Thermodynamics & Statistical Physics

Chapter 7. Boltzmann Statistics

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- For p and V, $đW = -p\mathrm{d}V$, so $p = \frac{N}{\beta} \frac{\partial \ln Z_1}{\partial V}$.
- As $\mathrm{d}\varepsilon_l = \sum_i \frac{\partial \varepsilon_l}{\partial y_i} \mathrm{d}y_i$, then $đW = \sum_i Y_i \mathrm{d}y_i$
$= \sum_i \mathrm{d}y_i \sum \frac{\partial \varepsilon_l}{\partial y_i} a_l = \sum (\sum_i \frac{\partial \varepsilon_l}{\partial y_i} \mathrm{d}y_i) a_l = \sum a_l \mathrm{d}\varepsilon_l$.
- $\because U = \sum \varepsilon_l a_l$, $\therefore \mathrm{d}U = \sum a_l \mathrm{d}\varepsilon_l + \sum \varepsilon_l \mathrm{d}a_l$
$= đW + đQ$.

Thermal quantities in statistics

- For each particle, the generalized force is $\frac{\partial \varepsilon_l}{\partial y}$, the whole force (Y_i): $Y = \sum \frac{\partial \varepsilon_l}{\partial y} a_l = \sum \frac{\partial \varepsilon_l}{\partial y} \omega_l e^{-\alpha-\beta\varepsilon_l}$
$= e^{-\alpha} \sum \omega_l \frac{\partial \varepsilon_l}{\partial y} e^{-\beta\varepsilon_l} = e^{-\alpha} \sum \omega_l (-\frac{1}{\beta}) \frac{\partial e^{-\beta\varepsilon_l}}{\partial y}$
$= e^{-\alpha} (-\frac{1}{\beta}) \frac{\partial}{\partial y} \sum \omega_l e^{-\beta\varepsilon_l} = \frac{N}{Z_1} (-\frac{1}{\beta}) \frac{\partial}{\partial y} Z_1 = -\frac{N}{\beta} \frac{\partial \ln Z_1}{\partial y}$.
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$= \sum_i \mathrm{d}y_i \sum \frac{\partial \varepsilon_l}{\partial y_i} a_l = \sum (\sum_i \frac{\partial \varepsilon_l}{\partial y_i} \mathrm{d}y_i) a_l = \sum a_l \mathrm{d}\varepsilon_l$.
- $\because U = \sum \varepsilon_l a_l$, $\therefore \mathrm{d}U = \sum a_l \mathrm{d}\varepsilon_l + \sum \varepsilon_l \mathrm{d}a_l$
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$đW$ changes the energy levels; $đQ$ changes $\{a_l\}$.

Thermal quantities in statistics — $\beta = \frac{1}{kT}$

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  $Z_1(\beta, \varepsilon_l)$, and $\varepsilon(y)$, so, $\mathrm{d}\ln Z_1 = \frac{\partial \ln Z_1}{\partial \beta}\mathrm{d}\beta + \frac{\partial \ln Z_1}{\partial y}\mathrm{d}y$.

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- $\therefore \beta = \frac{1}{kT}$, where k is a constant.

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$k = 1.381 \times 10^{-23}\mathrm{J}\cdot\mathrm{K}^{-1}$ can be measured.

Thermal quantities in statistics — entropy

- $\mathrm{d}S = \frac{1}{T} đQ$

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- Entropy statistical meaning: number of micro-states.
- $F = U - TS = -N\frac{\partial \ln Z_1}{\partial\beta} - TNk(\ln Z_1 - \beta\frac{\partial \ln Z_1}{\partial\beta})$
  $= -NkT\ln Z_1$.
- Conclusion: Given the partition function
  $Z_1 = \sum\omega_l e^{-\beta\varepsilon_l}$, thermal variables are determined.

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  Means, the wavelength should be much less than the distance of any two molecules. (Can be distinguished.)

