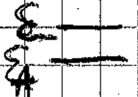
# TD 5 : Canonical ensemble

## 5.1) Crystal of spin 1/2

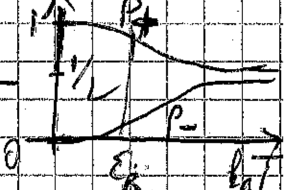


$\varepsilon_\pm = \mp \varepsilon_B$ with $\varepsilon_B = \gamma \hbar B/2 = m_0 B$

1) microstates of the crystal of spins $\{|\pm\rangle_1 \otimes |\pm\rangle_2 \otimes - - \otimes |\pm\rangle_N\}$

N spins independent
$$Z = \sum_{\sigma_1} \text{—} \sum_{\sigma_N} e^{-\beta \sum_{i=1}^{N} \sigma_i B} \quad \text{where } \varepsilon_i = \pm m_0$$
$$= \sum_{\sigma_1} e^{-\beta \sigma_1 B} \sum_{\sigma_2} e^{-\beta \sigma_i B} \text{—} \sum_{\sigma_N} e^{-\beta \sigma_N B} = (z_{spin})^N$$

$z_{spin} = 2\cosh \beta\varepsilon_B$ & $p_\pm = \dfrac{e^{-\beta \varepsilon_\pm}}{z_{spin}} = \dfrac{e^{\pm \beta \varepsilon_B}}{z_{spin}}$



When $T \to 0$, all spins are in the ground state $|+\rangle_1 \otimes — |+\rangle_N$

At $T \gg \varepsilon_B$, all states are equiprobable and $p_+ = p_- = 1/2$

2) $Z = (2\cosh \beta\varepsilon_B)^N$
$$\overline{E}^c = -\frac{\partial}{\partial \beta} \ln Z = \boxed{-N\varepsilon_B \tanh(\beta\varepsilon_B)}$$
$$\Leftrightarrow -\frac{\overline{E}^c}{N\varepsilon_B} = \frac{e^{2\beta\varepsilon_B} - 1}{e^{2\beta\varepsilon_B} + 1} \Leftrightarrow e^{2\beta\varepsilon_B} = \frac{1 - \frac{\overline{E}^c}{N\varepsilon_B}}{1 + \frac{\overline{E}^c}{N\varepsilon_B}}$$
$$\Leftrightarrow \frac{1}{T} = \frac{k_B}{2\varepsilon_B} \ln \frac{N\varepsilon_B - \overline{E}^c}{N\varepsilon_B + \overline{E}^c} = -\frac{k_B}{\varepsilon_B} \operatorname{argtanh}\left(\frac{\overline{E}^c}{N\varepsilon_B}\right)$$

$\Rightarrow$ corresponds to $T^*(E)$ if we replace $E$ by $\overline{E}^c$

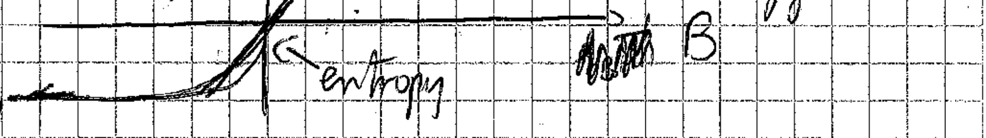
This illustrates the equivalence between ensembles!

3) $M = m_0 \overline{\sum_i \sigma_i} = -\dfrac{\partial F}{\partial B}$

or here (far simpler), $\overline{E}^c = -MB$ because the energy is only magnetic

$$\Rightarrow M = N m_0 \tanh(\beta\varepsilon_B)$$

For $\varepsilon_B \ll k_B T$
$M \sim 0$
For $\varepsilon_B \gg k_B T \to M = \pm N m_0$



Notice that in the $B \to 0$ regime, $M \simeq \chi(T) \cdot B$

where $\chi(T) = \frac{N m_0^2}{k_B T}$ (Curie law)

At large $B$, magnetization saturates

4) We have already commented about the equivalence of $T^*(\epsilon)$ and $T(\bar{E}^c)$

We see that the canonical ensemble allows access quickly to the results

Notice also that the use of canonical ensemble assumes the set of spins to be in equilibrium with a bath (typically the phonons)

Therefore $T = T_{ph}$

## 5.2) Monoatomic gas

Ideal gas treated classically

$$Z = \frac{1}{N!} \frac{1}{h^D} \int \prod_{i=1}^{D} dq_i \, dp_i \, e^{-\beta H(\{q_i, p_i\})}$$

where $D \equiv$ nb of degrees of freedom

1) The atoms are independent $\to D = 3N$ in dimension 3

$$Z = \frac{1}{N!} \left( Z_{atome} \right)^N$$

$$\text{with} \quad Z_{atom} = \frac{1}{h^3} \int dq_x dp_x \, dq_y dp_y \, dq_z dp_z \, e^{-\beta \left( \frac{\vec{p}^2}{2m} \right)}$$

$$= \frac{V}{h^3} \left( \int dp \; e^{-\beta p^2/2m} \right)^3$$

$$= \frac{V}{h^3} \, {}^{3/2}\!\sqrt{2\pi m k_B T} = \frac{V}{\left( \sqrt{\frac{2\pi \hbar^2}{m k_B T}} \right)^3} = \frac{V}{\Lambda_T^3}$$

$$\text{where } \Lambda_T = \left( \frac{2\pi \hbar^2}{m k_B T} \right)^{1/2}$$

Using Stirling $Z \approx e^N \left( \frac{Z_{atom}}{N} \right)^N$ where $Z_{atom} = \frac{V}{\Lambda_T^3}$

A.N $\Lambda_T = \left( \frac{2\pi \, 10^{-68}}{4 \cdot (1.67 \, 10^{-27})(1.38 \, 10^{-23})(300)} \right)^{1/2} \sim 5 \, 10^{-11} \, m$

2) $F = -k_BT\ln Z = -Nk_BT\left\{\ln\left[\frac{V}{N\Lambda_T^3}\right]+1\right\} = Nk_BT\left\{\ln(n\Lambda_T^3)-1\right\}$

Free energy/particle $f = \frac{F}{N} = k_BT\left\{\ln(n\Lambda_T^3)-1\right\}$.

$\hookrightarrow$ density $\frac{N}{V}$ (e-density)

3) $\overline{E}^c = -\frac{\partial}{\partial\beta}\ln Z = \frac{-\partial}{\partial\Lambda_T}\ln Z\,\frac{\partial\Lambda_T}{\partial\beta} = \frac{3N}{\Lambda_T}\frac{\partial}{\partial\beta}\left(\frac{2\pi\hbar^2}{m}\beta\right)^{1/2} = \frac{3N}{2\Lambda_T}\cdot\frac{\Lambda_T}{\beta} = \frac{3N}{2\beta}$

$$\Rightarrow \overline{E}^c = \frac{3N}{2}k_BT \,\|$$

$$C_V = \frac{\partial}{\partial T}\overline{E}^c = \frac{3}{2}Nk_B$$

$$var(E) = \overline{E^2}^c - (\overline{E}^c)^2 = \frac{\partial^2\ln Z}{\partial\beta^2} = -\frac{\partial}{\partial\beta}\overline{E}^c$$

Using $T\frac{\partial}{\partial T} = -\beta\frac{\partial}{\partial\beta} \Rightarrow var(E) = \frac{T}{\beta}\frac{\partial}{\partial T}\overline{E}^c$

$$\underline{var(E) = k_BT^2C_V}\,\| \Leftrightarrow C_V = \frac{1}{k_BT^2}var(E)$$

$$var(E) = \frac{3}{2}(k_BT)^2N$$

$\hookrightarrow \sigma_E = k_BT\sqrt{\frac{3}{2}N} \Rightarrow \frac{\sigma_E}{\overline{E}^c} \sim \frac{1}{\sqrt{N}}$ negligible

