Equilibrium Statistical Physics
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11. Canonical Ensemble II

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Abstract

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Paramagnetism [tln58]

Paramagnetic salts contain localized ions with permanent magnetic dipole moments associated with unpaired electron spins. The interaction between the electron spins is negligibly small and there is no kinetic energy associated with their orientational motion. Hence the internal energy vanishes: $U = 0$.

The microstate is specified by the instantaneous orientation of the magnetic moments $\mathbf{m}_i, i = 1, \ldots, N$ relative to some coordinate system. The localized moments can be treated as distinguishable particles. They do not need to have a definite permutation symmetry. The macroscopic equilibrium state in the canonical ensemble is characterized by random orientations of the moments $\mathbf{m}_i$. It has no magnetisation: $\mathbf{M} = \sum_i \langle \mathbf{m}_i \rangle = 0$.

An external magnetic field $\mathbf{H}$ causes a partial spin alignment. The interaction of the magnetic moments with a field in z-direction is represented by Hamiltonian (Zeeman energy) of the form:

$$\mathcal{H} = -\sum_{i=1}^{N} \mathbf{m}_i \cdot \mathbf{H} = -H \sum_{i=1}^{N} m_i^z.$$

Classical model: The permanent atomic magnetic moment is described as a 3-component vector of fixed length:

$$\mathbf{m}_i = (m_i^x, m_i^y, m_i^z) = m(\sin\theta_i \cos\phi_i, \sin\theta_i \sin\phi_i, \cos\theta_i).$$

Each $\mathbf{m}_i$ represents one degree of freedom described by one pair of canonical coordinates $q_i = \phi_i,\ p_i = m\cos\theta_i$. The canonical partition function is calculated in exercise [tex84].

Quantum model (spin 1/2): The permanent atomic magnetic moment originates from a single electron spin. This is a two-level system, which also has a host of realizations unrelated to paramagnetism. The magnetic moment in appropriate units is quantized as follows:

$$m_i^z = \pm\frac{1}{2}.$$

The canonical partition function is calculated in exercise [tex85].

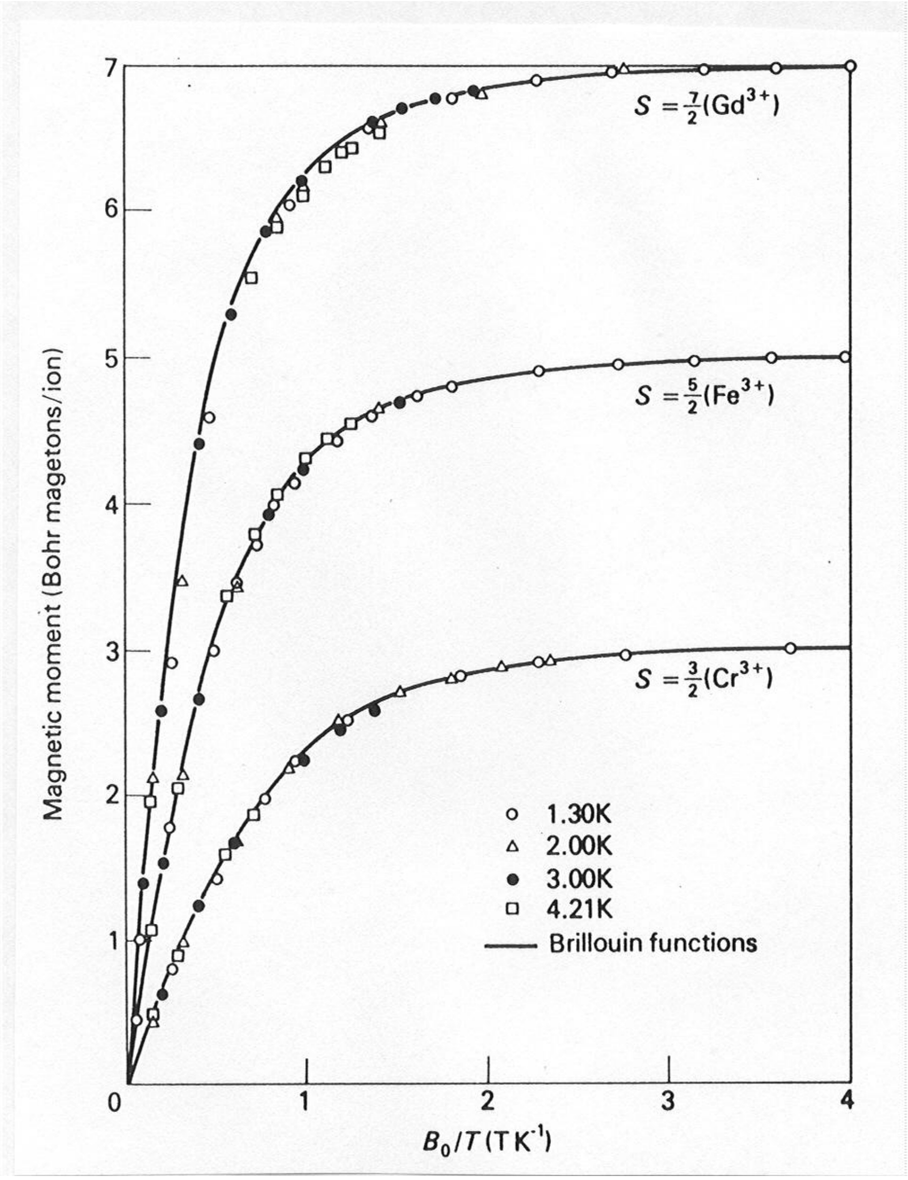
Quantum model (spin s): The permanent atomic magnetic moment originates from an effective spin of quantum number $s = \frac{1}{2}, 1, \frac{3}{2}, \ldots$ The magnetic moment in appropriate units is quantized as follows:

$$m_i^z = -s, -s+1, \ldots, s-1, s.$$

The canonical partition function is calculated in exercise [tex86].

Paramagnetic salts [tsl30]

Magnetization curves of paramagnetic salts
in comparison with Brillouin functions



[from Crangle 1977]

Fluctuations in a magnetic system [tln53]

Consider a system of N interacting magnetic moments m_i positioned in an external magnetic field of magnitude H.

Total magnetic moment: $M = \sum_{i=1}^{N} m_i$.

Hamiltonian: $\mathcal{H} = \mathcal{H}_{int} - HM$.

Canonical partition function: $Z_N = \mathrm{Tr}\, e^{-\beta\mathcal{H}}, \quad \beta = (k_BT)^{-1}$.

Gibbs free energy: $G(T,H,N) = -k_BT \ln Z_N$.

Magnetisation (average value of total magnetic moment):

$$\langle M\rangle = \frac{1}{Z_N}\mathrm{Tr}\left[M\, e^{-\beta\mathcal{H}}\right] = \beta^{-1}\frac{\partial}{\partial H}\ln Z_N \doteq M.$$

Enthalpy (average value of Hamiltonian):

$$\langle \mathcal{H}\rangle = \frac{1}{Z_N}\mathrm{Tr}\left[\mathcal{H}\, e^{-\beta\mathcal{H}}\right] = -\frac{\partial}{\partial \beta}\ln Z_N = U - HM = E$$

Energy fluctuations and heat capacity [tex109]:

$$\langle \mathcal{H}^2\rangle - \langle \mathcal{H}\rangle^2 = \frac{\partial^2}{\partial \beta^2}\ln Z_N = k_BT^2C_H.$$

Magnetisation fluctuations and susceptibility [tex109]:

$$\langle M^2\rangle - \langle M\rangle^2 = \beta^{-2}\frac{\partial^2}{\partial H^2}\ln Z_N = k_BT\chi_T.$$

[tex109] Fluctuations in a magnetic system

Consider a quantum magnet. The Hamiltonian is of the form $H = H_{int} - hm$, where H_{int} describes the (unspecified) interaction between microscopic magnetic moments, h is the magnitude of the external magnetic field (assumed constant) and m is the component of the total magnetic moment in the direction of the field. Given the Gibbs free energy $G(T, h, N) = -k_B T \ln Z_N$ as derived from the canonical partition function $Z_N = \mathrm{Tr}\, e^{-\beta H}$, where $\beta = (k_B T)^{-1}$, derive the following relations (a) between energy fluctuations and heat capacity at constant field,

$$\langle H^2 \rangle - \langle H \rangle^2 = \frac{\partial^2}{\partial \beta^2} \ln Z_N = k_B T^2 C_h,$$

and (b) between magnetisation fluctuations and isothermal susceptibility,

$$\langle m^2 \rangle - \langle m \rangle^2 = \beta^{-2} \frac{\partial^2}{\partial h^2} \ln Z_N = k_B T \chi_T.$$

Solution:

[tex84] Classical paramagnet (canonical ensemble)

Consider an array of N noninteracting localized magnetic dipole moments in the form of classical 3-component unit vectors $\mathbf{m}_i = (m_i^x, m_i^y, m_i^z) = (\sin\theta_i \cos\phi_i, \sin\theta_i \sin\phi_i, \cos\theta_i)$. In the presence of a magnetic field $\mathbf{H}$ pointing in z-direction, the Hamiltonian of this system represents the Zeeman energy:

$$\mathcal{H} = -\sum_{i=1}^{N} \mathbf{m}_i \cdot \mathbf{H} = -H \sum_{i=1}^{N} m_i^z.$$

(a) Calculate the canonical partition function Z_N of this system.
(b) Calculate the Gibbs free energy $G(T,H,N)$, the magnetization $M(T,H,N)$ (Langevin function), the isothermal susceptibility $\chi_T(T,H,N)$, and the heat capacity $C_H(T,H,N)$.
(c) Plot M/N versus H for three values of T. Plot C_H/N versus T for three values of H.
(d) Show that the leading term in an expansion of χ_T at small H is H-independent and represents Curie's law $\chi_T \simeq N/3k_BT$.