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- Object: gas. Obeys classical limit, so Boltzmann distribution: $a_l = \omega_l e^{-\alpha-\beta\varepsilon_l}$.
- Simple case: monatomic molecules.
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$$\frac{\mathrm{d}(e^{-\frac{m}{2kT}v^2} v^2)}{\mathrm{d}v} = e^{-\frac{m}{2kT}v^2}(-\frac{m}{2kT}) \cdot 2v \cdot v^2 + e^{-\frac{m}{2kT}v^2} \cdot 2v$$
$$= e^{-\frac{m}{2kT}v^2}(-\frac{m}{2\pi kT}v^2 + 1) \cdot 2v = 0, \Rightarrow v_m^2 = \frac{2kT}{m}.$$

- Average speed $\bar{v} = \int v f(v)/n \mathrm{d}v$

$$= 4\pi(\frac{m}{2\pi kT})^{\frac{3}{2}} \int_0^\infty v e^{-\frac{m}{2kT}v^2} v^2 \mathrm{d}v$$
$$= 4\pi(\frac{m}{2\pi kT})^{\frac{3}{2}} \cdot \frac{1}{2} \int_0^\infty e^{-\frac{m}{2kT}v^2} v^2 \mathrm{d}v^2$$
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$$= 4\pi(\frac{m}{2\pi kT})^{\frac{3}{2}} \cdot \frac{1}{2}(-\frac{2kT}{m})[(v^2 e^{-\frac{m}{2kT}v^2})|_0^\infty - \int_0^\infty e^{-\frac{m}{2kT}v^2} \mathrm{d}v^2]$$
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$$= 4\pi(\frac{m}{2\pi kT})^{\frac{3}{2}} \cdot \frac{1}{2}(\frac{2kT}{m})^2 = \sqrt{\frac{8kT}{\pi m}}.$$

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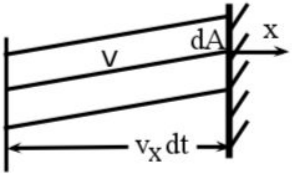
Γ : Number of colliding molecules on the surface in unit time unit area.



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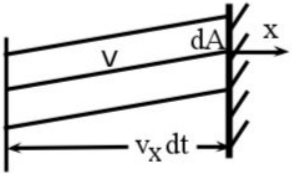

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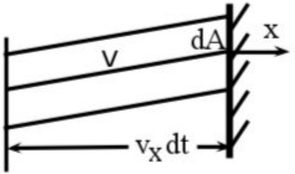

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$f(v_x, v_y, v_z)\mathrm{d}v_x\mathrm{d}v_y\mathrm{d}v_z \cdot v_x \mathrm{d}t\mathrm{d}A$.

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  $=nkT$.

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  $=2mn(\frac{m}{2\pi kT})^{\frac{3}{2}}(\frac{2kT}{m})^{\frac{3}{2}}\int_0^\infty(\frac{m}{2kT}v_x^2)e^{-\frac{m}{2kT}v_x^2}\mathrm{d}(\sqrt{\frac{m}{2kT}}v_x)\cdot$
  $\frac{2kT}{m}\iint_{-\infty}^{\infty}e^{-\frac{m}{2kT}(v_y^2+v_z^2)}\mathrm{d}(\sqrt{\frac{m}{2kT}}v_y)\mathrm{d}(\sqrt{\frac{m}{2kT}}v_z)$
  $=2mn(\frac{m}{2\pi kT})^{\frac{3}{2}}(\frac{2kT}{m})^{\frac{3}{2}}\cdot\frac{\sqrt{\pi}}{4}\cdot\frac{2kT}{m}\pi$
  $=nkT$.
  Same as eq (7.2.5).

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- $\overline{\frac{1}{2}a_1p_1^2} = \frac{1}{Z_1}\int \frac{1}{2}a_1p_1^2 \cdot e^{-\beta\varepsilon}\frac{\mathrm{d}q_1\ldots\mathrm{d}q_r\mathrm{d}p_1\ldots\mathrm{d}p_r}{h_0^r}$

$$= \int_{-\infty}^{\infty}\frac{1}{2}a_1p_1^2 e^{-\beta\frac{1}{2}a_1p_1^2}\mathrm{d}p_1 \cdot \frac{1}{Z_1}\int e^{-\beta(\varepsilon-\frac{1}{2}a_1p_1^2)}\frac{\mathrm{d}q_1\ldots\mathrm{d}q_r\mathrm{d}p_2\ldots\mathrm{d}p_r}{h_0^r}$$

