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Practice for Qualifying Exams

Solution based on advice from Diana.

Problem Source: **CMU February 2006 Qualifying Exam**

Consider an ideal gas of N atoms confined to a container of volume V and internal surface area A. Although you may neglect the interactions between atoms, there is an attraction between the atoms and the walls of the container that cannot be ignored. A simple model for the atoms adsorbed onto the surface is to treat them as a two-dimensional classical ideal gas, where the energy of an adsorbed atom is

$$\varepsilon(\vec{p}) = \frac{|\vec{p}|^2}{2m} - \varepsilon_0$$

and $\vec{p}$ is the two-dimensional momentum. Do not concern yourself with the details of the binding. Treat ε_0 as a known parameter.

(a) What is the classical partition function of the adsorbed atoms if N' atoms are bound to the surface?

The classical partition function is given for one atom by:

$$Z = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{-\beta H(\vec{p},\vec{q})} d^n p\, d^n q$$

In this case, then, I have:

$$Z = A\int_{-\infty}^{\infty} e^{-\beta\left(\frac{p^2}{2m}-\varepsilon_0\right)} d^n p = A\int_{0}^{\infty} e^{-\beta\left(\frac{r^2}{2m}-\varepsilon_0\right)} 2\pi r dr = 2\pi A e^{\beta\varepsilon_0}\int_{0}^{\infty} e^{-\beta\frac{r^2}{2m}} r dr$$

$$v = \beta\frac{r^2}{2m} \quad dv = \frac{\beta r}{m}dr \quad \int_0^\infty e^{-v}dv = 1$$

$$Z = 2\pi A\frac{m}{\beta}e^{\beta\varepsilon_0}$$

and so for N' particles, I have

$$Z_{N'} = \frac{1}{h^{2N'}N'!}\left(2\pi A\frac{m}{\beta}e^{\beta\varepsilon_0}\right)^{N'} = \frac{A^{N'}e^{N'\beta\varepsilon_0}}{N'!}\left(\frac{2\pi m}{h^2\beta}\right)^{N'} = \frac{A^{N'}e^{N'\beta\varepsilon_0}}{N'!}\left(\frac{mkT}{2\pi\hbar^2}\right)^{N'}$$

(b) What is the chemical potential μ_S of the adsorbed atoms?

From the Helmholtz free energy $dF = -SdT - pdV + \mu dN$, I see that:

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}$$

In this case,

$$F = -\frac{1}{\beta}\ln Z = -\frac{1}{\beta}\left[-\ln N'! + N'\ln A + N'\ln\left(\frac{m}{2\pi\hbar^2\beta}\right) + N'\beta\varepsilon_0\right]$$

$$\ln N! \approx N\ln N - N$$

$$\mu_S = \frac{\partial}{\partial N'}\left(-\frac{1}{\beta}\left[-\ln N'! + N'\ln A + N'\ln\left(\frac{m}{2\pi\hbar^2\beta}\right) + N'\beta\varepsilon_0\right]\right)$$

$$= \frac{\partial}{\partial N'}\left(-\frac{1}{\beta}\left[-N'\ln N' + N' + N'\ln A + N'\ln\left(\frac{m}{2\pi\hbar^2\beta}\right) + N'\beta\varepsilon_0\right]\right)$$

$$= -\frac{1}{\beta}\ln\left(\frac{mA}{N'2\pi\hbar^2\beta}\right) - \varepsilon_0$$

(c) What is the classical partition function of the N – N' atoms in the volume of the container?

Again, $Z = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{-\beta H(\bar{p},\bar{q})} d^n p\, d^n q$.

In three dimensions,

$$Z = V\int_{-\infty}^{\infty} e^{-\beta\left(\frac{\bar{p}^2}{2m}\right)} d^n p = V\int_{0}^{\infty} e^{-\beta\frac{r^2}{2m}} 4\pi r^2 dr = 4\pi V\int_{0}^{\infty} e^{-\beta\frac{r^2}{2m}} r^2 dr$$

$$u = \sqrt{\frac{\beta}{2m}}r \qquad du = \sqrt{\frac{\beta}{2m}}dr$$

$$Z = 4\pi V\left(\frac{2m}{\beta}\right)^{\frac{3}{2}}\int_{0}^{\infty} e^{-u^2}u^2 du = 4\pi V\left(\frac{2m}{\beta}\right)^{\frac{3}{2}}\left[\frac{\sqrt{\pi}}{4}\right] = V\left(\frac{2m\pi}{\beta}\right)^{\frac{3}{2}}$$

$$Z_{N-N'} = \frac{V^{N-N'}}{h^{3(N-N')}(N-N')!}\left(\frac{2m\pi}{\beta}\right)^{\frac{3}{2}(N-N')} = \frac{V^{N-N'}}{(N-N')!}\left(\frac{mkT}{2\pi\hbar^2}\right)^{\frac{3}{2}(N-N')}$$

(d) What is the chemical potential of the N – N' atoms in the volume of the container?

Again, $\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}$.

$$F = -\frac{1}{\beta}\ln Z = -\frac{1}{\beta}\left[-\ln(N-N')! + (N-N')\ln V + \frac{3}{2}(N-N')\ln\left(\frac{m}{2\pi\hbar^2\beta}\right)\right]$$

$$\approx = -\frac{1}{\beta}\left[-(N-N')\ln(N-N') + (N-N') + (N-N')\ln V + \frac{3}{2}(N-N')\ln\left(\frac{m}{2\pi\hbar^2\beta}\right)\right]$$

$$\mu_V = -\frac{1}{\beta}\left[-\ln(N-N') + \ln V + \frac{3}{2}\ln\left(\frac{m}{2\pi\hbar^2\beta}\right)\right] = -\frac{1}{\beta}\frac{3}{2}\ln\left(\left(\frac{V}{(N-N')}\right)^{\frac{2}{3}}\frac{m}{2\pi\hbar^2\beta}\right)$$

(e) When the atoms in the volume and those on the surface are in equilibrium with each other, what is the average number of atoms adsorbed as a function of the temperature T?

At equilibrium, $\mu_S = \mu_V$.

$$-\frac{1}{\beta}\ln\left(\frac{mA}{N'2\pi\hbar^2\beta}\right) - \varepsilon_0 = -\frac{1}{\beta}\frac{3}{2}\ln\left(\left(\frac{V}{(N-N')}\right)^{\frac{2}{3}}\frac{m}{2\pi\hbar^2\beta}\right)$$

$$\frac{mA}{N'2\pi\hbar^2\beta}e^{\beta\varepsilon_0} = \frac{V}{(N-N')}\left(\frac{m}{2\pi\hbar^2\beta}\right)^{\frac{3}{2}}$$

$$\frac{N-N'}{N'} = \frac{V}{A}\left(\frac{m}{2\pi\hbar^2\beta}\right)^{\frac{1}{2}}e^{-\beta\varepsilon_0}$$

gives the ratio of atoms in the volume to atoms stuck to the surface.

(f) How many atoms are adsorbed on the walls in the limits of high and low temperatures, according to your answer to (e)? Does your answer make sense in these two limits?

In the limit of a very low temperature, β becomes infinite and the right hand side of the solution in part (e) becomes zero, indicating that the particles are all sticking to the walls. In the limit of a very high temperature, β goes to zero and the right hand side becomes infinite, indicating that all of the particles are floating about the volume.