4) $p^c = -\frac{\partial F}{\partial V} = Nk_BT/V = nk_BT \rightarrow$ recover perfect gas

5) $S^c = -\frac{\partial F}{\partial T} = Nk_B\left\{\ln\left(\frac{V}{N\Lambda_T^3}\right)+\frac{5}{2}\right\}$

$\rightarrow$ recover Sackur-Tetrode

6) $\mu^c = \frac{\partial F}{\partial N} = k_BT\ln\left(\frac{N}{V}\Lambda_T^3\right) = k_BT\ln\left(n\Lambda_T^3\right)$

7) We want $S \geq 0 \rightarrow \ln\left(\frac{1}{n\Lambda_T^3}\right) > 0 \Rightarrow n\Lambda_T^3 < 1$

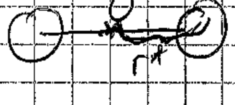
$$\Leftrightarrow \underline{n < n^* = \Lambda_T^{-3}}\,\|$$

equivalently $n\left(\frac{2\pi\hbar^2}{mk_BT}\right)^{1/2} < 1$

$$\rightarrow \frac{2\pi\hbar^2}{mk_BT} < \frac{1}{n^2} \Rightarrow T > T^* = \frac{2\pi n^2\hbar^2}{mk_B}\,\|$$

## 5.3) The diatomic perfect gas

1) $$H = \frac{\vec{P}^2}{2M} + \frac{\vec{l}^2}{2I} + \frac{p_r^2}{2m_r} + \frac{1}{2} m\omega^2 (r-r_*)^2 - E_{\text{bonding}}$$



$$= H_{\text{transl}} + H_{\text{rot}} + H_{\text{vib}} - E_{\text{bonding}}$$

$H_{\text{transl}} \to E_k = \frac{\hbar^2 k_n^2}{2M}$ with $k_n = \frac{2\pi p}{L}$ for $V = L^3$, $p \in \mathbb{N}$

$H_{\text{rot}} \to E_\ell = \frac{\hbar^2 \ell(\ell+1)}{2I}$ with $\ell \in \mathbb{N}$ and degeneracy $g_\ell = 2\ell+1$

$H_{\text{vib}} \to E_n = \hbar\omega(n+\frac{1}{2})$ with $n \in \mathbb{N}$ (degeneracy 1)

$$Z = \frac{z_{\text{mol}}^N}{N!} \text{ with } z_{\text{mol}} = \int \frac{d^3\vec{p}\, d^3\vec{R}}{(2\pi\hbar)^3} \sum_{\ell,n=0}^{\infty} (2\ell+1) e^{-\beta\left(\frac{p^2}{2m} + E_\ell + E_n\right)} e^{\beta E_{\text{bond}}}$$

$$= z_{\text{trans}}\, z_{\text{rot}}\, z_{\text{vib}}\, e^{\beta E_{\text{bond}}}$$

Comes from separability of the Hamiltonian

$$z_{\text{rot}} = \sum_\ell (2\ell+1) e^{-\beta\hbar^2 \ell(\ell+1)/2I} \; ; \; z_{\text{vib}} = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega(n+\frac{1}{2})}$$

$$z_{\text{trans}} = \frac{V}{h^3} \int d^3p\, e^{-\frac{\beta p^2}{2m}} = \frac{V}{\Lambda_T^3} \text{ with } \Lambda_T = \frac{h}{\sqrt{2\pi m k_B T}} = \sqrt{\frac{2\pi\hbar^2}{m k_B T}}$$

2) High T limit

$$z_{\text{vib}} = \sum_n e^{-\beta\hbar\omega(n+\frac{1}{2})} \simeq \int_0^{+\infty} dn\, e^{-\beta\hbar\omega n} = \frac{k_B T}{\hbar\omega} = \frac{T}{T_{\text{vib}}}$$

$$z_{\text{rot}} = \sum_\ell (2\ell+1) e^{-\beta\hbar^2 \frac{\ell(\ell+1)}{2I}} \simeq \int_0^{+\infty} d\ell\, (2\ell+1) e^{-\frac{\beta\hbar^2}{2I}\ell(\ell+1)}$$

$$\simeq \int_0^{+\infty} du\, e^{-\frac{\beta\hbar^2}{2I} u} = \frac{k_B T}{\hbar^2/2I} = \frac{T}{T_{\text{rot}}}$$

We expect this approx to be valid

when $T \gg \max(T_{\text{vib}}, T_{\text{rot}})$

b) $\overline{E}_{vib} = -N\frac{\partial \ln z_{vib}}{\partial \beta} = N\frac{\partial}{\partial \beta}\ln(\hbar\omega\beta) = k_B T N$

$\Rightarrow C_{vib} = k_B \cdot N$ (equipartit° of energy)

$\overline{E}_{rot} = k_B T \cdot N \Rightarrow C_{rot} = N k_B$ (equipartit° ——)

$E_{transl} = \frac{3}{2} N k_B T \rightarrow C_{tran} = \frac{3}{2} N k_B$

$C_{V,total} = \frac{7}{2} N k_B$

in agreement with experiment for $T \gg \max(T_{rot}, T_{vib})$

$\Rightarrow$ Actually, at very high T, the agreement is not that good

The exp. curve seems to go higher than $\frac{7}{2} N k_B$

$\Rightarrow$ it means we excite new d° of freedom that we have neglected: $T \sim 10^4 K \sim O(eV) \rightarrow$ comparable to electronic energy scales

$\Rightarrow$ we can start exciting electrons from their ground states!

3) Quantum freezing

a) If $k_B T \ll \hbar\omega$ or $k_B T \ll \frac{\hbar^2}{2I}$

The system is in the ground state

We expect $\begin{cases} E_{rot} \simeq 0 & (l=0) \\ E_{vib} \simeq \hbar\omega/2 & (n=0) \end{cases}$

b) $z_{vib} = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega(n+\frac{1}{2})} = \frac{e^{-\beta\hbar\omega/2}}{1-e^{\beta\hbar\omega}} = \frac{1}{2\,\mathrm{sh}(\beta\frac{\hbar\omega}{2})}$

$\overline{\varepsilon}_{vib} = -\frac{\partial}{\partial\beta}\ln z_{vib} = \frac{\hbar\omega}{2}\coth\left(\beta\frac{\hbar\omega}{2}\right) = \hbar\omega\left(\bar{n} + \frac{1}{2}\right)$

with $\bar{n} = \frac{1}{e^{\beta\hbar\omega} - 1}$

If $k_B T \ll \hbar\omega \Rightarrow \bar{n} \simeq e^{-\beta\hbar\omega}$

$\overline{\varepsilon}_{vib} \simeq \frac{\hbar\omega}{2}\left(1 + 2e^{-\beta\hbar\omega}\right)$

Actually, we could have recovered this result by writing

$$Z_{vib} \simeq e^{-\beta\frac{\hbar}{2}\omega} + e^{-\frac{3}{2}\beta\hbar\omega} = e^{-\beta\hbar\omega/2}\left(1+e^{-\beta\hbar\omega}\right)$$

$$E_{vib} \simeq -\frac{\partial}{\partial\beta}\left(-\frac{\beta\hbar\omega}{2} + \ln\left(1+e^{-\beta\hbar\omega}\right)\right) = \frac{\hbar\omega}{2} + \hbar\omega e^{-\beta\hbar\omega}$$