Solution:

[tex85] Quantum paramagnet (two−level system)

Consider an array of N noninteracting localized magnetic dipole moments $\mathbf{m}_i$ produced by localized electron spins in a paramagnetic insulator. In the presence of a magnetic field $\mathbf{H}$ pointing in z-direction, the Hamiltonian of this system represents the Zeeman energy:

$$\mathcal{H} = -\sum_{i=1}^{N} \mathbf{m}_i \cdot \mathbf{H} = -H \sum_{i=1}^{N} m_i^z, \quad m_i^z = \pm\frac{1}{2}.$$

(a) Calculate the canonical partition function Z_N of this system.
(b) Calculate the Gibbs free energy $G(T,H,N)$, the magnetization $M(T,H,N)$, the isothermal susceptibility $\chi_T(T,H,N)$, and the heat capacity $C_H(T,H,N)$.
(c) Show that the internal energy U is identically zero.
(d) Show that the leading term in an expansion of χ_T at small H is H-independent and represents Curie's law $\chi_T \simeq N/4k_BT$.

Solution:

[tex86] Quantum paramagnet (Brillouin function)

Consider an array of N noninteracting localized magnetic dipole moments $\mathbf{m}_i$ produced by localized effective atomic spins in a paramagnetic insulator. In the presence of a magnetic field $\mathbf{H}$ pointing in z-direction, the Hamiltonian of this system represents the Zeeman energy:

$$\mathcal{H} = -\sum_{i=1}^{N} \mathbf{m}_i \cdot \mathbf{H} = -H \sum_{i=1}^{N} m_i^z,$$

where m_i^z can assume the $2s+1$ values $(-s, -s+1, \ldots, s-1, s)$ for fixed $s = \frac{1}{2}, 1, \frac{3}{2}, \ldots$.
(a) Calculate the canonical partition function Z_N of this system.
(b) Calculate the Gibbs free energy $G(T, H, N)$. Calculate the magnetization $M(T, H, N)$ (Brillouin function).
(c) Set $s = \frac{1}{2}$ to recover the result of [tex85]. Take the limit $s \to \infty$ and recover the result of [tex84] for the rescaled quantities $\tilde{M} = M/s, \tilde{H} = Hs$.

Solution:

[tex142] Ising trimer

Three spins at the corners of an equilateral triangle interact with each other and with a magnetic field. The Hamiltonian is of the form

$$\mathcal{H} = -J(s_1 s_2 + s_2 s_3 + s_3 s_1) - H(s_1 + s_2 + s_3),$$

where $s_n = \pm 1$, $n = 1, 2, 3$, and J, H are energy units representing the interaction and the magnetic field, respectively.
(a) Calculate the canonicl partition function Z and infer from it the Gibbs free energy $G(T, H)$.
(b) Write detailed instructions for the derivation, from Z or G, of the magnetization M, the entropy S, and the internal energy U.

Solution:

Negative temperatures [tsl31]

Consider N noninteracting 2-level systems with energies $\pm\epsilon$.

$$N = N_+ + N_-, \quad U = (N_+ - N_-)\epsilon \quad \Rightarrow N_+ = \frac{1}{2}\left(N + \frac{U}{\epsilon}\right), \quad N_- = \frac{1}{2}\left(N - \frac{U}{\epsilon}\right).$$

Degeneracy of state with energy U: $N_U(U, N) = \dfrac{N!}{N_+!N_-!}$.

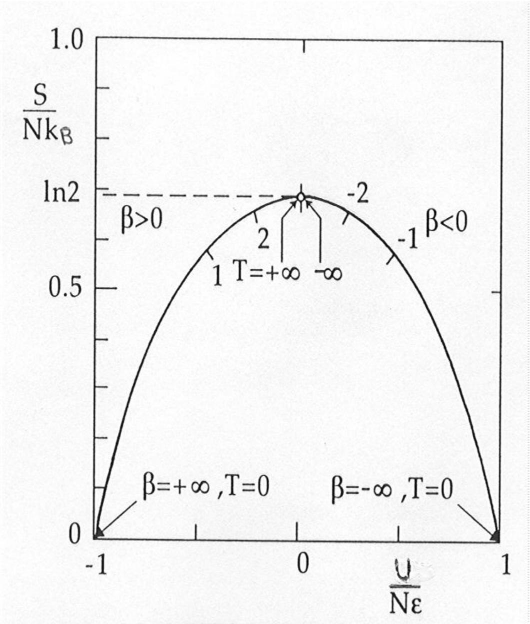
Entropy:

$$\begin{aligned} S(U,N) = k_B \ln N_U(U,N) = k_B N \ln N \quad &- \quad \frac{1}{2}k_B\left(N + \frac{U}{\epsilon}\right)\ln\left[\left(N + \frac{U}{\epsilon}\right)\right] \\ &- \quad \frac{1}{2}k_B\left(N - \frac{U}{\epsilon}\right)\ln\left[\left(N - \frac{U}{\epsilon}\right)\right]. \end{aligned}$$

Inverse temperature:

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_N = \frac{k_B}{2\epsilon}\ln\left(\frac{N - U/\epsilon}{N + U/\epsilon}\right).$$

Inversion of level occupancy corresponds to negative temperature.



