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Problem Set 1
Adsorption of a gas on a surface

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Reminder

Partition function of the grand-canonical ensemble

$\Xi(T, \mu, V)$ is the partition function of the grand-canonical ensemble, defined by

$$\Xi(T, \mu, V) \equiv \sum_l \exp[-\beta(E_l - \mu N_l)]$$

Grand potential

We define the grand potential Ω by

$$\Omega \equiv -k_B T \ln \Xi$$

Particles' number mean value

The mean value of the number of particles is defined by

$$\langle N \rangle \equiv \frac{N_l}{\Xi} \exp[-\beta(E_l - \mu N_l)]$$

Mean energy

$$\langle E \rangle = \sum_l \frac{E_l}{\Xi} \exp[-\beta(E_l - \mu N_l)]$$

Entropy

$$S = -\frac{\partial \Omega}{\partial T}$$

1 Statistical analysis of the adsorbed atoms

An ideal gas of N monatomic molecules with spin zero and mass m is contained in a box of constant volume V , maintained at the temperature T . The gas is in contact with a surface that can absorb molecules in A traps. In what follows, we assume that $N \gg A$. We call $-\epsilon_0$ the atom-trap binding energy, and it is assumed that only one atom can be adsorbed per trap.

(a) Which formalism is most suitable for studying the adsorbed atoms ? What is the relationship between the chemical potential μ_g of the gas and the one of the adsorbed atoms μ ?

The gas will play the role of a potential tank that will maintain the system made of atoms at a temperature T. We will study this system in the *grand-canonical ensemble*.
In order to have the system at an equilibrium state, it is needed to have $\mu = \mu_g$. If we were in the situation of multiple species in the system, then all the chemical potential associated with all the species should respect $\mu_i = \mu_{g_i}$.

(b) What is the sign of ϵ_0 ? Show that the total energy of the system can be written as

$$E = -\epsilon_0 \sum_{i=1}^{A} n_i$$

where n_i is the occupation number of the i^{th} trap. What are the possible values of n_i ?

The bonding energy between an atom and a trap is $-\epsilon_0$ and the energy of an atom has to be diminished if its trapped, we get that $\epsilon_0 > 0$ in order to have $-\epsilon_0$ to diminish the energy.

We suppose that if no atoms is trapped, then $E = 0$. There is A traps and there can be only one atom trapped by traps, so it means that $n_i = 0$ or $n_i = 1$. We can deduce that

$$E = -\epsilon_0 \sum_{i=1}^{A} n_i$$

We can also write

$$N_l = \sum_{i=1}^{A} n_i$$

(c) Calculate the grand-canonical partition function Ξ.

We wants to calculate the grand-canonical partition function Ξ,

$$\begin{aligned}
\Xi &= \sum_l \exp[-\beta(E_l - \mu N_l)] && \text{where } l = (n_1, ..., n_A) \\
&= \sum_{\{n_i\}} \exp\left[-\beta\left(-\epsilon_0 \sum_{j=1}^{A} n_j - \mu \sum_{j=1}^{A} n_j\right)\right] \\
&= \sum_{\{n_i\}} \exp\left[\beta(\epsilon_0 + \mu) \sum_{j=1}^{A} n_j\right] \\
&= \sum_{\{n_i\}} \prod_{j=1}^{A} \exp[\beta(\epsilon_0 + \mu) n_j] && \text{because it's discernable} \\
&= \prod_{j=1}^{A} \sum_{n_j=0}^{1} \exp[\beta(\epsilon_0 + \mu) n_j] \\
&= \prod_{j=1}^{A} (1 + \exp[\beta(\epsilon_0 + \mu)]) \\
&= (1 + \exp[\beta(\epsilon_0 + \mu)])^A
\end{aligned}$$

We are happy because Ξ does depend on the fixed quantities β, μ and A.

(d) Calculate the grand-canonical potential Ω. Deduce from the previous result the average number N_a of adsorbed atoms. Check your result by calculating N_a directly from Ξ.

$$\begin{aligned}
\Omega &= -k_B T \ln \Xi \\
&= -A k_B T \ln(1 + \exp[\beta(\epsilon_0 + \mu)])
\end{aligned}$$

If we write the grand-potential in thermodynamics we get,

$$\Omega = E - TS - N_a \mu$$

But in statistical physics, it then would be

$$\Omega = \langle E \rangle - T\langle S \rangle - \langle N_a \rangle \mu$$

Meaning that

$$\langle N_a \rangle = -\left(\frac{\partial \Omega}{\partial \mu}\right)_T$$

So we get,

$$\begin{aligned}\langle N_a\rangle &= +Ak_BT\frac{\partial}{\partial\mu}\left(\ln(1+\exp[\beta(\epsilon_0+\mu)])\right)\\ &= Ak_BT\frac{\beta\exp[\beta(\epsilon_0+\mu)]}{1+\exp[\beta(\epsilon_0+\mu)]}\\ &= \frac{A}{1+\exp[-\beta(\epsilon_0+\mu)]}\end{aligned}$$