Basically, we took into account the ground state and 1st excited state

We can therefore do the same for $E_{rot}$

$$Z_{rot} \simeq 1 + 3e^{-\beta\hbar^2/I} \rightarrow E_{rot} = -\frac{\partial}{\partial\beta}\ln\left(1+3e^{-\beta\hbar^2/I}\right) \simeq +\frac{3\hbar^2}{I}e^{-\beta\hbar^2/I}$$

c) Assume $\frac{\hbar^2}{I} \ll \hbar\omega$

$$C_{vib} = \frac{\partial E_{vib}}{\partial T}N = Nk_B\left(\frac{\hbar\omega}{k_BT}\right)^2 e^{-\frac{\hbar\omega}{k_BT}}$$

$$C_{rot} = 3\left(\frac{\hbar^2}{k_BTI}\right)^2 Nk_B e^{-\frac{\hbar^2}{Ik_BT}}$$

We expect three plateaus for $T \ll T_{rot} = \frac{\hbar^2}{2k_BI} \rightarrow C_V \rightarrow 3/2$

$T_{rot} \ll T < T_{vib} = \frac{\hbar\omega}{k_B} \rightarrow C_V \sim 5/2$

$T \gg T_{vib} \longrightarrow C_V \rightarrow 7/2$

$\sim$ more or less in agreement with the plot (except the overshooting around $T_{rot}$ which can be also obtained theoretically by ~~[illegible]~~ really plotting $C_{vib}$

## 4) The Langevin paramagnet

N atoms with a magnetic moment $\vec{m}$ → classical

1) $H_{mag} = -\vec{m}\cdot\vec{B} = -m_0 B\cos\theta$ with $m_0 = \|\vec{m}\|$

$$H = \frac{1}{2I}\left(p_\theta^2 + \frac{p_\varphi^2}{\sin^2\theta}\right) + H_{mag} \rightarrow \underline{\text{Ham separable}}$$

This can be found from classical mechanics: $\vec{u_r} = (\cos\varphi\,\vec{u_x} + \sin\varphi\,\vec{u_y})\sin\theta + \cos\theta\,\vec{u_z}$

$$\vec{r} = R\,\vec{u_r}$$

$$\hookrightarrow \dot{\vec{r}} = R\left(\dot\theta\,\vec{u_\theta} + \dot\varphi\sin\theta\,\vec{u_\varphi}\right)$$

$$E_{cin} = \frac{1}{2}m\dot{\vec{r}}^2 = \frac{1}{2}\underbrace{mR^2}_{I}\left(\dot\theta^2 + \sin^2\theta\,\dot\varphi^2\right) = \frac{1}{2I}\left(p_\theta^2 + \frac{p_\varphi^2}{\sin^2\theta}\right)$$

Phase space: $\begin{cases}\theta\in[0,\pi] \,;\, \varphi\in[0,2\pi] \\ p_\theta\in\mathbb{R} \,;\, p_\varphi\in\mathbb{R}\end{cases}$

$(\theta, p_\theta); (\varphi, p_\varphi) \rightarrow h^2$

$$z = \frac{1}{h^2}\int_0^\pi d\theta\int_0^{2\pi}d\varphi\int_{-\infty}^{+\infty}dp_\theta\int_{-\infty}^{+\infty}dp_\varphi\, e^{-\beta\left(H(\theta,\varphi,p_\theta,p_\varphi)\right)} = z_{kin}^{(B=0)}\, z_{mag}$$

$\underline{\text{For } B=0}$ $z = z_{kin} = \frac{1}{h^2}\int_0^\pi d\theta\int_0^{2\pi}d\varphi \times \sqrt{\frac{2\pi I}{\beta}}\sqrt{\frac{2\pi I\sin^2\theta}{\beta}} = \frac{(2\pi I)}{\beta h^2}\times 2\pi\underbrace{\int_0^\pi d\theta\sin\theta}_{2}$

$$z_{kin} = \frac{8\pi^2 I}{\beta h^2} = \frac{8\pi^2 mR^2}{\beta h^2} = \frac{4\pi R^2}{\Lambda_T^2} \quad (\text{here } I = mR^2)$$

$$\Lambda_T = \left(\frac{2\pi m k_B T}{h^2}\right)^{-\frac{1}{2}}$$

In general: $z = \frac{1}{h^2}\int_0^\pi d\theta\int_0^{2\pi}d\varphi \times \frac{2\pi I}{\beta}\times\sin\theta\, e^{\beta m_0 B\cos\theta}$

$$= z_{kin}\left(\frac{1}{4\pi}\right)\int_0^\pi d\theta\int_0^{2\pi}d\varphi\,\sin\theta\, e^{\beta m_0 B\cos\theta}$$

$$= z_{kin}\frac{-1}{2\beta m_0 B}\left[e^{\beta m_0 B\cos\theta}\right]_0^\pi = z_{kin}\underbrace{\text{sinhc}(\beta m_0 B)}_{z_{mag}}$$

where $\text{sinhc}(x) = \frac{\sinh(x)}{x} \xrightarrow[x\to 0]{} 1$

2)

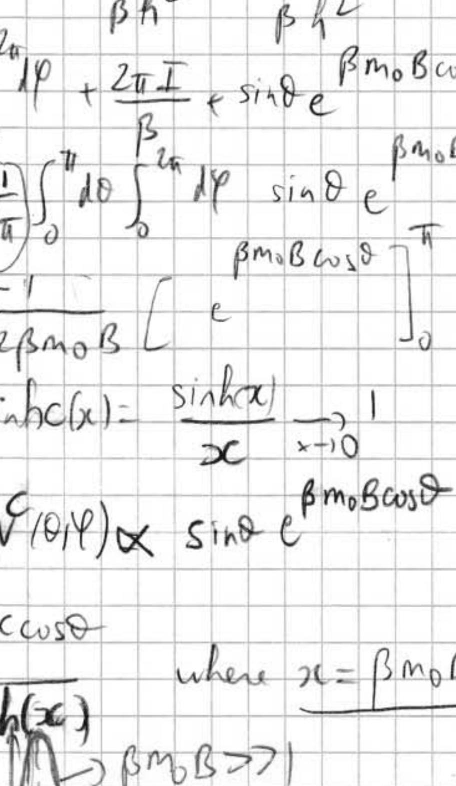
$\rho^c(\theta,\varphi) \propto \int d\theta d\varphi \int dp_\theta\, e^{\dots} \rightarrow W^c(\theta,\varphi) \propto \sin\theta\, e^{\beta m_0 B\cos\theta}$ We fix the normalization by $\int_0^\pi d\theta\int_0^{2\pi}d\varphi\, W^c(\theta,\varphi) = 1$

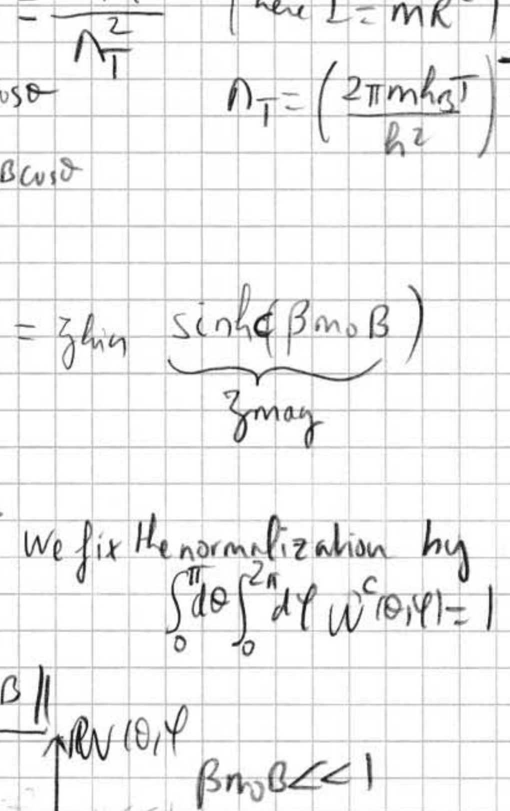
$$W^c(\theta,\varphi) = \frac{x\sin\theta\, e^{x\cos\theta}}{4\pi\sinh(x)} \quad \text{where } \underline{x = \beta m_0 B}\,\|$$