[from Greiner et al. 1995]

Applications: laser pumping to metastable states, nuclear magnetism.

Gases with internal degrees of freedom [tln59]

Assumptions: molecules are noninteracting; translational, rotational, and vibrational degrees of freedom are independent:

$$H = \sum_{i=1}^{N} \left[H_T^{(i)} + H_R^{(i)} + H_V^{(i)} \right] \;\Rightarrow\; Z_N = \frac{1}{N!}\tilde{Z}^N, \;\; \tilde{Z} = \tilde{Z}_T \tilde{Z}_R \tilde{Z}_V .$$

Translational motion (classical):

$$H_T^{(i)} = \frac{p_i^2}{2m} \;\Rightarrow\; \tilde{Z}_T = V\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \;\Rightarrow\; C_V^{(T)} = \frac{3}{2} N k_B \quad \text{[tex76]}.$$

Rotational motion (classical):

(a) NH_3 (multi-atomic molecule):
Euler angles θ, ϕ, ψ; canonical conjugate momenta p_θ, p_ϕ, p_ψ.
Uniaxially symmetric inertia tensor with principal moments $I_1 = I_2, I_3$.

Hamiltonian: $H_R^{(i)} = \dfrac{p_{i\theta}^2}{2I_1} + \dfrac{p_{i\psi}^2}{2I_3} + \dfrac{(p_{i\phi} - p_{i\psi}\cos\theta_i)^2}{2I_1 \sin^2\theta_i}$.

Ranges: $0 \leq \theta_i \leq \pi,\; 0 \leq \phi_i, \psi_i \leq 2\pi,\; -\infty < p_{i\theta}, p_{i\phi}, p_{i\psi} < +\infty$.

$$\Rightarrow\; \tilde{Z}_R = \frac{1}{\pi\hbar^3}\sqrt{(2\pi I_1 k_B T)^2 (2\pi I_3 k_B T)} \;\Rightarrow\; C_V^{(R)} = \frac{3}{2} N k_B \quad \text{[tex87]}.$$

(b) HCl (two-atomic heteronuclear molecule):
The rotation about the molecular axis is suppressed due to quantum effect.

Hamiltonian: $H_R^{(i)} = \dfrac{p_{i\theta}^2}{2I_1} + \dfrac{p_{i\phi}^2}{2I_1 \sin^2\theta_i}, \quad 0 \leq \theta_i \leq \pi,\; 0 \leq \phi_i \leq 2\pi.$

$$\Rightarrow\; \tilde{Z}_R = \frac{2 I_1 k_B T}{\hbar^2} \;\Rightarrow\; C_V^{(R)} = N k_B \quad \text{[tex88]}.$$

(c) N_2 (two-atomic homonuclear molecule):
Minor modification: range of one variable ($0 \leq \phi \leq \pi$).
This change does affect the entropy but not the heat capacity ⇒ [tex88].

Rotational motion (quantum):

Consider a two-atomic molecule.

Angular momentum operator: $\mathbf{L}$. Hamiltonian operator: $H_R = \frac{1}{2I}\mathbf{L}^2$.

Energy levels: $E_{lm} = \frac{l(l+1)\hbar^2}{2I}$; $l = 0, 1, 2, \ldots$; $m = -l, -l+1, \ldots, l$.

Degeneracy: $(2l+1)$-fold.

$$\Rightarrow \ \tilde{Z}_R = \sum_{l=0}^{\infty}\sum_{m=-l}^{+l} e^{-\beta E_{lm}} = \sum_{l=0}^{\infty}(2l+1)e^{-\beta l(l+1)\hbar^2/2I} \quad \Rightarrow \quad \text{[tsl32]}$$

Characteristic temperature: $k_B\Theta_R = \frac{\hbar^2}{2I}$.

Low-temperature analysis ($T \ll \Theta_R$) $\Rightarrow$ [tex89].

High-temperature analysis ($T \gg \Theta_R$) $\Rightarrow$ [tex90].

Vibrational motion (quantum):

Hamiltonian: $H_V = \sum_{l=1}^{f}\left(\frac{p_l^2}{2m_l} + \frac{1}{2}m_l\omega_l^2 q_l^2\right)$.