> Let's get $\langle N_a\rangle$ from Ξ,
>
> $$\begin{aligned}\langle N_a\rangle &= \sum_l N_l P_l\\ &= \sum_l \frac{N_l}{\Xi}\exp[-\beta(\epsilon_0 E_l+\mu N_l)]\\ &= \frac{1}{\Xi}\sum_{\{n_i\}}(n_1+...+n_A)\exp[-\beta(\epsilon_0+\mu)(n_1+...+n_A)]\\ &= \frac{1}{\Xi}\frac{1}{\epsilon_0+\mu}\frac{\partial}{\partial\beta}\sum_{\{n_i\}}\exp[-\beta(\epsilon_0+\mu)(n_1+...+n_A)]\\ &= \frac{1}{\Xi}\frac{1}{\epsilon_0+\mu}\frac{\partial}{\partial\beta}\left(1+\exp[\beta(\epsilon_0+\mu)]\right)^A\\ &= \frac{1}{\Xi}\frac{\epsilon_0+\mu}{\epsilon_0+\mu}A\exp[\beta(\epsilon_0+\mu)]\left(1+\exp[\beta(\epsilon_0+\mu)]\right)^{A-1}\\ &= \frac{A\exp[\beta(\epsilon_0+\mu)]}{1+\exp[\beta(\epsilon_0+\mu)]}\\ &= \frac{A}{1+\exp[-\beta(\epsilon_0+\mu)]}\end{aligned}$$

So,

$$\langle N_a\rangle = \frac{A}{1+\exp[-\beta(\epsilon_0+\mu)]}$$

(e) Calculate the ensemble-average energy of the adsorbed atoms.

$$\langle E\rangle = \left\langle\sum_{i=1}^{A} n_i(-\epsilon_0)\right\rangle = -\epsilon_0\langle N_a\rangle = -\frac{A\epsilon_0}{1+\exp[-\beta(\epsilon_0+\mu)]}$$

(f) Deduce from the previous results the expression of the entropy S_a of the adsorbed atoms as a function of A and N_a. Comment on your result.

$$S_a = -\left(\frac{\partial\Omega}{\partial T}\right)_\mu = \frac{1}{T}\left[\langle E\rangle - \mu\langle N_a\rangle - \Omega\right]$$

$$\begin{aligned}
S_a &= -\frac{\partial}{\partial T}\left(-k_B T\ln\{(1+\exp[\beta(\epsilon_0+\mu)])^A\}\right)\\
&= \frac{\partial}{\partial T}\left(Ak_B T\ln(1+\exp[\beta(\epsilon_0+\mu)])\right)\\
&= Ak_B\ln(1+\exp[\beta(\epsilon_0+\mu)]) + Ak_B T\frac{\partial}{\partial T}\ln(1+\exp[\beta(\epsilon_0+\mu)])\\
&= Ak_B\ln(1+\exp[\beta(\epsilon_0+\mu)]) - Ak_B T k_B\beta^2\frac{\partial}{\partial \beta}\ln(1+\exp[\beta(\epsilon_0+\mu)])\\
&= Ak_B\ln(1+\exp[\beta(\epsilon_0+\mu)]) - Ak_B\beta(\epsilon_0+\mu)\exp[\beta(\epsilon_0+\mu)]\frac{1}{1+\exp[\beta(\epsilon_0+\mu)]}\\
&= Ak_B\left(\ln(1+\exp[\beta(\epsilon_0+\mu)]) - \frac{\beta(\epsilon_0+\mu)}{1+\exp[-\beta(\epsilon_0+\mu)]}\right)\\
&= -k_B\langle N_a\rangle\ln\left(\frac{\langle N_a\rangle}{A-\langle N_a\rangle}\right) + Ak_B\ln\left(\frac{A}{A-\langle N_a\rangle}\right)\\
&= k_B\ln\left(\frac{A!}{\langle N_a\rangle!(A-\langle N_a\rangle)!}\right)
\end{aligned}$$

Which does look like the micro-canonical entropy.

2 Thermodynamical properties

Within the Maxwell–Boltzmann approximation, the free energy of the ideal gas described in the introduction of the Problem takes the form

$$F = Nk_BT\left[\ln\left(\frac{N}{V}\Lambda_T^3\right) - 1\right] \tag{1}$$

where $\Lambda_T = (2\pi\hbar^2/mk_BT)^{1/2}$ is the thermal de Broglie wavelength.