$$= \int_{-\infty}^{\infty}\frac{1}{4}a_1p_1 e^{-\beta\frac{1}{2}a_1p_1^2}\mathrm{d}p_1^2 \cdot \frac{1}{Z_1}\int e^{-\beta(\varepsilon-\frac{1}{2}a_1p_1^2)}\frac{\mathrm{d}q_1\ldots\mathrm{d}q_r\mathrm{d}p_2\ldots\mathrm{d}p_r}{h_0^r}$$

$$= \int_{-\infty}^{\infty}\frac{1}{4}a_1p_1 \cdot (\frac{-2}{\beta a_1})\mathrm{d}e^{-\beta\frac{1}{2}a_1p_1^2} \cdot$$

$$\frac{1}{Z_1}\int e^{-\beta(\varepsilon-\frac{1}{2}a_1p_1^2)}\frac{\mathrm{d}q_1\ldots\mathrm{d}q_r\mathrm{d}p_2\ldots\mathrm{d}p_r}{h_0^r}$$

$$= \frac{1}{2\beta}\int_{-\infty}^{\infty} e^{-\beta\frac{1}{2}a_1p_1^2}\mathrm{d}p_1 \cdot \frac{1}{Z_1}\int e^{-\beta(\varepsilon-\frac{1}{2}a_1p_1^2)}\frac{\mathrm{d}q_1\ldots\mathrm{d}q_r\mathrm{d}p_2\ldots\mathrm{d}p_r}{h_0^r}$$

$$= \frac{1}{2\beta}\frac{1}{Z_1}\int e^{-\beta\varepsilon}\frac{\mathrm{d}q_1\ldots\mathrm{d}q_r\mathrm{d}p_1\ldots\mathrm{d}p_r}{h_0^r}$$

$$= \frac{1}{2\beta}$$

Energy equipartition theorem

- $$\begin{aligned}
\overline{\tfrac{1}{2}a_1p_1^2} &= \frac{1}{Z_1}\int \tfrac{1}{2}a_1p_1^2 \cdot e^{-\beta\varepsilon}\frac{\mathrm{d}q_1 \ldots \mathrm{d}q_r \mathrm{d}p_1 \ldots \mathrm{d}p_r}{h_0^r} \\
&= \int_{-\infty}^{\infty} \tfrac{1}{2}a_1p_1^2 e^{-\beta\frac{1}{2}a_1p_1^2}\mathrm{d}p_1 \cdot \frac{1}{Z_1}\int e^{-\beta(\varepsilon-\frac{1}{2}a_1p_1^2)}\frac{\mathrm{d}q_1 \ldots \mathrm{d}q_r \mathrm{d}p_2 \ldots \mathrm{d}p_r}{h_0^r} \\
&= \int_{-\infty}^{\infty} \tfrac{1}{4}a_1p_1 e^{-\beta\frac{1}{2}a_1p_1^2}\mathrm{d}p_1^2 \cdot \frac{1}{Z_1}\int e^{-\beta(\varepsilon-\frac{1}{2}a_1p_1^2)}\frac{\mathrm{d}q_1 \ldots \mathrm{d}q_r \mathrm{d}p_2 \ldots \mathrm{d}p_r}{h_0^r} \\
&= \int_{-\infty}^{\infty} \tfrac{1}{4}a_1p_1 \cdot \left(\frac{-2}{\beta a_1}\right)\mathrm{d}e^{-\beta\frac{1}{2}a_1p_1^2} \cdot \\
&\quad \frac{1}{Z_1}\int e^{-\beta(\varepsilon-\frac{1}{2}a_1p_1^2)}\frac{\mathrm{d}q_1 \ldots \mathrm{d}q_r \mathrm{d}p_2 \ldots \mathrm{d}p_r}{h_0^r} \\
&= \frac{1}{2\beta}\int_{-\infty}^{\infty} e^{-\beta\frac{1}{2}a_1p_1^2}\mathrm{d}p_1 \cdot \frac{1}{Z_1}\int e^{-\beta(\varepsilon-\frac{1}{2}a_1p_1^2)}\frac{\mathrm{d}q_1 \ldots \mathrm{d}q_r \mathrm{d}p_2 \ldots \mathrm{d}p_r}{h_0^r} \\
&= \frac{1}{2\beta}\frac{1}{Z_1}\int e^{-\beta\varepsilon}\frac{\mathrm{d}q_1 \ldots \mathrm{d}q_r \mathrm{d}p_1 \ldots \mathrm{d}p_r}{h_0^r} \\
&= \frac{1}{2\beta} = \frac{1}{2}kT.
\end{aligned}$$