Here f is the number of vibrational normal modes, each expressed by a pair (q_l, p_l) of canonical normal mode coordinates.

$$\Rightarrow \ \tilde{Z}_V = \prod_{l=1}^{f}\left[\frac{e^{-\beta\hbar\omega_l}}{1-e^{-\beta\hbar\omega_l}}\right] \ \Rightarrow \ C_V^{(V)} \overset{T\gg\Theta_V}{\longrightarrow} fNk_B \quad \text{[tex82]}.$$

Characteristic temperature: $k_B\Theta_V = \hbar\omega_l$.

Vibrational modes require much higher temperatures to be activated:

$$\Theta_R = \frac{\hbar^2}{2Ik_B} \sim 10\text{K}, \quad \Theta_V = \frac{\hbar\omega_l}{k_B} \sim 1000\text{K} \quad \Rightarrow \text{[tsl32]}.$$

Fine structure:

If the atomic ground state has zero *orbital* angular momentum ($l = 0$) and nonzero *spin* angular momentum ($s \neq 0$), the entropy acquires an additive constant, $\Delta S = Nk_B \ln(2s+1)$. The heat capacity remains unaffected.

In the presence of an external magnetic field, this system is a paramagnetic gas. The thermodynamics of dilute paramagnetic gases are the theme of [tex22] and [tex133].

If the atomic ground state has $l \neq 0$ and $s \neq 0$, then the L-S coupling produces a fine-structure splitting of the ground-state degeneracy:

$$\tilde{Z}_{FS} = \sum_j (2j+1)e^{-\beta\epsilon_j}, \qquad |l-s| \leq j \leq l+s,$$

where j is the quantum number of the total angular momentum. If the lowest level has $j = j_0$, then the entropy of the atomic gas increases by

$$\Delta S = Nk_B \ln \frac{(2s+1)(2l+1)}{(2j_0+1)}$$

over a temperature range $0 < k_BT \lesssim \Delta E_{LS}$, where ΔE_{LS} measures the total L-S level splitting.

The contribution to the heat capacity, $C_V^{(FS)}$, is a function of T that rises from zero exponentially, exhibits a smooth maximum at $k_BT \sim \Delta E_{LS}$, and then dips back down to zero algebraically.[1]

The functional dependence of $C_V^{(FS)}$ on T is very similar to that of the heat capacity of a Langevin paramagnet as analyzed in [tex85] and [tex86].

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[1] In practical reality, atomic gases with $l \neq 0, s \neq 0$ tend to form molecules or condense at temperatures far above $k_BT \sim \Delta E_{LS}$.

[tex87] Classical rotational free energy of NH_3 gas

Under the assumption that the NH_3 molecule is a rigid body with uniaxially symmetric inertia tensor and principal moments $I_1 = I_2 \neq I_3$, the one-particle Hamiltonian of the free rotational motion reads

$$H_R = \frac{p_\theta^2}{2I_1} + \frac{p_\psi^2}{2I_3} + \frac{(p_\phi - p_\psi \cos\theta)^2}{2I_1 \sin^2\theta},$$

where $(\theta, p_\theta; \phi, p_\phi; \psi, p_\psi)$ are the Euler angles and their conjugate generalized momenta. The range of these canonical coordinates is $0 \leq \theta \leq \pi$, $0 \leq \phi, \psi \leq 2\pi$, $-\infty < p_\theta, p_\phi, p_\psi < +\infty$.
(a) Show that the canonical partition function for the rotational motion of N molecules is

$$Z_R^N = \pi^{-N}(2\pi k_B T/\hbar^2)^{3N/2} I_1^N I_3^{N/2}.$$

(b) Calculate the rotational Helmholtz free energy $A_R(T, N)$, the rotational entropy $S_R(T, N)$, and the rotational internal energy $U_R(T, N)$.

Solution:

[tex88] Classical rotational entropies of HCl and N_2 gases

Under the assumption (to be justified quantum mechanically) that only the rotational modes perpendicular to the axis of a two-atomic molecule are activated, its classical rotational motion is described by a Hamiltonian with two degrees of freedom,

$$H_R = \frac{p_\theta^2}{2I_1} + \frac{p_\phi^2}{2I_1 \sin^2\theta},$$

where $0 \leq \theta \leq \pi$, $-\infty < p_\theta, p_\phi < +\infty$. The range of the other angle is $0 \leq \phi \leq 2\pi$ for heteronuclear molecules (e.g. HCl) and $0 \leq \phi \leq \pi$ for homonuclear molecules (e.g. N_2).
(a) Calculate the canonical partition function Z_R^N for the rotational motion of a gas of N HCl molecules and a gas of N N_2 molecules.
(b) Calculate the difference in rotational entropy and in rotational internal energy of the two gases when both are at the same temperature.

