i \frac{z_i^2 e^2 n_{i,0}}{\epsilon_r \epsilon_0 k_B T}$$

The solution to this differential equation with the spherical symmetry created by the ball is of the form.

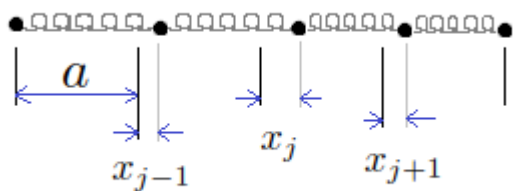
$$\phi = A \frac{e^{-\kappa r}}{r}$$

g)

The length $1/\kappa$ is the Debye screening length used to model polyelectrolyte solutions where the ball itself is replaced with a charged ion. This gives a chemical potential for the ion in solution. What approximations does this model make?

Phonon Dispersion relation

Here we will find the dispersion relation for phonons in a one dimensional solid. We model the solid as atoms with mass m connected with springs of spring constant K .



a)

What is the acceleration of the j^{th} atom in terms of the offsets $\{x\}$?

$$m \frac{d^2}{dt^2} x_j = -K(x_j - x_{j-1}) + K(x_{j+1} - x_j)$$

$$m \frac{d^2}{dt^2} x_j = K(x_{j+1} - 2x_j + x_{j-1})$$

b)

Let's take the as ansatz

$$x_j(t) = A e^{\pm i k a j + i \omega t}$$

Plug this into the difference equation you found in part a) to show that it is a solution and find the relationship between k and ω . Hint: $\sin(x) = (e^{ix} - e^{-ix}) / 2i$.

$$-\omega^2 m x_j = K(e^{\pm i k a} - 2 + e^{\mp i k a}) x_j$$

$$\omega^2 = \frac{4K}{m} \left(\frac{e^{i k a/2} - e^{-i k a/2}}{2i} \right) \left(\frac{e^{i k a/2} - e^{-i k a/2}}{2i} \right)$$

$$\omega^2 = \frac{4K}{m} \sin^2 \left(\frac{k a}{2} \right)$$

c)

Under the approximation that the wavelength of the sound waves is much larger than the atom spacing, simplify your result. Write the result in term of the velocity of a sound wave.

$$\omega^2 \approx \frac{4K}{m} \left(\frac{k a}{2} \right)^2$$

$$\omega \approx \sqrt{\frac{K}{m}} k a$$

d)

Would the above approximation affect the low temperature or high temperature results?

The above approximation affects the highest k and therefore highest ω modes. These modes are only excited at high temperature.

e)

In the worse case scenario by what factor does the above approximation deviate from the correct value for $\omega(k)$?

The worse case scenario is when $ka = \pi$ which is the highest frequency wave where each atom is moving opposite of its neighbors. The correction factor is

$$\left(\frac{\sin(\pi/2)}{\pi/2} \right)^2 = \frac{4}{\pi^2}$$