Energy equipartition theorem

- $\overline{\frac{1}{2}a_1p_1^2} = \frac{1}{Z_1}\int \frac{1}{2}a_1p_1^2 \cdot e^{-\beta\varepsilon}\frac{\mathrm{d}q_1\ldots\mathrm{d}q_r\mathrm{d}p_1\ldots\mathrm{d}p_r}{h_0^r}$
  $= \int_{-\infty}^{\infty}\frac{1}{2}a_1p_1^2 e^{-\beta\frac{1}{2}a_1p_1^2}\mathrm{d}p_1 \cdot \frac{1}{Z_1}\int e^{-\beta(\varepsilon-\frac{1}{2}a_1p_1^2)}\frac{\mathrm{d}q_1\ldots\mathrm{d}q_r\mathrm{d}p_2\ldots\mathrm{d}p_r}{h_0^r}$
  $= \int_{-\infty}^{\infty}\frac{1}{4}a_1p_1 e^{-\beta\frac{1}{2}a_1p_1^2}\mathrm{d}p_1^2 \cdot \frac{1}{Z_1}\int e^{-\beta(\varepsilon-\frac{1}{2}a_1p_1^2)}\frac{\mathrm{d}q_1\ldots\mathrm{d}q_r\mathrm{d}p_2\ldots\mathrm{d}p_r}{h_0^r}$
  $= \int_{-\infty}^{\infty}\frac{1}{4}a_1p_1 \cdot (\frac{-2}{\beta a_1})\mathrm{d}e^{-\beta\frac{1}{2}a_1p_1^2} \cdot$
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  $= \frac{1}{2\beta}\int_{-\infty}^{\infty} e^{-\beta\frac{1}{2}a_1p_1^2}\mathrm{d}p_1 \cdot \frac{1}{Z_1}\int e^{-\beta(\varepsilon-\frac{1}{2}a_1p_1^2)}\frac{\mathrm{d}q_1\ldots\mathrm{d}q_r\mathrm{d}p_2\ldots\mathrm{d}p_r}{h_0^r}$
  $= \frac{1}{2\beta}\frac{1}{Z_1}\int e^{-\beta\varepsilon}\frac{\mathrm{d}q_1\ldots\mathrm{d}q_r\mathrm{d}p_1\ldots\mathrm{d}p_r}{h_0^r}$
  $= \frac{1}{2\beta} = \frac{1}{2}kT.$
- Similar for the other quadratic term.

Energy equipartition theorem

- $\overline{\frac{1}{2}a_1p_1^2} = \frac{1}{Z_1}\int \frac{1}{2}a_1p_1^2 \cdot e^{-\beta\varepsilon}\frac{\mathrm{d}q_1\ldots\mathrm{d}q_r\mathrm{d}p_1\ldots\mathrm{d}p_r}{h_0^r}$
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$= \frac{1}{2\beta} = \frac{1}{2}kT.$
- Similar for the other quadratic term.
- Application: internal energy U, thermal capacity C_V.

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  Eq. (7.2.6), $\frac{V}{N}(\frac{2\pi mkT}{h^2})^{3/2}$, classical limit.

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  $\bar{\varepsilon} = 3kT$, $U = 3NkT$, $C_V = 3Nk$.
  Consistent with the experiment at high temperature.

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Application 4. Equilibrium radiation

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  Degeneracy: $\omega_l = 2l + 1$.