Solution:

[tex89] Quantum rotational heat capacity of a gas at low temperature

The rotational spectrum of two-atomic molecules consists of energy levels

$$E_{lm} = \frac{l(l+1)\hbar^2}{2I}; \quad l = 0, 1, 2, \ldots; \quad m = -l, -l+1, \ldots, l.$$

Show that the leading term of the rotational heat capacity of a gas of N molecules at low temperature ($T \ll \Theta$) has the form

$$C_R(T) \simeq 12Nk_B \left(\frac{\Theta}{T}\right)^2 e^{-2\Theta/T}, \quad \Theta = \frac{\hbar^2}{2Ik_B}.$$

Solution:

[tex90] Quantum rotational heat capacity of a gas at high temperature

The rotational spectrum of two-atomic molecules consists of energy levels

$$E_{lm} = \frac{l(l+1)\hbar^2}{2I}; \quad l = 0, 1, 2, \ldots; \quad m = -l, -l+1, \ldots, +l.$$

(a) Use the Euler-McLaurin summation formula

$$\sum_{n=0}^{\infty} f(n) = \int_0^{\infty} dx\, f(x) + \frac{1}{2}f(0) - \frac{1}{12}f'(0) + \frac{1}{720}f'''(0) + \ldots$$

to calculate the first three terms of a high-temperature expansion of $Z_R = \sum_{lm} e^{-\beta E_{lm}}$.
(b) Use the result of (a) to show that the first two terms in a high-temperature expansion of the rotational heat capacity read

$$C_R \simeq N k_B \left[1 + \frac{1}{45}\left(\frac{\Theta}{T}\right)^2 + \ldots\right], \qquad \Theta = \frac{\hbar^2}{2Ik_B}.$$

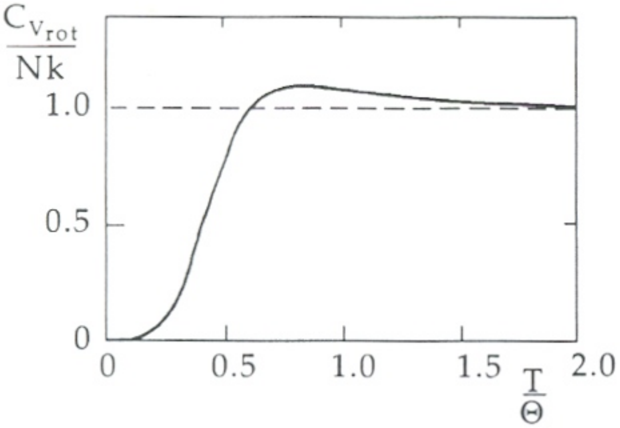
Solution:

Rotational and vibrational heat capacities

Rotational heat capacity of two-atomic gas:

$$T \ll \Theta: \qquad C \simeq 12Nk_B\left(\frac{\Theta}{T}\right)^2 e^{-2\Theta/T}; \quad \Theta \equiv \frac{\hbar^2}{2Ik_B}$$

$$T \gg \Theta: \qquad C \simeq Nk_B\left[1+\frac{1}{45}\left(\frac{\Theta}{T}\right)^2+\ldots\right]$$

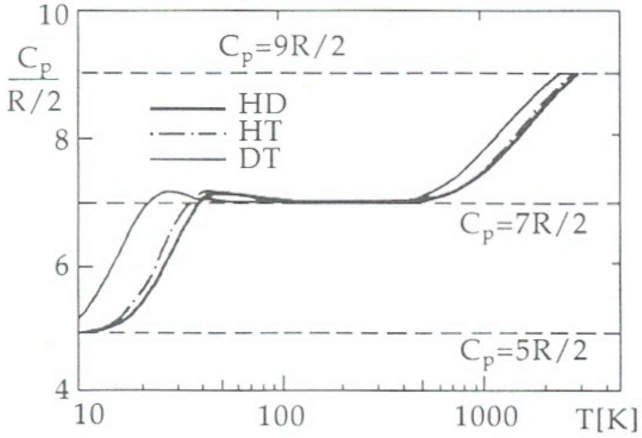


Rotational and vibrational heat capacities of hydrogen molecules:

H: ^{1}H (hydrogen)

D: ^{2}H (deuterium)

T: ^{3}H (tritium)



[from Greiner et al. 1995]

Orthohydrogen and parahydrogen [tln81]

Molecular hydrogen (H_2) comes in two (nuclear) spin isomers.

The electronic and nuclear wave functions must both be antisymmetric. The electronic ground state has a symmetric space part and an antisymmetric spin part (spin singlet). Electronic excited states have much higher energies.

Nuclear wave functions with symmetric spin part and antisymmetric space part or vice versa are energetically close to each other. The space part is described by rotational modes with orbital quantum numbers $l = 0, 1, 2, \ldots$ Vibrational modes have much higher energies.

- **Orthohydrogen**: Nuclear spin part is symmetric (spin triplet) and nuclear space part is antisymmetric (odd l).
- **Parahydrogen**: Nuclear spin part is antisymmetric (spin singlet) and nuclear space part is symmetric (even l).

At high T, the H_2 gas at equilibrium contains 75% orthohydrogen and 25% parahydrogen. The 3:1 ratio is a reflection of the nuclear spin degeneracy.