High T: $W(\theta,\varphi) \sim \sin(\theta)/4\pi$

low T: $W(\theta,\varphi) \sim \frac{x\theta}{4\pi}e^{-\frac{x\theta^2}{2}}$

Gaussian





3) $\vec{M}$ and $\vec{B}$ are conjugate variabl. $E = -\vec{\mu}\cdot\vec{B}$

$$\begin{cases} dE = TdS - pdV - MdB \\ dF = -SdT - pdV - MdB \Rightarrow M = -\dfrac{\partial F}{\partial B} \end{cases}$$

More specifically

Here $\vec{M}$ is along $\vec{u_z}$ by symmetry.

$$\langle m_z \rangle = m_0 \langle \cos\theta \rangle = \frac{m_0}{z_{mag}} \int d\Omega \cos\theta \, e^{\beta m_0 B \cos\theta}$$

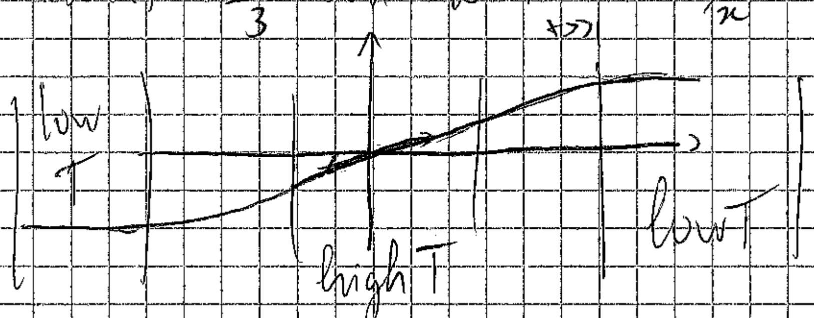
$$= m_0 \frac{\partial}{\partial(\beta m_0 B)} \int d\Omega \, e^{\beta m_0 B \cos\theta}$$

$$= \frac{1}{\beta} \frac{\partial}{\partial B} \ln z_{mag} = -\frac{\partial F}{\partial B} \rightarrow \underline{\text{general}}$$

$$\langle m_z \rangle = \frac{1}{\beta}\frac{\partial}{\partial B} \ln\left(\frac{\sinh(\beta m_0 B)}{\beta m_0 B}\right) = m_0 \frac{\partial}{\partial x}\left(\ln\left(\frac{\sinh(x)}{x}\right)\right)$$

$$\underline{\langle m_z \rangle = m_0 \mathcal{L}(x)} \Big\| \text{ where } \mathcal{L}(x) = \coth(x) - \frac{1}{x}$$

4) $\mathcal{L}(x) \underset{}{\overset{x\to 0}{\sim}} \frac{x}{3}$ and $\mathcal{L}(x) \underset{x\gg 1}{\sim} 1 - \frac{1}{x}$ $\quad (\mathcal{L}(-x) = -\mathcal{L}(x))$



high T : $M \simeq N m_0^2 \frac{B}{k_B T}$ $\quad$ Curie law

## 5.5 Brillouin paramagnet

$\vec{m} = g\mu_B \vec{J}/\hbar$ $\qquad J_z = m\hbar$ with $m \in [-J, J]$ and $m$ integer

1) $\hat{H} = -\vec{m}\cdot\vec{B} = -g\mu_B \frac{B}{\hbar}\hat{J}_z \rightarrow 2J+1$ eigenvalues $E = -g\mu_B B m$ $\quad$ $\equiv$ $+m$ … $-m$

2) $z = \sum_m e^{\beta g \mu_B B m}$

$(x = \beta g \mu_B B)$
$$= \sum_{m=-J}^{m=+J} e^{xm} = e^{-xJ} \sum_{m=-J}^{J} e^{x(m+J)} = e^{-xJ} \sum_{m'=0}^{2J} e^{xm'} = e^{-xJ} \frac{1-e^{(2J+1)x}}{1-e^{x}}$$

$$z = \frac{\sinh(J+\frac{1}{2})x}{\sinh\frac{x}{2}} = \underline{\frac{\sinh\left(1+\frac{1}{2J}\right)y}{\sinh\left(\frac{y}{2J}\right)}} \Big\| \text{ where } y = \frac{g\mu_B J B}{k_B T}$$

For $J = \frac{1}{2} \Rightarrow z = 2\cosh(y) = \underset{|\uparrow\rangle}{e^{y}} + \underset{|\downarrow\rangle}{e^{-y}} \longrightarrow$ expected

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# STATISTICAL PHYSICS

# TD 5

March 19, 2025

## 5.1 The crystal of spin $1/2$ (*)

## 5.2 Monoatomic ideal gas (*)

## 5.3 The diatomic perfect gas (*)

## 5.4 The Langevin paramagnet (*)

The spatial orientation of the magnetic moment of each atom is specified by two angles $\theta$ and $\varphi$. When a magnetic field $\vec{B}$ is applied along the $z$ axis, each atom acquires a potential energy

$$H_{\text{mag}} = -\vec{\mathfrak{m}} \cdot \vec{\mathcal{B}} = -\mathfrak{m}_0 \, \mathcal{B} \, \cos\theta \ , \tag{5.1}$$

where $\mathfrak{m}_0 = ||\vec{\mathfrak{m}}||$. The kinetic energy reads

$$H_{\text{kin}} = \frac{I}{2}[\dot{\theta}^2 + \dot{\varphi}^2 \sin^2\theta], \tag{5.2}$$

$$= \frac{1}{2\,I}\left(p_\theta^2 + \frac{p_\varphi^2}{\sin^2\theta}\right) \tag{5.3}$$

1. The phase space is defined by $(\theta, p_\theta), (\varphi, p_\varphi)$. We thus have two pairs of conjugate variables therefore D=2 degrees of freedom in the semi-classical formula.

   The canonical partition function associated with $H$ in the semi-classical limit is

   $$z = \frac{1}{h^2}\int_0^\pi d\theta \int_0^{2\pi} d\varphi \int dp_\theta \int dp_\varphi e^{-\beta H}$$

   We first fix B=0 and perform the two Gaussian integrals over the momenta (we use the formula 0.1 of the text):

   $$z(B=0) = \frac{1}{h^2}\int_0^\pi d\theta \int_0^{2\pi} d\varphi \sqrt{\frac{2\pi I}{\beta}}\sqrt{\frac{2\pi I \sin^2\theta}{\beta}}$$

   And we make the final integration over angles to find

   $$z(B=0) = \frac{8\pi^2 I}{\beta h^2} = \frac{4\pi R^2}{\Lambda_T^2}$$

with $I = mR^2$ and $\Lambda_T = \sqrt{\frac{h^2}{2\pi m k_B T}}$

Notice that $Vol = 4\pi R^2$ corresponds to the surface of a sphere of radius $R$.