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  $Z_1^r = \int_0^{\infty}(2l+1)e^{-x}\frac{\mathrm{d}x}{(2l+1)(\theta_r/T)} = \frac{T}{\theta_r}\int_0^{\infty}e^{-x}\mathrm{d}x = \frac{T}{\theta_r}$
  $= T\frac{2Ik}{\hbar^2} = \frac{2I}{\beta\hbar^2}$.
- $U^r = -N\frac{\partial}{\partial\beta}\ln Z_1^r = N(\frac{2I}{\beta\hbar^2})^{-1}\cdot\frac{2I}{\beta^2\hbar^2} = \frac{N}{\beta}$

Internal energy and heat capacity of the ideal gas

- Partition function: $Z_1^r = \sum_{l=0}^{\infty}(2l+1)e^{-\frac{l(l+1)\hbar^2}{2IkT}}$.
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- $C_V^r = Nk$.
- At normal temperature (Table 7.5), $\frac{\theta_r}{T} \ll 1$ holds.

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Internal energy and heat capacity of the ideal gas

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- If $\theta_r \ll T$, the hydrogen molecule is in high l state, $l \sim l+1$, then $\sum\limits_{l=0,2\ldots}^{\infty} \ldots \simeq \sum\limits_{l=1,3\ldots}^{\infty} \ldots \simeq \frac{1}{2}\sum\limits_{l=0,1\ldots}^{\infty} \ldots$

Internal energy and heat capacity of the ideal gas

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Internal energy and heat capacity of the ideal gas

- $Z^r_{1o} \simeq Z^r_{1p} \simeq \frac{1}{2} \sum\limits_{l=0,1\ldots} (2l+1) e^{-\frac{l(l+1)\theta_r}{T}}$
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- $C_V^r = Nk$.
- If $\theta_r \ll T$ does not hold, the summation is necessary.

General processes for **classical** statistics

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- $Z_1 = \int \dots \int e^{-\beta\varepsilon(q,p)}\frac{\mathrm{d}q_1\dots\mathrm{d}q_r\mathrm{d}p_1\dots\mathrm{d}p_r}{h_0^r}$,

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- Integration:
  $Z_1^t = V\left(\frac{2\pi m}{h_0^2\beta}\right)^{3/2}$.

General processes for classical statistics

- $Z_1^r = \int e^{-\frac{\beta}{2I}(p_\theta^2 + \frac{1}{\sin^2\theta} p_\varphi^2)} \frac{\mathrm{d}p_\theta \mathrm{d}p_\varphi \mathrm{d}\theta \mathrm{d}\varphi}{h_0^2}$

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$= \frac{1}{h_0^2} \int_0^{2\pi} \mathrm{d}\varphi \int_0^{\pi} \mathrm{d}\theta \int_{-\infty}^{\infty} e^{-\frac{\beta}{2I} p_\theta^2} \mathrm{d}p_\theta \int_{-\infty}^{\infty} e^{-\frac{\beta}{2I\sin^2\theta} p_\varphi^2} \mathrm{d}p_\varphi$

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  $= \frac{1}{h_0^2}\int_0^{2\pi}\mathrm{d}\varphi \int_0^{\pi}\mathrm{d}\theta \int_{-\infty}^{\infty} e^{-\frac{\beta}{2I}p_\theta^2}\mathrm{d}p_\theta \int_{-\infty}^{\infty} e^{-\frac{\beta}{2I\sin^2\theta}p_\varphi^2}\mathrm{d}p_\varphi$
  $=$
  $\frac{2\pi}{h_0^2}\int_0^{\pi}\mathrm{d}\theta\sqrt{\frac{2I}{\beta}}\sqrt{\pi}\cdot\sqrt{\frac{2I\sin^2\theta}{\beta}}\int_{-\infty}^{\infty} e^{-\frac{\beta}{2I\sin^2\theta}p_\varphi^2}\mathrm{d}\sqrt{\frac{\beta}{2I\sin^2\theta}}p_\varphi$