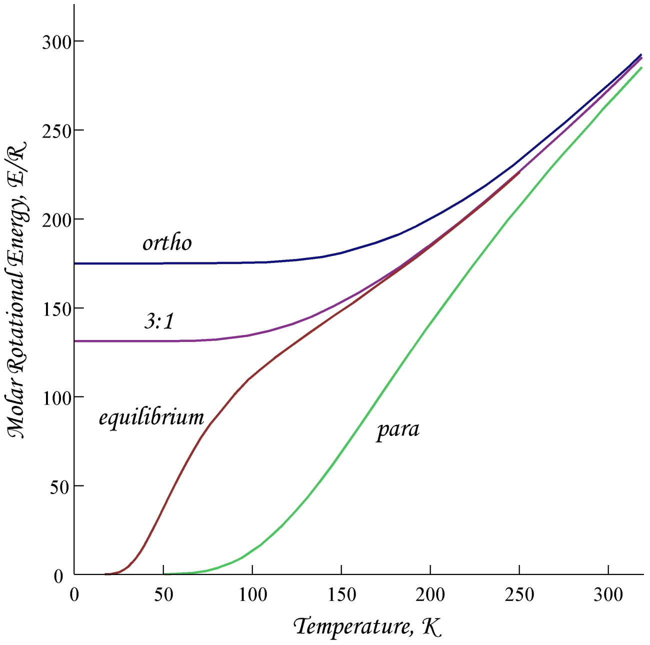
The lowest parahydrogen level is lower than the lowest orthohydrogen level by $\Delta E/k_B = \hbar^2/k_B I \simeq 175$K. Conversion is slow in the absence of catalysts. Cooling and condensing hydrogen may leave the majority of molecules in a metastable state. The transition to equilibrium at low T releases significant amounts of energy.

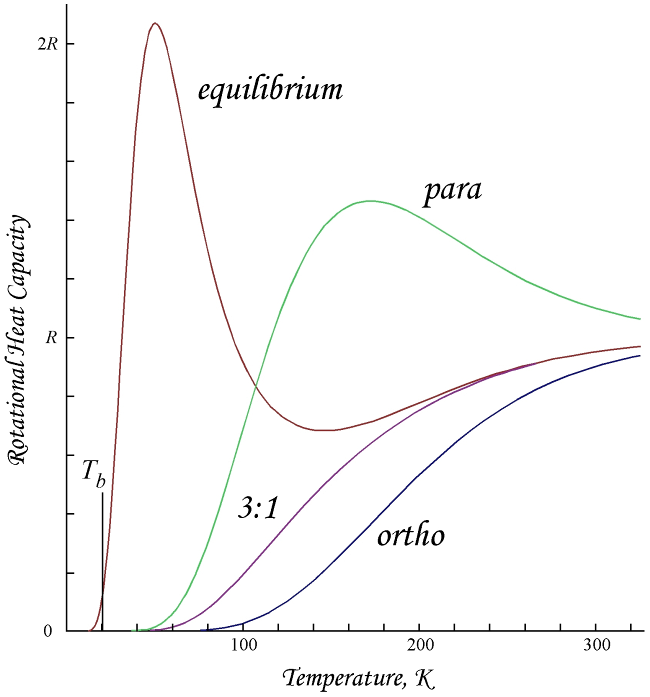
Rotational factors of canonical partition function under two conditions:

- {eq} Slow temperature variation with catalysts present.
- {3:1} More rapid temperature reduction with catalysts absent.

$$\tilde{Z}_R^{eq} = \big(\tilde{Z}_o + \tilde{Z}_p\big)^N, \qquad \tilde{Z}_R^{3:1} = \big(\tilde{Z}_o\big)^{3N/4}\big(\tilde{Z}_p\big)^{N/4}.$$

$$\tilde{Z}_o = 3\sum_{\text{odd } l}(2l+1)e^{-\beta l(l+1)\hbar^2/2I}, \qquad \tilde{Z}_p = \sum_{\text{even } l}(2l+1)e^{-\beta l(l+1)\hbar^2/2I},$$





[from Wikipedia]

[tex91] Relativistic ideal gas (canonical partition function)

Consider a classical ideal gas of N atoms confined to a box of volume V in thermal equilibrium with a heat reservoir at a very high temperature T. The Hamiltonian of the system,

$$H = \sum_{l=1}^{N} \left[\sqrt{m^2c^4 + p_l^2c^2} - mc^2 \right],$$

reflects the relativistic kinetic energy of N noninteracting particles. Here c is the speed of light and $p_l = |\mathbf{p}_l|$ is the magnitude of the momentum of particle l.
(a) Show that the canonical partition function can be expressed in the form

$$Z_N = \frac{1}{N!}\left[4\pi V \left(\frac{mc}{h}\right)^3 \frac{e^u}{u} K_2(u)\right]^N, \quad u \equiv \beta mc^2, \quad K_\gamma(u) = \frac{u}{\gamma}\int_0^\infty dx\, \sinh x \sinh(\gamma x) e^{-u\cosh x}$$

where $K_\gamma(u)$ is a modified Bessel function.
(b) Recover the result from [tex76] for Z_N of the nonrelativistic ideal gas at $k_BT \ll mc^2$ by using the asymptotic expression $K_2(u) \simeq \sqrt{\pi/2u}e^{-u}$ for $u \gg 1$.
(c) Recover the result from [tex77] for Z_N of the ultrarelativistic ideal gas at $k_BT \gg mc^2$ by using the asymptotic expression $K_2(u) \simeq 2/u^2$ for $u \ll 1$.