In the general case, we follow the same path by first integrating over the momenta:

$$z = \frac{1}{h^2} \int_0^\pi d\theta \int_0^{2\pi} d\varphi \frac{2\pi I}{\beta} \sin\theta e^{\beta m_0 B \cos(\theta)}$$

We can thus write the result in the form $z = z_{\text{kin}} z_{\text{mag}}$ where

$$z_{\text{kin}} = z(B = 0) = \frac{4\pi R^2}{\Lambda_T^2}$$

and

$$z_{\text{mag}} = \frac{1}{4\pi} \int_0^\pi d\theta \int_0^{2\pi} d\varphi \sin\theta e^{\beta m_0 B \cos(\theta)}$$

The latter integral gives

$$z_{\text{mag}} = \frac{\text{sh}(\beta m_0 B)}{\beta m_0 B} = \frac{\text{sh}(x)}{x}$$

where $x = \beta m_0 B$.

2. Give the expression for the probability density $w(\theta, \varphi)$ that the magnetic moment points in the direction $(\theta, \varphi)$.

   In the canonical ensemble, the probability density is defined by

   $$P^c(p_\theta, p_\varphi, \theta, \varphi) \propto e^{-\beta(H_{\text{kin}} + H_{\text{mag}})}$$

   We are only interested in the probability density that the magnetic moment points in the direction defined by the two angles $\theta, \varphi$. Therefore, we need to integrate $P^c(p_\theta, p_\varphi, \theta, \varphi)$ over the two momenta variables $p_\theta, p_\varphi$.

   $$w(\theta, \varphi) \propto \int dp_\theta \int dp_\varphi \, P^c(p_\theta, p_\varphi, \theta, \varphi) \propto \sin\theta e^{\beta m_0 B \cos\theta}$$

   This probability density should verify

   $$\int_0^\pi d\theta \int_0^{2\pi} d\varphi \, w(\theta, \varphi) = 1.$$

   This thus fix the proportionality constant. Using the previous calculation, we find that

   $$w(\theta, \varphi) = \frac{\beta m_0 B}{4\pi \, \text{sh}(\beta m_0 B)} \sin\theta e^{\beta m_0 B \cos\theta}$$

   or equivalently

$$w(\theta,\varphi) = \frac{x\sin\theta e^{x\cos\theta}}{4\pi\,\mathrm{sh}(x)}$$

At low temperature, $x \gg 1$ and

$$w(\theta,\varphi) \sim \frac{x\sin\theta e^{-x(1-\cos\theta)}}{2\pi} \sim \frac{x\theta e^{-x\theta^2/2}}{2\pi}$$

This looks like a Gaussian which is peaked around a value $\theta^* \sim 0$.

At high temperature, $x \ll 1$,

$$w(\theta,\varphi) \sim \sin\theta(1 + x\cos\theta)/4\pi \sim \sin\theta/4\pi$$

3. Calculate the average magnetic moment, $\overline{\mathfrak{m}_z}^{\mathrm{c}}$ per atom. We will refer to $M = N\,\overline{\mathfrak{m}_z}^{\mathrm{c}}$ as the total magnetization of the material.

   we have

$$\overline{\mathfrak{m}_z}^{c} = -\frac{\partial F}{\partial B}$$

$$\overline{\mathfrak{m}_z}^{c} = \frac{1}{\beta}\frac{\ln\left(\frac{\mathrm{sh}(x)}{x}\right)}{\partial B}$$

$$\overline{\mathfrak{m}_z}^{c} = m_0\mathcal{L}(x)$$

   where $\mathcal{L}(x) = coth(x) - \frac{1}{x}$ is the Langevin function.

   At high temperature, $\mathcal{L}(x) \sim x/3$ and we recover the Curie law.

   At low temperature, $\mathcal{L}(x) \sim 1 - 1/x$. The system progressively gets magnetized.

## 5.5 Brillouin paramagnet

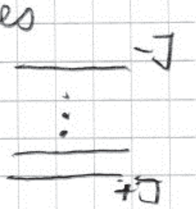
(8')

1) $\vec{m} = g\mu_B \frac{\vec{J}}{\hbar}$ ; $\mu_B$ = Bohr magneton

$J^z = m\hbar$ with $m \in [-J, J]$ and we have $2J+1$ values

$\hat{H} = -\vec{m}\cdot\vec{B} = -g\mu_B \frac{B}{\hbar} J^z \rightarrow (2J+1)$ eigenvalues

$\hookrightarrow \boxed{E = -g\mu_B B m}$ with $m \in [-J, J]$



2) $$Z = \sum_{m=-J}^{+J} e^{\beta g\mu_B B m} = \sum_{m=-J}^{+J} e^{xm} \quad \text{with } x = \beta g\mu_B B$$

$$= e^{-xJ} \sum_{m=-J}^{+J} e^{x(m+J)}$$

$$= e^{-xJ} \sum_{m'=0}^{2J} e^{xm'} = e^{-xJ} \frac{1-e^{x(2J+1)}}{1-e^{x}}$$

$$= e^{-xJ} \frac{e^{x(J+\frac{1}{2})}}{e^{x/2}} \frac{e^{-x(J+\frac{1}{2})} - e^{x(J+1/2)}}{e^{-x/2} - e^{x/2}}$$

$$= \frac{2\sinh\left(x(J+\frac{1}{2})\right)}{2\sinh\left(\frac{x}{2}\right)} = \frac{\sinh\left(1+\frac{1}{2J}\right)y}{\sinh(y/2J)}$$

with $y = \frac{g|\mu_B| J B}{k_B T} = Jx$

For $J = \frac{1}{2} \Rightarrow Z = 2\cosh(y) = e^{y} + e^{-y}$ as expected

3) $P_m^c \propto e^{\beta g\mu_B B m} = e^{ym/J}$

Fiting the normalization ; $P_m^c = \frac{e^{ym/J}}{Z}$

4) We need to be careful with the two types of averages we consider here.

We have $\vec{m} = g\mu_B \frac{\hat{\vec{J}}}{\hbar} \Rightarrow \langle m^x \rangle = g\mu_B \frac{\langle \hat{J}^x \rangle}{\hbar}$

quantum average
or expectation value of an observable

Now, we are working at finite temperature. The statistical average will be a statistical average of expectation values

namely $\overline{m_x}^c = \frac{g\mu_B}{\hbar} \underbrace{\sum_m P_m^c}_{\text{stat. average}} \underbrace{\langle J,m | \hat{J}^x | Jm \rangle}_{\text{quantum average.}}$

Here $\underline{\overline{m_x}^c = 0}\,\|$

However $\overline{m_z}^c = g\mu_B \sum_m m\, P_m^c = \frac{g\mu_B}{Z}\sum_m m\, e^{\beta g\mu_B B m}$

$$= \frac{1}{Z\beta}\frac{\partial}{\partial B}\sum_m e^{\beta g\mu_B B m} = \frac{1}{\beta}\frac{\partial \ln Z}{\partial B} = -\frac{\partial F}{\partial B}$$