(a) Quickly rederive the result of Eq. (1).

The gas is at temperature T and number of particles N constant, so we are in the situatipon of the canonical ensemble. So,

$$Z = \frac{1}{N!}z^N$$

with Z the partition function of the system for the N particles and z the partition function for one particle.

$$\begin{aligned} z &= \frac{1}{\hbar^3}\int \mathrm{d}^3\vec{x}\mathrm{d}^3\vec{p}\exp\left(-\beta\left(\frac{\vec{p}^2}{2m}\right)\right) \\ &= \frac{V}{\hbar^3}\left(\frac{2m}{\beta}\right)^{3/2}\int \mathrm{d}^3\vec{p}\exp\left(-\vec{p}^2\right) \\ &= \frac{V}{\hbar^3}\left(\frac{2m}{\beta}\right)^{3/2}\pi^{3/2} \end{aligned}$$

So,

$$Z = \frac{1}{N!}\left(V\left(\frac{2mk_BT\pi}{\hbar^2}\right)^{3/2}\right)^N$$

$$\begin{aligned} F^c = k_BT\ln(Z) &= k_BT\ln\left(\frac{1}{N!}\left(V\left(\frac{2mk_BT\pi}{\hbar^2}\right)^{3/2}\right)^N\right) \\ &= -k_BT\left(N\ln V - N\ln\Lambda_T^3 - N\ln N + N\right) \\ &= Nk_BT\left(\ln\left(\frac{N}{V}\Lambda_T^3\right) - 1\right) \end{aligned}$$

(b) Give a definition of the adsorbtion rate of the gas θ. Show that it takes the form

$$\theta = \frac{P}{P + P_0(T)}$$

where P is the pressure of the gas. Give an expression for $P_0(T)$ as a function of the parameters of the problem.

The adsorbtion rate of the gas θ is the number of atom adsorbed divided by the total number of traps

$$\theta = \frac{N_a}{A}$$

So,

$$\theta = \frac{1}{1 + \exp[-\beta(\epsilon_0 + \mu)]}$$

The gas is at the temperature T and its particle number is constant. As $\mu = \mu_g$, let's look for μ_g and get an other expression of θ as defined before.

$$\begin{aligned}\mu = \frac{\partial F}{\partial N} &= k_B T \left[\ln\left(\frac{N}{V}\Lambda_T^3\right) - 1\right] + k_B T \\ &= k_B T \ln\left(\frac{N}{V}\Lambda_T^3\right)\end{aligned}$$

$$\begin{aligned}p = -\frac{\partial F}{\partial V} &= \frac{\partial}{\partial V}\left(N k_B T \left[\ln\left(\frac{V}{N}\frac{1}{\Lambda_T^3}\right) + 1\right]\right) \\ &= \frac{N k_B T}{V}\end{aligned}$$

$$\begin{aligned}\theta &= \frac{1}{1 + \exp\left[-\beta\left(\epsilon_0 - k_B T \ln\left(\frac{V}{N}\frac{1}{\Lambda_T^3}\right)\right)\right]} \\ &= \frac{1}{1 + \exp[-\beta\epsilon_0]\exp\left[\ln\left(\frac{V}{N}\frac{1}{\Lambda_T^3}\right)\right]} \\ &= \frac{1}{1 + \exp[-\beta\epsilon_0]\left(\frac{N\Lambda_T^3}{V}\right)^{-1}}\end{aligned}$$

$$\begin{aligned}\frac{N}{V}\Lambda_T^3 &= \frac{N}{V}\left(\frac{2\pi\hbar^2}{m k_B T}\right)^{3/2}\frac{k_B T}{k_B T} \\ &= p\frac{(2\pi)^{3/2}\hbar^3}{m^{3/2}(k_B T)^{5/2}} \\ &= \frac{p}{\alpha(T)}\end{aligned}$$