Solution:

[tex92] Relativistic ideal gas (entropy and internal energy)

(a) Derive from the result for the canonical partition function Z_N of the relativistic classical ideal gas as calculated in [tex91] the Helmholtz free energy $A(T,V,N)$, the equation of state $p(T,V,N)$, the chemical potential $\mu(T,V,N)$, and the entropy $S(T,V,N)$.
(b) Use the recursion relation, $K_n'(u) = -K_{n-1}(u) - (n/u)K_n(u)$, for the modified Bessel functions to derive the following expression for the internal energy:

$$U(T,N) = Nk_BTu\left[\frac{K_1(u)}{K_2(u)} + \frac{3}{u} - 1\right], \quad u \equiv \beta mc^2, \quad \beta = \frac{1}{k_BT}.$$

Solution:

[tex93] Relativistic ideal gas (heat capacity)

(a) Derive from the result for the internal energy $U(T,N)$ of the relativistic classical ideal gas as calculated in [tex92] the heat capacity in the form

$$C_V(T,N) = Nk_Bu\left[u + \frac{3}{u} - \frac{K_1(u)}{K_2(u)}\left(3 + u\frac{K_1(u)}{K_2(u)}\right)\right], \quad u \equiv \beta mc^2, \quad \beta = \frac{1}{k_BT}.$$

by using the recursion relations $K_n'(u) = -K_{n-1}(u) - (n/u)K_n(u)$ and $K_{n-1}(u) = K_{n+1}(u) - (2/u)K_n(u)$ for modified Bessel functions.
(b) Use the asymptotic results

$$\frac{K_1(u)}{K_2(u)} \simeq 1 - \frac{3}{2u} + \frac{15}{8u^2} \quad (u \gg 1), \qquad \frac{K_1(u)}{K_2(u)} \simeq \frac{u}{2} \quad (u \ll 1)$$

to recover the the results $C_V = \frac{3}{2}Nk_B$ and $C_V = 3Nk_B$ in the nonrelativistic and ultrarelativistic limits, respectively.

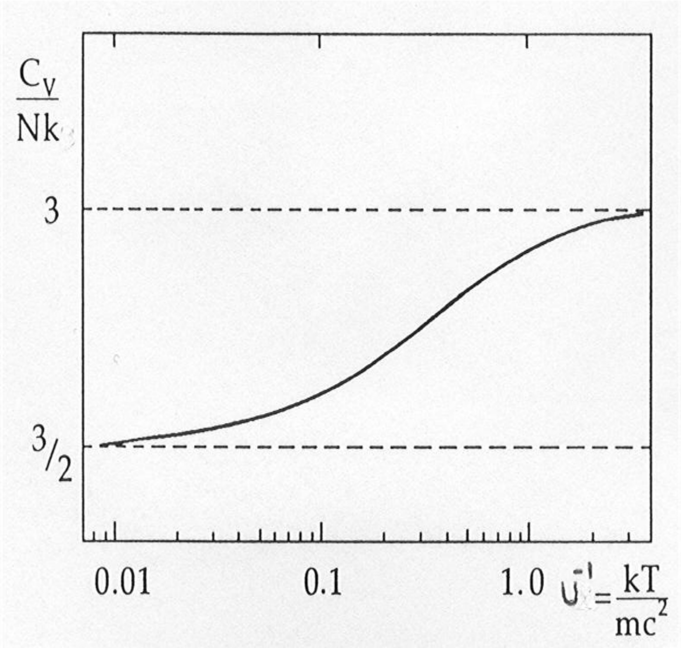
Solution:

Relativistic classical ideal gas [tsl34]

Heat capacity:

$$C_V = Nk_B u \left[u + \frac{3}{u} - \frac{K_1(u)}{K_2(u)} \left(3 + u\frac{K_1(u)}{K_2(u)} \right) \right]$$

$K_n(u)$: modified Bessel function; $u \equiv \beta mc^2$.



Nonrelativistic limit ($u \gg 1$): $\dfrac{K_1(u)}{K_2(u)} = 1 - \dfrac{3}{2u} + \dfrac{15}{8u^2} + \ldots$

Ultrarelativistic limit ($u \ll 1$): $\dfrac{K_1(u)}{K_2(u)} = \dfrac{u}{2} + \ldots$

[from Greiner et al. 1995]