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  $= \frac{1}{h_0^2}\int_0^{2\pi}\mathrm{d}\varphi \int_0^{\pi}\mathrm{d}\theta \int_{-\infty}^{\infty} e^{-\frac{\beta}{2I}p_\theta^2}\mathrm{d}p_\theta \int_{-\infty}^{\infty} e^{-\frac{\beta}{2I\sin^2\theta}p_\varphi^2}\mathrm{d}p_\varphi$
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  $\frac{2\pi}{h_0^2}\int_0^{\pi}\mathrm{d}\theta\sqrt{\frac{2I}{\beta}}\sqrt{\pi}\cdot\sqrt{\frac{2I\sin^2\theta}{\beta}}\int_{-\infty}^{\infty} e^{-\frac{\beta}{2I\sin^2\theta}p_\varphi^2}\mathrm{d}\sqrt{\frac{\beta}{2I\sin^2\theta}}p_\varphi$
  $= \frac{2\pi}{h_0^2}\int_0^{\pi}\mathrm{d}\theta\sqrt{\frac{2I}{\beta}}\sqrt{\pi}\cdot\sqrt{\frac{2I\sin^2\theta}{\beta}}\sqrt{\pi}$

General processes for classical statistics

- $Z_1^r = \int e^{-\frac{\beta}{2I}(p_\theta^2+\frac{1}{\sin^2\theta}p_\varphi^2)} \frac{\mathrm{d}p_\theta \mathrm{d}p_\varphi \mathrm{d}\theta \mathrm{d}\varphi}{h_0^2}$
  $= \frac{1}{h_0^2}\int_0^{2\pi}\mathrm{d}\varphi\int_0^{\pi}\mathrm{d}\theta\int_{-\infty}^{\infty}e^{-\frac{\beta}{2I}p_\theta^2}\mathrm{d}p_\theta\int_{-\infty}^{\infty}e^{-\frac{\beta}{2I\sin^2\theta}p_\varphi^2}\mathrm{d}p_\varphi$
  $=$
  $\frac{2\pi}{h_0^2}\int_0^{\pi}\mathrm{d}\theta\sqrt{\frac{2I}{\beta}}\sqrt{\pi}\cdot\sqrt{\frac{2I\sin^2\theta}{\beta}}\int_{-\infty}^{\infty}e^{-\frac{\beta}{2I\sin^2\theta}p_\varphi^2}\mathrm{d}\sqrt{\frac{\beta}{2I\sin^2\theta}}p_\varphi$
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  $= \frac{2\pi^2}{h_0^2}\frac{2I}{\beta}\int_0^{\pi}\sin\theta \mathrm{d}\theta$
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- Introduce typical temperature θ_E: $k\theta_E = \hbar\omega$.

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Paramagnetic solid

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Negative temperature $\boxed{N_\pm = \frac{N}{2}(1 \pm \frac{E}{N\varepsilon})}$

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$$= k\{N\ln N - \frac{N}{2}(1+\frac{E}{N\varepsilon})[\ln\frac{N}{2} + \ln(1+\frac{E}{N\varepsilon})] - \frac{N}{2}(1-\frac{E}{N\varepsilon})[\ln\frac{N}{2} + \ln(1-\frac{E}{N\varepsilon})]\}$$
$$= k\{N\ln N - \frac{N}{2}\ln\frac{N}{2}[(1+\frac{E}{N\varepsilon}) + (1-\frac{E}{N\varepsilon})] - \frac{N}{2}(1+\frac{E}{N\varepsilon})\ln(1+\frac{E}{N\varepsilon}) - \frac{N}{2}(1-\frac{E}{N\varepsilon})\ln(1-\frac{E}{N\varepsilon})\}$$