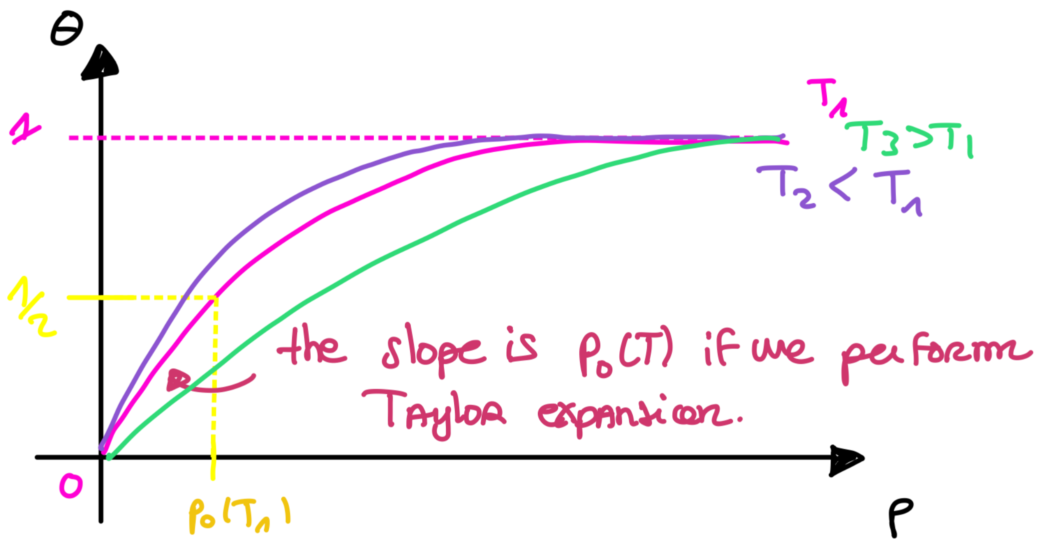
with

$$\alpha(T) = \frac{m^{3/2}(k_B T)^{5/2}}{(2\pi)^{3/2}\hbar^3}$$

So,

$$\begin{aligned}\theta &= \frac{1}{1 + \frac{\alpha(T)\exp[-\beta\epsilon_0]}{p}} \\ &= \frac{p}{p + \alpha(T)\exp[-\beta\epsilon_0]} \\ &= \frac{p}{p + p_0(T)} \qquad\qquad p_0(T) = \left(\frac{m}{2\pi\hbar^2}\right)^{3/2}(k_B T)^{5/2}\end{aligned}$$

(c) Plot the curves $\theta(P)$, called the Langmuir adsorbtion isotherms, for different values of the temperature T.



(d) Calculate the ensemble-average energy E_T of the total system.

$$\langle E_g\rangle = k_B T^2 \frac{\partial \ln Z}{\partial T} = -k_B T^2 \frac{\partial}{\partial T}\left(N \ln\left(\frac{N}{V}\lambda_T^3\right)\right)$$
$$= -\frac{3Nk_B T^2}{\Lambda_T}\frac{\partial \Lambda_T}{\partial T}$$

We know that

$$\Lambda_T \propto \frac{\text{coef}}{T^{1/2}} \Longrightarrow \frac{\partial}{\partial T}\Lambda_T \propto -\frac{1}{2}\frac{\text{coef}}{T^{3/2}} = -\frac{\Lambda_T}{2T}$$

So,

$$\langle E_g \rangle = +\frac{3Nk_BT}{2}$$

$$\begin{aligned}
\langle E_{\text{tot}} \rangle &= \langle E \rangle + \langle E_g \rangle \\
&= \frac{3}{2}(N - N_a)k_BT - \frac{A\epsilon_0}{1 + \exp[-\beta(\epsilon_0 + \mu)]} \\
&= \frac{3}{2}\left(N - \frac{A}{1 + \exp[-\beta(\epsilon_0 + \mu)]}\right)k_BT - \frac{A\epsilon_0}{1 + \exp[-\beta(\epsilon_0 + \mu)]} \\
&= \frac{3}{2}Nk_BT - \frac{\frac{3}{2}k_BT + \epsilon_0}{1 + \exp[-\beta(\epsilon_0 + \mu)]}A \\
&= \frac{3}{2}Nk_BT - \frac{3}{2}N_ak_BT - A\epsilon_0
\end{aligned}$$

Which we can rewrite,

$$\langle E_{\text{tot}} \rangle = \frac{3}{2}Nk_BT - \frac{3}{2}N_ak_BT - N_a\epsilon_0$$

(e) Deduce from the previous question the heat capacity of the total system C_V . (In your calculation, do not seek for an explicit expression of $\mathrm{d}Na/\mathrm{d}T$). Interprete your result.

$$C_V = \frac{\partial \langle E \rangle}{\partial T} = \frac{3}{2}k_B - \frac{3}{2}N_ak_B - \frac{\mathrm{d}N_a}{\mathrm{d}T}\left[\frac{3}{2}k_BT + \epsilon_0\right]$$

$$\begin{aligned}
\frac{3}{2}k_B &\longrightarrow \text{ system without any adsorbtion.} \\
-\frac{3}{2}N_ak_B &\longrightarrow \text{ absence of } N_a \text{ atoms.} \\
\frac{\mathrm{d}N_a}{\mathrm{d}T}\left[\frac{3}{2}k_BT + \epsilon_0\right] &\longrightarrow \text{ the traps are diminishing the energy.}
\end{aligned}$$