Chemical Potential: problems and solutions (Blundell-Blundell))

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(Date: October 15, 2018)

1. Blundell-Blundell: Thermal Physics

Problem 22.2

The fugacity z is defined as $z = e^{\beta\mu}$. Using

$$\mu = k_B T \ln(n\lambda_{th}{}^3)$$

show that

$$z = n\lambda_{th}{}^3$$

for an ideal gas, and comment on the limits $z << 1$ and $z >> 1$.

((**Solution**))

The chemical potential is given by

$$\mu = k_B T \ln(\frac{N\lambda_T{}^3}{V}) = k_B T \ln(n\lambda_T{}^3)$$

The fugacity z is defined as

$$z = e^{\beta\mu}.$$

Then we have

$$\ln z = \beta\mu = \ln(n\lambda_T{}^3),$$

leading to the relation

$$z = n\lambda_T{}^3 = \frac{n}{n_Q},$$

where the quantum concentration n_Q is defined by

$$n_Q = \frac{1}{\lambda_T{}^3} = \left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2}.$$

For $z >> 1$ (high density limit; $n >> n_Q$): quantum effect (low temperatures)is dominant.
For $z << 1$ (low density limit: $n << n_Q$), classical effect (high temperatures)is dominant.

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2. Blundell-Blundell: Thermal Physics
Problem 21-4
An atom in a solid has two energy levels: a ground state of degeneracy g_1 and an excited state of degeneracy g_2 at an energy Δ above the ground state. Show that the partition function Z_{atom} is

$$Z_{atom} = g_1 + g_2 e^{-\beta\Delta}$$

Show that the heat capacity of the atom is given by

$$C = \frac{g_1 g_2 \Delta^2 e^{-\beta\Delta}}{k_B T^2 (g_1 + g_2 e^{-\beta\Delta})^2}$$

A monatomic gas of such atoms has a partition function given by

$$Z_N = \frac{(Z_1)^N}{N!}$$

where $Z_1 = Z_{atom} Z_{translation}$ and $Z_{translation} = \frac{V}{\lambda_{th}{}^3}$ is the partition function due to the translational motion of the gas atom. Show that the heat capacity of such a gas is

$$C = N[\frac{3}{2}k_B + \frac{g_1 g_2 \Delta^2 e^{-\beta\Delta}}{k_B T^2 (g_1 + g_2 e^{-\beta\Delta})^2}]$$

((**Solution**))
The particle partition function of atom is

$$Z_{atom} = g_1 + g_2 e^{-\beta\Delta}$$

The internal energy

$$U_{atom} = -\frac{\partial}{\partial \beta} \ln Z_{atom} = \frac{\Delta g_2 e^{-\beta\Delta}}{g_1 + g_2 e^{-\beta\Delta}}$$

The heat capacity:

$$\begin{aligned} C_{atom} &= \frac{dU_{atom}}{dT} \\ &= -\frac{1}{k_B T^2} \frac{dU_{atom}}{d\beta} \\ &= \frac{g_1 g_2 \Delta^2 e^{-\beta\Delta}}{k_B T^2 (g_1 + g_2 e^{-\beta\Delta})^2} \end{aligned}$$

The partition function of the system including the translational motion is

$$Z_{tot} = \frac{(Z_1)^N}{N!},$$

where

$$Z_1 = Z_{atom} Z_{translation}$$

and

$$Z_{translation} = \frac{V}{\lambda_{th}{}^3}.$$

We note that

$$\ln Z_{tot} = N \ln Z_1 - \ln N!$$

The internal energy:

$$U = -\frac{\partial}{\partial \beta} \ln Z_{tot}$$
$$= -N \frac{\partial}{\partial \beta} (\ln Z_{atom} + \ln \frac{V}{\lambda_{th}^3})$$
$$= -N \frac{\partial}{\partial \beta} \ln Z_{atom} + \frac{3}{2} N \frac{\partial}{\partial \beta} \ln \beta$$
$$= -N \frac{\partial}{\partial \beta} \ln Z_{atom} + \frac{3}{2} N k_B T$$

where

$$\lambda_{th} = \left(\frac{2\pi\hbar^2 \beta}{m} \right)^{1/2}, \qquad \ln \lambda_{th} = \frac{1}{2} [\ln \beta + \ln \left(\frac{2\pi\hbar^2}{m} \right)]$$