For N spins,

$$M = N\,\overline{m_z}^c = \frac{N}{Z\beta}\frac{\partial}{\partial B}\left(\sum_m e^{\beta g\mu_B B m}\right)$$

$$= \frac{N g\mu_B J}{Z}\frac{\partial}{\partial y}\left(\sum_m e^{my/J}\right)$$

$$\underline{M = M_{max}\, B_J(y)}\,\|$$

with $y = \beta g\mu_B J B = \frac{T_B}{T}$

Large T $\Rightarrow y \sim 0 \rightarrow B_J(y) \approx \frac{J+1}{3J}\, y + O(y^3)$

$$\Rightarrow M = \frac{N\mu_B^2 g^2 J^2}{k_B T}\frac{J+1}{3J}\, B \quad \text{Curie law}$$

$$= N(m_0)^2 \frac{J+1}{3J}\frac{B}{k_B T}$$

où $\underline{m_0 = g\mu_B J}$

Low T (Quantum regime)

$$\text{th}\,x \underset{x \gg 1}{\sim} 1 - 2e^{-2x}$$

Therefore $B_J(y \gg 1) \sim \left(1+\frac{1}{2J}\right)\left(1+2e^{-2\left(1+\frac{1}{2J}\right)y}\right)$

$$- \frac{1}{2J}\left(1+2e^{-y/2J}\right)$$

$$\approx 1 + \left(2+\frac{1}{J}\right)e^{-2\left(1+\frac{1}{2J}\right)y} - \frac{e^{-y/J}}{J}$$

$\approx 1 +$ exponentially small corrections

$\neq$ classical behaviour

RQ: For $J=\frac{1}{2}$ $B_{1/2}(y) = \tanh y \rightarrow$ we recover spin $\frac{1}{2}$ case

Indeed $B_{\frac{1}{2}}(y) = \frac{2}{\text{th}(2y)} - \frac{1}{\text{th}\,y} = \frac{2\,\text{ch}2y}{\text{sh}2y} - \frac{\text{ch}y}{\text{sh}y}$

use trigonometry

5) At large $\frac{B}{T}$ $M \rightarrow g\mu_B J = 2\mu_B J$

Therefore Max $\rightarrow \begin{cases} 3\mu_B & \text{for } J = 3/2 \\ 5\mu_B & — \; J = 5/2 \\ 7\mu_B & — \; J = 7/2 \end{cases}$

3) $P_m^c = \frac{e^{ym/J}}{z}$    4) $\langle \hat{m}_x \rangle = g\frac{\mu_B}{\hbar}\langle J_x \rangle = \gamma \langle \hat{J}_x \rangle$

$$\langle \hat{m}_x \rangle = \gamma \underbrace{\sum_m P_m^c}_{\text{stat average}} \underbrace{\langle J,m | \hat{J}_x | J,m \rangle}_{\text{quant. average}}$$

$$\to \langle \hat{m}_x \rangle = 0$$

$$\langle \hat{m}_z \rangle = \gamma\hbar \sum m P_m^c = \hbar\gamma = -\frac{\partial F}{\partial B} = \frac{1}{\beta}\frac{\partial}{\partial B}\ln z$$

$$\Rightarrow M = N\langle \hat{m}_z \rangle = \frac{N}{\beta} = \underbrace{N g \mu_B J}_{M_{max}} \frac{\partial}{\partial y}\ln z = \underline{M_{max}\, B_J(y)}$$

$$y = \beta g |\mu_B| J B = \frac{T_B}{T}$$

Large T → $y \sim 0$ → $M \simeq \frac{N\mu^2}{k_B T}\frac{J+1}{3J}$   Curie Law

Low T → $y \gg 1$   $M \sim \pm M_{max}$ → all polarized.

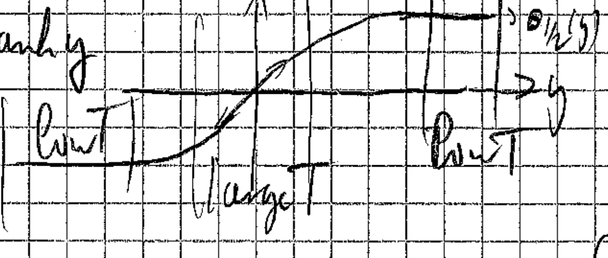
Expand $\text{th}\,x \underset{x \gg 1}{\sim} 1 - 2e^{-2x}$

$$B_J(y \gg 1) \sim \left(1+\frac{1}{2J}\right)\left(1+2e^{-2(1+\frac{1}{2J})y}\right) - \frac{1}{2J}\left(1+2e^{-y/J}\right)$$

$$= 1 + \left(2+\frac{1}{J}\right)e^{-2(1+\frac{1}{2J})y} - \frac{1}{J}e^{-y/J}$$

We have exponential small corrections at large y ≠ classical case where $\mathcal{L}(x) \sim 1 - 1/x$

For $J = 1/2$   $B_{1/2}(y) = \tanh y$



At large $\frac{B}{T}$ → $M \to g|\mu_B| J = 2|\mu_B| J$ → $\begin{cases} J_I = 3/2 \\ J_{II} = 5/2 \\ J_{III} = 7/2 \end{cases}$ consistent with caption

5.6 Ideal, confined, non-ideal, etc gases

1) Microstates $\{\vec r_i, \vec p_i\}$ → $\rho^c = \frac{1}{Z h^3} e^{-\beta H(\{\vec r_i, \vec p_i\})}$

$$f(\vec r, \vec p)\, d\vec r\, d\vec p = \frac{e^{-\beta\left(\frac{p^2}{2m} + U(\vec r)\right)}\, dr\, dp}{h^3 \int \frac{d\vec r\, d\vec p}{h^3}\, e^{-\beta\left(\frac{p^2}{2m} + U(\vec r)\right)}}$$

2) a) $Z = \frac{1}{N!} z^N$ with $z = \frac{V}{\Lambda_T^3}$ (see main lecture) $\Rightarrow \underline{U(\vec{r}) = 0}$

valid providing particles are independent $\rightarrow$ needs $\Lambda_T << d_{\text{part-part}}$

b) $$f(\vec{r},\vec{p}) = \frac{e^{-\beta \frac{\vec{p}^2}{2m}} e^{-\beta U(\vec{r})}}{h^3 \left(\frac{V}{\Lambda_T^3}\right)\left(\frac{1}{V}\int d\vec{r}\, e^{-\beta U(r)}\right)}$$

velocities distribution

$$f(\vec{v})d^3\vec{v} = d^3p \int d^3\vec{r}\, f(\vec{r},\vec{p}) = d^3p \frac{e^{-\beta \frac{\vec{p}^2}{2m}} \cancel{\int d^3r\, e^{-\beta U(r)}}}{h^3 \Lambda_T^{-3} \cancel{\int d^3r\, e^{-\beta U(r)}}}$$

$$\hookrightarrow f(\vec{v}) = \frac{m^3}{h^3 \left(\frac{2\pi m k_B T}{h}\right)^{3/2}} e^{-\beta v^2/2m} \Rightarrow \underline{f(\vec{v}) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\beta \frac{1}{2} m v^2}} \;\Big\|$$

3) a) Gas in a potential $\Rightarrow$ The pb remains separable (5.10) holds and we find the Maxwell Boltzmann distrib.

