

Phys 7230

Midterm

March 13

An atom-absorbing site is located on a wall of a container filled with an ideal gas. The site can absorb an arbitrary number of atoms from the gas, at an energy cost of $E = n\epsilon$, if exactly n atoms were absorbed (ϵ is some constant having units of energy). The site is in equilibrium with an ideal monoatomic gas of atoms of mass m kept in the container under pressure P at temperature T . Find the average number of atoms absorbed by the site.

Please write your answer as a function of P , T , m , and of whatever fundamental constants might also enter the expression for the answer.

Solution

We write the grand canonical partition function for the site. If the site absorbed n atoms, its energy is $n\epsilon$. Thus the grand canonical partition function is

$$Z = \sum_{n=0}^{\infty} \exp\left(-\frac{n\epsilon - n\mu}{T}\right) = \frac{1}{1 - \exp\left(\frac{\mu - \epsilon}{T}\right)}. \quad (1)$$

The grand canonical potential is then

$$\Omega = -T \ln Z = T \ln \left(1 - \exp\left(\frac{\mu - \epsilon}{T}\right)\right). \quad (2)$$

The number of absorbed atoms is given by

$$N = -\frac{\partial \Omega}{\partial \mu} = \frac{1}{\exp\left(\frac{\epsilon - \mu}{T}\right) - 1}. \quad (3)$$

Looks like a Bose-Einstein distribution.

This is in equilibrium with a gas at temperature T , thus the temperature of the site is the same T . The gas also has chemical potential μ , which must be equal to μ in this

expression. We are told that the free energy of the gas is

$$F = -TN \ln \left[\frac{eV}{N} \left(\frac{mT}{2\pi\hbar^2} \right)^{\frac{3}{2}} \right]. \quad (4)$$

The chemical potential is then

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{T,V} = -T \ln \left[\frac{V}{N} \left(\frac{mT}{2\pi\hbar^2} \right)^{\frac{3}{2}} \right]. \quad (5)$$

We don't know the volume V or the particle number of the gas, but we know its equation of state

$$P = - \left(\frac{\partial F}{\partial V} \right)_{T,N} = \frac{TN}{V}. \quad (6)$$

Thus

$$\mu = -T \ln \left[\frac{T}{P} \left(\frac{mT}{2\pi\hbar^2} \right)^{\frac{3}{2}} \right]. \quad (7)$$

Finally we substitute this in (3). We find

$$N = \frac{1}{\frac{T}{P} \left(\frac{mT}{2\pi\hbar^2} \right)^{\frac{3}{2}} \exp \left(\frac{\epsilon}{T} \right) - 1}. \quad (8)$$

Grading guidelines

Can compute N as a function of μ and ϵ : 4 points.

Can compute μ of an ideal gas: 3 points.

Can substitute μ of an ideal gas into the expression for N : 3 points.

Total: 10 points

Useful formulae

It may be helpful to recall that the ideal gas is characterized by the Helmholtz free energy given by

$$F = -TN \ln \left[\frac{e}{N} \int \frac{V d^3p}{(2\pi\hbar)^3} e^{-\frac{p^2}{2mT}} \right] = -TN \ln \left[\frac{eV}{N} \left(\frac{mT}{2\pi\hbar^2} \right)^{\frac{3}{2}} \right]. \quad (9)$$

Other properties of the ideal gas, such as its equation of state, heat capacity and so on, can be derived from

$$P = - \left(\frac{\partial F}{\partial V} \right)_{T,N}, \quad S = - \left(\frac{\partial F}{\partial T} \right)_{V,N}, \quad \mu = \left(\frac{\partial F}{\partial N} \right)_{T,V}, \quad (10)$$

and so on.

Other helpful formulae are given below.

Thermodynamic potentials

- Energy $E(S, V, N)$: $dE = TdS - PdV + \mu dN$.
- Enthalpy $H(S, P, N)$: $H = E + PV$, $dH = TdS + VdP + \mu dN$.
- Helmholtz free energy $F(T, V, N)$: $F = E - TS$, $dF = -SdT - PdV + \mu dN$.
- Gibbs free energy $G(T, P, N)$: $G = E - TS + PV$, $dG = -SdT + VdP + \mu dN$.
 $G = N\mu$.
- Grand canonical potential $\Omega(T, V, \mu)$: $\Omega = E - TS - \mu N$, $d\Omega = -SdT - pdV - Nd\mu$.
 $\Omega = -PV$.

Canonical ensemble.

- Partition function $Z = \sum_n e^{-\frac{E_n}{T}}$, where E_n are the energy levels of the system.
- Free energy $F = -T \ln Z$. Energy of the system $E = F + TS$. $dF = -SdT - PdV + \mu dN$, $dE = TdS - PdV + \mu dN$.
- Probability that the system's energy is equal to E_n is $p_n = \frac{1}{Z} e^{-\frac{E_n}{T}}$.

Grand canonical ensemble.

- Partition function $Z = \sum_{N,n} e^{-\frac{E_{N,n}}{T} + \frac{\mu N}{T}}$, where $E_{N,n}$ are the energy levels of the system on the assumption that the system has exactly N particles.

- Grand canonical free energy $\Omega = -T \log Z$. $d\Omega = -SdT - PdV - Nd\mu$. $\Omega = F - \mu N$. $\Omega = -PV$.
- Probability that the system's energy is equal to $E_{N,n}$ if it has N particles is $p_n = \frac{1}{Z} e^{-\frac{E_{N,n}}{T} + \frac{\mu N}{T}}$.

Other formulae

- Heat capacity is the amount of heat pumped into the system to increase its temperature by dT . At fixed volume it is given by $c_v = T \left(\frac{\partial S}{\partial T} \right)_V$. At fixed pressure it is given by $c_p = T \left(\frac{\partial S}{\partial T} \right)_P$. Specific heat is the heat capacity per particle.
- Maxwell relations are relations between derivatives which follow from the fact that partial second derivatives of thermodynamic potentials do not depend on the order of differentiation. For example,

$$dE = TdS - PdV \rightarrow \left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_V .$$

- Quasiclassical approximation to the partition function of a particle

$$Z = \int \frac{d^3x d^3p}{(2\pi\hbar)^3} e^{-\frac{p^2}{2mT}}$$

- Equipartition theorem: specific heat of a quasiclassical system is equal to 1/2 per degree of freedom which enters its energy quadratically.
- Fermi-Dirac and Bose-Einstein grand canonical free energy $\Omega = -Tsg \sum_n \ln \left(1 + s e^{-\frac{\epsilon_n}{T} + \frac{\mu}{T}} \right)$, where $s = 1$ for Fermi-Dirac and $s = -1$ for Bose-Einstein distributions and ϵ_n are energy levels of one particle. g is a degeneracy of each single particle level (due to spin, for example).
- Bose-Einstein distribution $N = N_0 + \int \frac{d^3p d^3x}{(2\pi\hbar)^3} \frac{1}{e^{\frac{p^2}{2mT} - \frac{\mu}{T}} - 1}$, where N is the total number of particles, and N_0 are the particles in the condensate. $N_0 = 0$ at $T > T_c$, while $\mu = 0$ at $T < T_c$. It is assumed here that $g = 1$.