The heat capacity is obtained as

$$C = N[\frac{3}{2} k_B + \frac{g_1 g_2 \Delta^2 e^{-\beta\Delta}}{k_B T^2 (g_1 + g_2 e^{-\beta\Delta})^2}]$$

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3. Blundell-Blundell: Thermal Physics

Problem 21-6

Show that the single-particle partition function Z_1 of a gas of hydrogen atoms is given approximately by

$$Z_1 = Z_{translation} Z_{atom} = \frac{V}{\lambda_{th}^3} e^{\beta R}$$

where R = 13.6 eV and the contribution due to excited states has been neglected.

((Solution))

We assume that the energy of hydrogen atom is given by -R. The partition function of atom is given by

$$Z_{atom} = e^{\beta R}.$$

The partition function of hydrogen atom including the translational motion is given by

$$Z_1 = Z_{atom} Z_{translation}$$
$$= e^{\beta R} \frac{V}{\lambda_{th}{}^3}$$

where

$$Z_{translation} = \frac{V}{\lambda_{th}{}^3}$$

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4. Blundell and Blundell: Thermal Physics
Problem 20-8

The internal levels of an isolated hydrogen atom are given by $-\frac{R}{n^2}$, where R = 13.6 eV. The degeneracy of each level is given by $2n^2$.
(a) Sketch the energy levels.
(b) Show that

$$Z_{atom} = \sum_{n=1}^{\infty} 2n^2 \exp(\frac{\beta R}{n^2})$$

Note that when $T \neq 0$, this expression for Z_{atom} diverges. This is because of the large degeneracy of the hydrogen atom's highly excited states. If the hydrogen atom were to be confined in a box of finite size, this would cut off the highly excited states and Z_{atom} would not then diverge. By approximating Z_{atom} as follows:

$$Z_{atom} = \sum_{n=1}^{2} 2n^2 \exp(\frac{\beta R}{n^2})$$

i.e. by ignoring all but the n = 1 and n = 2 states estimate the mean energy of a hydrogen atom at 300 K.

((**Solution**))

n = 1, l = 0 (s) degeneracy = 1
total degeneracy = 2 x1 = 2 (factor 2; spin degeneracy)

$n = 2$ $\quad$ $l = 1$ (p) $\quad$ degeneracy = 3

$\quad$ $l = 0$ (s) $\quad$ degeneracy = 1

$\quad$ total degeneracy = 2 x 4 = 8 (factor 2; spin degeneracy)

$n = 3$ $\quad$ $l = 2$ (d) $\quad$ degeneracy = 5

$\quad$ $l = 1$ (p) $\quad$ degeneracy = 3

$\quad$ $l = 0$ (s) $\quad$ degeneracy = 1

$\quad$ total degeneracy = 2 x 9 = 18 (factor 2; spin degeneracy)

$$Z_{atom} = \sum_{n=1}^{\infty} 2n^2 \exp(\frac{\beta R}{n^2})$$

where $R = 13.6$ eV. When $T = 0$, Z diverges. For $T = 300\ K$, we assume that

$$Z_{atom} = \sum_{n=1}^{2} 2n^2 \exp(\frac{\beta R}{n^2}) = 2\exp(\beta R) + 8\exp(\frac{\beta R}{4})$$

The internal energy:

$$U = -\frac{\partial \ln Z_{atom}}{\partial \beta} = -R\left(\frac{\exp(\beta R) + \exp(\frac{\beta R}{4})}{\exp(\beta R) + 4\exp(\frac{\beta R}{4})}\right)$$

$$\beta R = 526.071$$

$U = -R$=-13.6 eV.