$\rightarrow$ Gaussian law of the profile

b) Gas of interacting particles

$$Z = \frac{1}{N!} \int \frac{d\vec{p}_1 \ldots d\vec{p}_N}{h^{3N}} e^{-\beta \sum \frac{p_i^2}{2m}} \int dr_1 \ldots dr_N\, e^{-\beta U(\vec{r}_1, \ldots \vec{r}_N)}$$

$\Rightarrow$ no $\underline{\text{factorizat}^\circ}$

However, we can still separate kinetic and potential contributions

$\rightarrow$ Maxwell Boltzman still holds

c) $E = \sqrt{p^2c^2 + m^2c^4}$ Factorizat° $\underline{\text{OK}}$

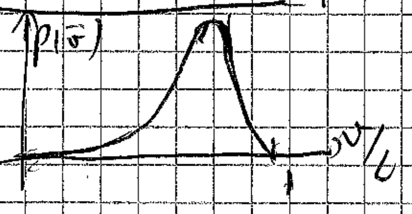
$$z = \frac{1}{h^3} \int d\vec{r} \int d\vec{p}\, e^{-\beta\left(\sqrt{p^2c^2 + m^2c^4}\right)}$$ we have $E = \frac{mc^2}{\sqrt{1 - v^2/c^2}}$ ; $p = \frac{mv}{\sqrt{1 - v^2/c^2}}$

$$\overset{4\pi}{\widehat{d\Omega}}\, v^2 f(\vec{v})\, dv = f(\vec{v})\, d^3\vec{v} \propto d^3\vec{p}\, e^{-\beta(p^2c^2 + m^2c^4)^{1/2}}$$

$$d^3\vec{p} = d\Omega\, p^2 dp = \overset{4\pi}{\widehat{d\Omega}}\, p^2 \frac{dp}{dv} dv$$

$$\frac{dp}{dv} = \frac{m}{\left(1 - \frac{v^2}{c^2}\right)^{3/2}} \quad \text{etc} \ldots \quad \underline{f(\vec{v}) \propto \frac{1}{\left(1 - \frac{v^2}{c^2}\right)^{5/2}} e^{-\frac{\beta mc^2}{\sqrt{1 - v^2/c^2}}}} \;\Big\|$$

$p(\vec{v}) = 4\pi v^2 f(\vec{v})$



d) $E = pc \Rightarrow$ $f(\vec{v}) = \frac{\delta(\|\vec{v}\| - c)}{4\pi v^2}$

$p(\vec{v}) = \delta(\vec{v} - c)$

(I stop here)

**Introduction à la Physique Statistique LP357**
2010-2011

# Corrigé TD 5 : L'ensemble canonique II

## 1 Chaleur spécifique d'un gaz parfait diatomique

▷ **1-1** Le Hamiltonien d'une molécule diatomique se décompose en 7 termes quadratiques indépendants : 3 pour l'énergie cinétique de translation, 2 pour l'oscillateur harmonique décrivant la vibration et 2 pour l'énergie cinétique de rotation décrite par deux angles. L'énergie moyenne du gaz diatomique est donc

$$< E >= 7N\frac{kT}{2}$$

et sa chaleur spécifique

$$C = \frac{7}{2}Nk.$$

Pourtant, la courbe de la Figure 1 montre que la chaleur spécifique dépend de la température et semble tendre vers le résultat obtenu seulement dans la limite des (très) hautes températures.

▷ **1-2** Puisque les particules sont indépendantes et indiscernables :

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

où $z$ est la fonction de partition d'une molécule. Le couplage entre degrés de liberté internes (vibration et rotation) et de translation intervient au moment des collisions, à faible densité, dans l'approximation du gaz parfait, l'influence des collisions est négligeable. En revanche, il peut y avoir des couplages entre degrés de liberté internes (rotation et vibration). En négligeant les couplages entre les divers degrés de liberté, on a donc

$$\epsilon = \epsilon_t + \epsilon_v + \epsilon_r,$$

donc

$$z = \sum_{etat} e^{-\beta\epsilon} = \sum_{t,v,r} e^{-\beta(\epsilon_t+\epsilon_v+\epsilon_r)} = z_t\ z_v\ z_r.$$

Remarque : On ne tient pas compte des degrés de liberté électroniques car les énergies en jeu (typiquement $1eV$) correspondant à des températures de l'ordre de 12 000 K. À “basse” température, ces degrés de liberté sont gelés en général.

### 1.1 Mouvement de translation

▷ **1-3** La fonction de partition d'une particule associée au mouvement de translation est

$$z_t = \int \frac{d^3\mathbf{q}d^3\mathbf{p}}{h^3}\ e^{-\beta\frac{\mathbf{p}^2}{2m}} = \frac{V}{\lambda^3} \sim \beta^{-\frac{3}{2}},$$

donc

$$< \epsilon_t >= -\frac{\partial \ln z_t}{\partial \beta} = \frac{3}{2}kT$$

et

$$C_t = \frac{3}{2}k.$$

## 1.2 Mouvement de vibration

▷ **1-4** L'énergie $-u_0$ est donc l'énergie minimale entre les atomes de la molécules et on considère les oscillations autour de cette position d'équilibre. En première approximation (2eme ordre), les vibrations sont donc harmoniques et décrites par un oscillateur harmonique quantique. Alors

$$z_v = \sum_{n=0}^{\infty} e^{-\beta\left(-u_0+(n+\frac{1}{2})\hbar\omega_0\right)} = e^{\beta(u_0-\frac{1}{2}\hbar\omega_0)}\frac{1}{1-e^{-\beta\hbar\omega_0}} = \frac{e^{\beta u_0}}{2\sinh\frac{\beta\hbar\omega_0}{2}}.$$

Donc

$$< \epsilon_v >= -\frac{\partial \ln z_v}{\partial \beta} = -u_0 + \frac{\frac{\hbar\omega_0}{2}}{\tanh\frac{\beta\hbar\omega_0}{2}}$$

et

$$C_v = \frac{\partial < \epsilon_v >}{\partial T} = -k\beta^2\frac{\partial < \epsilon_v >}{\partial \beta} = k\left(\frac{\frac{\beta\hbar\omega_0}{2}}{\sinh\frac{\beta\hbar\omega_0}{2}}\right)^2 = k\left(\frac{\frac{T_v}{2T}}{\sinh\frac{T_v}{2T}}\right)^2,$$

où $T_v = \hbar\omega_0/k$ est la température caractéristique des vibrations. Par exemple $T_v = 6215K$ pour $H_2$, $T_v = 4227K$ pour $HCl$ et $T_v = 808K$ pour $Cl_2$. Plus les atomes sont lourds, plus la fréquence de vibration ($\omega \sim \sqrt{k/m}$) et donc la température de vibration est faible.

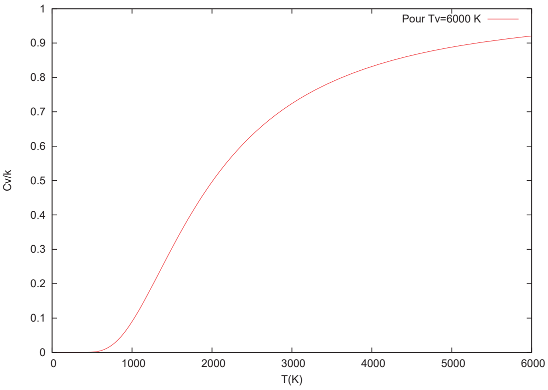


Fig. 1 – Chaleur spécifique de vibration $C_v$ pour $T_v = 6000K$ (hydrogène).

Et pour $T \to \infty$ ($\beta \to 0$), on retrouve bien l'équipartition de l'énergie :

$$C_v \simeq k.$$

▷ **1-5** Pour $T \to 0$ ($\beta \to \infty$) :

$$C_v \simeq k(\frac{T_v}{T})^2 e^{-T_v/T} \ll k.$$

On retrouve le comportement des anomalies de Schottky, typique des systèmes à deux niveaux. Ici, pour $T \ll T_v$, $kT \ll \hbar\omega_0$, la vibration de la molécule a donc deux états possibles, d'énergies $E_0$ et $E_0 + \hbar\omega_0$.