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&\simeq k[N(\ln N - 1) - N_+(\ln N_+ - 1) - N_-(\ln N_- - 1)] \\
&= k(N \ln N - N_+ \ln N_+ - N_- \ln N_-) \\
&= k\{N \ln N - \frac{N}{2}(1 + \frac{E}{N\varepsilon}) \ln[\frac{N}{2}(1 + \frac{E}{N\varepsilon})] \\
&\quad - \frac{N}{2}(1 - \frac{E}{N\varepsilon}) \ln[\frac{N}{2}(1 - \frac{E}{N\varepsilon})]\} \\
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&\quad - \frac{N}{2}(1 - \frac{E}{N\varepsilon})[\ln \frac{N}{2} + \ln(1 - \frac{E}{N\varepsilon})]\} \\
&= k\{N \ln N - \frac{N}{2} \ln \frac{N}{2}[(1 + \frac{E}{N\varepsilon}) + (1 - \frac{E}{N\varepsilon})] \\
&\quad - \frac{N}{2}(1 + \frac{E}{N\varepsilon}) \ln(1 + \frac{E}{N\varepsilon}) - \frac{N}{2}(1 - \frac{E}{N\varepsilon}) \ln(1 - \frac{E}{N\varepsilon})\} \\
&= k\{N \ln N - N \ln \frac{N}{2} \\
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  $- \frac{N}{2}(1 + \frac{E}{N\varepsilon}) \ln(1 + \frac{E}{N\varepsilon}) - \frac{N}{2}(1 - \frac{E}{N\varepsilon}) \ln(1 - \frac{E}{N\varepsilon})\}$
  $= k\{N \ln N - N \ln \frac{N}{2}$
  $- \frac{N}{2}(1 + \frac{E}{N\varepsilon}) \ln(1 + \frac{E}{N\varepsilon}) - \frac{N}{2}(1 - \frac{E}{N\varepsilon}) \ln(1 - \frac{E}{N\varepsilon})\}$
  $= Nk[\ln 2 - \frac{1}{2}(1 + \frac{E}{N\varepsilon}) \ln(1 + \frac{E}{N\varepsilon}) - \frac{1}{2}(1 - \frac{E}{N\varepsilon}) \ln(1 - \frac{E}{N\varepsilon})].$

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$$= -\frac{k}{2\varepsilon}[\ln(1+\frac{E}{N\varepsilon}) - \ln(1-\frac{E}{N\varepsilon})] = \frac{k}{2\varepsilon}\ln\frac{N\varepsilon-E}{N\varepsilon+E}.$$

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$$
\begin{aligned}
\frac{1}{T} &= \left(\frac{\partial S}{\partial E}\right)_B \\
&= \frac{\partial}{\partial E}\left\{Nk\left[\ln 2-\frac{1}{2}\left(1+\frac{E}{N\varepsilon}\right)\ln\left(1+\frac{E}{N\varepsilon}\right)-\frac{1}{2}\left(1-\frac{E}{N\varepsilon}\right)\ln\left(1-\frac{E}{N\varepsilon}\right)\right]\right\} \\
&= -\frac{Nk}{2}\left[\left(1+\frac{E}{N\varepsilon}\right)\cdot\frac{\frac{1}{N\varepsilon}}{1+\frac{E}{N\varepsilon}}+\frac{1}{N\varepsilon}\ln\left(1+\frac{E}{N\varepsilon}\right)+\left(1-\frac{E}{N\varepsilon}\right)\cdot\frac{-\frac{1}{N\varepsilon}}{1-\frac{E}{N\varepsilon}}-\frac{1}{N\varepsilon}\ln\left(1-\frac{E}{N\varepsilon}\right)\right] \\
&= -\frac{Nk}{2}\left[\frac{1}{N\varepsilon}+\frac{1}{N\varepsilon}\ln\left(1+\frac{E}{N\varepsilon}\right)-\frac{1}{N\varepsilon}-\frac{1}{N\varepsilon}\ln\left(1-\frac{E}{N\varepsilon}\right)\right] \\
&= -\frac{k}{2\varepsilon}\left[\ln\left(1+\frac{E}{N\varepsilon}\right)-\ln\left(1-\frac{E}{N\varepsilon}\right)\right] = \frac{k}{2\varepsilon}\ln\frac{N\varepsilon-E}{N\varepsilon+E}.
\end{aligned}
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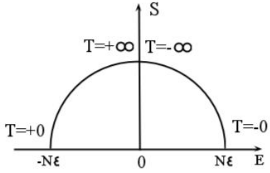

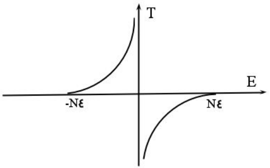

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