((**Mathematica**))

```
Clear["Global`*"];

rule1 = {eV → 1.602176487 × 10^-19, kB → 1.3806504 × 10^-23,
   h → 6.62606896 × 10^-34, ℏ → 1.05457162853 × 10^-34,
   T → 300, R → 13.6 eV};

h1 = R/(kB T) //. rule1

526.071

U11 = -((Exp[h1] + Exp[h1/4])/(Exp[h1] + 4 Exp[h1/4])) //. rule1

-1.
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5. Blundell-Blundell: Thermal Physics

Problem 22-5

If the partition function Z_N of a gas of N indistinguishable particles is given by

$$Z_N = \frac{(Z_1)^N}{N!}$$

where Z_1 is the single-particle partition function, show that the chemical potential is given by

$$\mu = -k_B T \ln\left(\frac{Z_1}{N}\right)$$

((**Solution**))

The partition function is given by

$$Z_{CN} = \frac{Z_{C1}{}^N}{N!}$$

$$
\begin{aligned}
F &= -k_B T \ln Z_{CN} \\
&= -k_B T \ln \frac{Z_{C1}{}^N}{N!} \\
&= -k_B T(N \ln Z_{C1} - \ln N!) \\
&= -k_B T[N \ln Z_{C1} - N \ln N + N)
\end{aligned}
$$

We note that

$$F = U - ST$$

$$
\begin{aligned}
dF &= dU - SdT - TdS \\
&= TdS - \mu dN - SdT - TdS \\
&= -\mu dN - SdT
\end{aligned}
$$

The chemical potential:

$$\mu = (\frac{\partial F}{\partial N})_T = -k_B T(\ln Z_{C1} - \ln N) = -k_B T \ln \frac{Z_{C1}}{N}$$

where

$$Z_{C1} = \frac{V}{\lambda_{th}{}^3} = V n_Q$$

and

$$\frac{1}{\lambda_{th}{}^3} = n_Q = \left(\frac{m k_B T}{2\pi\hbar^2}\right)^{3/2}, \qquad \lambda_{th} = \left(\frac{2\pi\hbar^2}{m k_B T}\right)^{1/2}.$$

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6. Blundell-Blundell

Problem 22-6

(a) Consider the ionization of atomic hydrogen governed by the equation

$$H = p^+ + e^-$$

where p^+ is a proton (equivalently a positively ionized hydrogen) and e^- is an electron. Explain why

$$\mu_H = \mu_p + \mu_e$$

Using the partition function for hydrogen atoms from Eq.(21.50), and using Eq.(22.92) show that

$$-k_B T \ln\left(\frac{Z_1^p}{N_p}\right) - k_B T \ln\left(\frac{Z_1^e}{N_e}\right) = -k_B T \ln\left(\frac{Z_1^H}{N_H} e^{\beta R}\right)$$

where Z_1^x and N_x are the single-particle partition function and number of particles for species *x*, and where R = 13.6 eV. Hence show that

$$\frac{n_e n_p}{n_H} = (\frac{2\pi m_e k_B T}{h^2})^{3/2} \exp(-\beta R) \qquad \textbf{(Saha equation)}$$

where $n_x = \frac{N_x}{N}$ is the number density of species *x*, stating any approximations you make. Equation (22.96 is known as the **Saha** equation.