## 1.3 Mouvement de rotation

▷ **1-6** On considère ici la molécule comme un rotateur rigide. En classique, il faut deux degrés de liberté, $\theta$ et $\phi$ , pour décrire la rotation de la molécule linéaire et l'énergie de rotation est donnée par

$$\epsilon_r = \frac{1}{2}I(\dot{\theta}^2 + \dot{\phi}^2\sin^2\theta) = \frac{1}{2I}\vec{\mathcal{L}}^2,$$

où $I = m_r d^2$ est le moment d'inertie et $\vec{\mathcal{L}}$ le moment cinétique. En quantique, le Hamiltonien est

$$H = \frac{1}{2I}\vec{L}^2.$$

Pour $HCl$, $m_r \simeq m_H = 1$ gmol$^{-1}$ et $d \simeq 1$ $A$ donc

$$T_r = \frac{\hbar^2}{2kI} \simeq 20K$$

On mesure en fait $T_r = 15$ K et $T_r = 85$ K pour $H_2$, $T_r = 0.35$ K pour $Cl_2$. À l'ambiante,

$$\frac{T}{T_r} \sim 15,$$

on a donc $T \gg T_r$. Contrairement aux degrès de liberté de vibration, les degrès de liberté de rotation ne sont pas gelés à l'ambiante.

▷ **1-7** La fonction de partition de rotation s'écrit :

$$z_r = \sum_{l,m_l} e^{-\beta\epsilon_r} = \sum_{l=0}^{\infty}(2l+1)e^{-\beta\frac{\hbar^2}{2I}l(l+1)}.$$

Pour calculer cette somme dans l'hypothèse où $T \gg T_r$ on traite $l$ comme une variable continue (deux termes consécutifs de la somme sont en effet très proches) :

$$z_r = \int_0^\infty dl(2l+1)\; e^{-\frac{T_r}{T}l(l+1)} = \int_0^\infty dx\; e^{-\frac{T_r}{T}x} = \frac{T}{T_r}.$$

Donc

$$< \epsilon_r >= kT,$$

et on retrouve l'équipartition de l'énergie, puisque classiquement,

$$\epsilon_r = \frac{1}{2I}(p_\theta^2 + \frac{1}{\sin\theta}p_\phi^2)$$

Et

$$C_r = k.$$

▷ **1-8** À très basse température, pour $T \ll T_r$ seuls les premiers termes de la fonction de partition vont contribuer :

$$z_r = 1 + 3e^{-2\frac{T_r}{T}} + ...$$

Donc

$$\ln z_r \simeq \ln(1 + 3e^{-2\frac{T_r}{T}} + ...) \simeq 3e^{-2\frac{T_r}{T}}.$$

C'est un développement basse température. Ainsi

$$< \epsilon_r >\simeq 6kT_r e^{-2\frac{T_r}{T}}.$$

Et

$$C_r \simeq 12k\left(\frac{T_r}{T}\right)^2 e^{-2\frac{T_r}{T}},$$

qui augmente avec la température pour $T \ll T_r$.

## 1.4 Conclusion

▷ **1-9** Pour $T \gg T_r$ on a

$$z = \frac{V}{\lambda^3}\;\frac{e^{\beta u_0}}{2\sinh\frac{\beta\hbar\omega_0}{2}}\;\frac{T}{T_r}.$$

La pression du gaz est donnée par

$$p = -\frac{\partial F}{\partial V} = kT\frac{\partial \ln Z}{\partial V} = NkT\frac{\partial \ln z_t}{\partial V},$$

la dépendance en $V$ est la même que dans le cas du gaz parfait monoatomique. Donc

$$PV = NkT.$$

▷ **1-10** L'énergie moyenne étant additive, la capacité calorifique l'est aussi :

$$C_V = N(c_t + c_v + c_r) = \frac{3}{2}Nk + N(c_v + c_r).$$

La courbe présente trois plateaux quand la température augmente :

- pour $T \ll T_r = 85$ K (pour $H_2$), $C \simeq C_t = 1.5k$ (seulement la translation),
- pour $T_r \ll T \ll T_v = 6215$ K (pour $H_2$), $C \simeq C_t + C_r = 2.5k$, (translation et rotation)
- pour $T_v \ll T$, $C \simeq C_t + C_r + C_v = 3.5k$ (translation, rotation et vibration).

Ainsi, à l'ambiante, les degrés de liberté de vibration sont gelés ce qui explique le comportement en $\frac{5}{2}R$ de la capacité calorifique molaire observé sur la figure 1. À très haute température ($T > 1000$ K), le modèle ne reproduit pas les données expérimentales à cause des effets d'anharmonicité de la vibration (l'approximation harmonique n'est valable qu'à faible énergie comparée au niveau fondamental) et à son couplage avec la rotation (la force centrifuge due à la rotation va modifier la pulsation de vibration et inversement, les vibrations modifient la distance entre les atomes et donc le moment d'inertie de la molécule).

Remarque dans le cas d'une molécule polyatomique constituée de $n$ atomes, il y a 3 degrés de liberté de translation, 3 pour les angles (2 si la molécules est linéaire) et donc $3n - 6$ pour ddl de vibration ($3n - 5$ pour une molécule linéaire). Par exemple, pour $C0_2$ : 4 ddl de vibration (de températures associées aux modes normaux 954 (2 fois), 1890 et 3360 K). Pour $H_20$ : 3 ddl (2290, 5160 et 5360 K).

# 2 Chaleur spécifique des solides

## 2.1 Loi de Dulong et Petit

▷ **2-1** À haute température, on peut traiter ce problème classiquement. Le Hamiltonien de l'oscillateur harmonique a deux termes quadratiques, l'énergie moyenne est donc $kT$ et la chaleur spécifique de $3N$ oscillateurs $3Nk$. Soit pour une mole, $C_V = 3R \simeq 24.9$. La loi de Dulong et Petit (1819) est en très bon accord avec les résultats expérimentaux, sauf pour le diamant...(pour les solides, la chaleur spécifique à pression constante et très proche de la chaleur spécifique à volume constant. Typiquement, $C_V \simeq 0.95C_P$).

## 2.2 Modèle d'Einstein

▷ **2-2** Les $3N$ oscillateurs harmoniques étant indépendants et discernables :

$$Z = z^{3N},$$

où $z$ est la fonction de partition d'un oscillateur harmonique quantique qui s'exprime :

$$\begin{aligned} z &= \sum_{n=0}^{\infty} e^{-\beta(n+\frac{1}{2})\hbar\omega_0)} = e^{-\frac{\beta}{2}\hbar\omega_0} \sum_{n=0}^{\infty} e^{-n\beta\hbar\omega_0} \\ &= e^{-\frac{\beta}{2}\hbar\omega_0} \frac{1}{1 - e^{-\beta\hbar\omega_0}} = \frac{1}{2\sinh\beta\hbar\omega_0/2}. \end{aligned}$$

Donc

$$Z = \frac{1}{(2\sinh\beta\hbar\omega_0/2)^{3N}}.$$

On en déduit l'énergie moyenne :

$$< E >= -\frac{\partial \ln Z}{\partial\beta} = 3N\frac{\hbar\omega_0/2}{\tanh\beta\hbar\omega_0/2}.$$

L'énergie libre est donnée par

$$F = -kT\ln Z = 3NkT\ \ln(2\sinh\beta\hbar\omega_0/2),$$

et l'entropie :

$$S = -\frac{\partial F}{\partial T} = 3Nk\left( - \ln(2\sinh\hbar\omega_0/2kT) + \frac{\hbar\omega_0/2kT}{\tanh(\hbar\omega_0/2kT)}\right).$$

Quand $T \to 0$ $S \to 0$ et $S$ est croissante avec la température comme il se doit.