(b) Explain why charge neutrality implies that $n_e = n_P$ and conservation of nucleus implies $n = n_H + n_P$, where *n* is the total number density of hydrogen (neutral and ionized). Writing $y = n_P / n$ as the degree of ionization, show that

$$\frac{y^2}{1-y} = \frac{1}{n} n_Q \exp(-\beta R)$$

Find the degree of ionization at 10000 K and density 10^{20} m^{-3}.

((**Solution**))

Chemical reaction:

$$H \rightarrow p^+ + e^-$$

$$\mu_H = \mu_P + \mu_e$$

or

$$-k_B T \ln\left(\frac{Z_1^H}{N_H} e^{\beta R}\right) = -k_B T \ln\left(\frac{Z_1^P}{N_P}\right) - k_B T \ln[\frac{Z_1^e}{N_e}]$$

where

$$\mu_H = -k_B T \ln[\frac{Z_1^H}{N_H} e^{\beta R}], \qquad \mu_P = -k_B T \ln[\frac{Z_1^P}{N_P}]$$

$$\mu_e = -k_B T \ln[\frac{Z_1^e}{N_e}]$$

Thus we have

$$\frac{N_P N_e}{N_H} e^{\beta R} = \frac{Z_1^P Z_1^e}{Z_1^H} = Z_1^e = V\left(\frac{m k_B T}{2\pi\hbar^2}\right)^{3/2}$$

or

$$\frac{n_P n_e}{n_H} = n_Q e^{-\beta R} = \left(\frac{m k_B T}{2\pi\hbar^2}\right)^{3/2} e^{-\beta R}$$

since $Z_1^P = Z_1^H$, where $n_P = \frac{N_P}{V}$, $n_e = \frac{N_e}{V}$, $n_H = \frac{N_H}{V}$, and

$$n_Q = \frac{1}{\lambda_{th}{}^3} = \left(\frac{m k_B T}{2\pi\hbar^2}\right)^{3/2}$$

We assume that *n* is the number density of nucleus.

$$n = n_H + n_P, \qquad n_P = n_e = ny$$

$$n_H = n - n_p = n(1-y)$$

Then we have

$$\frac{n^2 y^2}{n(1-y)} = n_Q \exp(-\beta R)$$

$$\frac{y^2}{1-y} = \frac{1}{n} n_Q \exp(-\frac{R}{k_B T})$$
$$= \frac{1}{n} (\frac{2\pi m k_B T}{h^2})^{3/2} \exp(-\frac{R}{k_B T})$$

where $R = 13.6$ eV. $n = 10^{14}$ cm^{-3}.

$$x = \frac{T(\mathrm{K})}{10^4}.$$

When $f(x=1) = 3.37886$, we have y =0.807174.

We make a ContourPlot of y vs x;

$$\frac{y^2}{1-y} = f(x)$$

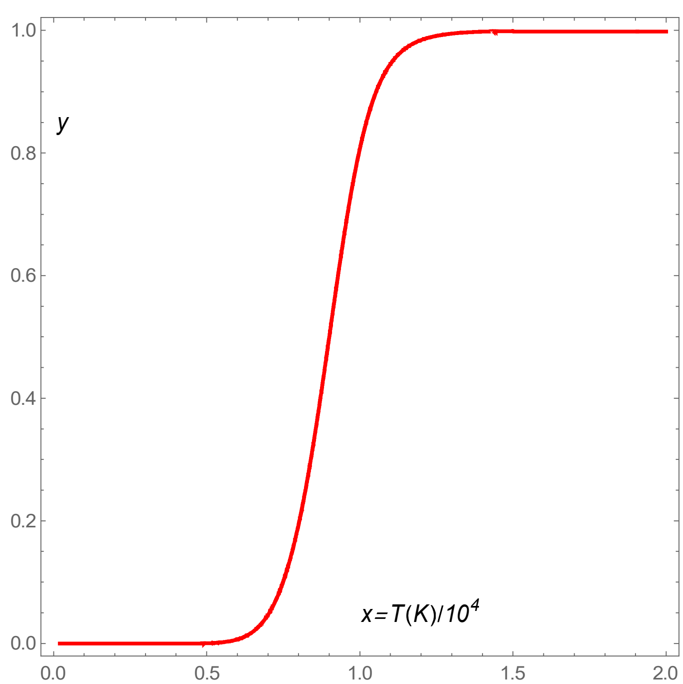

Fig. $n_P / n = y$ vs $x = T(K)/10^4$.

The fraction y increases with increasing temperature T.

((**Mathematica**))

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Clear["Global`*"];

rule1 = {kB → 1.3806504 × 10^-16, NA → 6.02214179 × 10^23,
   c → 2.99792 × 10^10, ℏ → 1.054571628 10^-27, h → 2 π ℏ,
   me → 9.10938215 10^-28, mp → 1.672621637 × 10^-24,
   mn → 1.674927211 × 10^-24, qe → 4.8032068 × 10^-10,
   eV → 1.602176487 × 10^-12, n1 → 10^14};

f1[T1_] :=
  1/n1 ((2 π me kB T)/h^2)^(3/2) Exp[-(13.6 eV)/(kB T)] /. {T → 10^4 T1} //.
   rule1

f1[1]

3.37886

eq1 = ContourPlot[y^2/(1 - y) == f1[x], {x, 0, 2},
  {y, 0, 1}, ContourStyle → {Red, Thick},
  PlotPoints → 300]
```