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): $Y = \sum \frac{\partial \varepsilon_l}{\partial y} a_l = \sum \frac{\partial \varepsilon_l}{\partial y} \omega_l e^{-\alpha-\beta\varepsilon_l}$
$= e^{-\alpha} \sum \omega_l \frac{\partial \varepsilon_l}{\partial y} e^{-\beta\varepsilon_l} = e^{-\alpha} \sum \omega_l (-\frac{1}{\beta}) \frac{\partial e^{-\beta\varepsilon_l}}{\partial y}$
$= e^{-\alpha}(-\frac{1}{\beta}) \frac{\partial}{\partial y} \sum \omega_l e^{-\beta\varepsilon_l} = \frac{N}{Z_1}(-\frac{1}{\beta}) \frac{\partial}{\partial y} Z_1 = -\frac{N}{\beta} \frac{\partial \ln Z_1}{\partial y}$.
- 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 $đW = \sum_i Y_i \mathrm{d}y_i$
$= \sum_i \mathrm{d}y_i \sum \frac{\partial \varepsilon_l}{\partial y_i} a_l = \sum (\sum_i \frac{\partial \varepsilon_l}{\partial y_i} \mathrm{d}y_i) a_l = \sum a_l \mathrm{d}\varepsilon_l$.
- $\because U = \sum \varepsilon_l a_l$, $\therefore \mathrm{d}U = \sum a_l \mathrm{d}\varepsilon_l + \sum \varepsilon_l \mathrm{d}a_l$
$= đW + đQ$.

$đW$ changes the energy levels; $đQ$ changes $\{a_l\}$.

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

Thermal quantities in statistics — entropy

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- 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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  Degeneracy: $\omega = \frac{V}{h^3}\mathrm{d}p_x\mathrm{d}p_y\mathrm{d}p_z$.
- $a = \frac{V}{h^3}e^{-\alpha-\frac{1}{2mkT}(p_x^2+p_y^2+p_z^2)}\mathrm{d}p_x\mathrm{d}p_y\mathrm{d}p_z$.
- $N = \sum a_l = \frac{V}{h^3}\iiint e^{-\alpha-\frac{1}{2mkT}(p_x^2+p_y^2+p_z^2)}\mathrm{d}p_x\mathrm{d}p_y\mathrm{d}p_z =$
  $e^{-\alpha}\frac{V}{h^3}(2mkT)^{\frac{3}{2}}\int e^{-\frac{p_x^2}{2mkT}}\mathrm{d}\frac{p_x}{\sqrt{2mkT}}\int e^{-\frac{p_y^2}{2mkT}}\mathrm{d}\frac{p_y}{\sqrt{2mkT}}\int e^{-\frac{p_z^2}{2mk}}$
  $= e^{-\alpha}\frac{V}{h^3}(2mkT)^{\frac{3}{2}}(\sqrt{\pi})^3 \Rightarrow e^{-\alpha} = \frac{N}{V}\left(\frac{h^2}{2\pi mkT}\right)^{\frac{3}{2}}$.

7.3 Maxwell speed distribution

- Object: gas. Obeys classical limit, so Boltzmann distribution: $a_l = \omega_l e^{-\alpha-\beta\varepsilon_l}$.
- Simple case: monatomic molecules.
- Energy: $\varepsilon = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2)$; Degeneracy: $\omega = \frac{V}{h^3}\mathrm{d}p_x\mathrm{d}p_y\mathrm{d}p_z$.
- $a = \frac{V}{h^3}e^{-\alpha-\frac{1}{2mkT}(p_x^2+p_y^2+p_z^2)}\mathrm{d}p_x\mathrm{d}p_y\mathrm{d}p_z$.
- $N = \sum a_l = \frac{V}{h^3}\iiint e^{-\alpha-\frac{1}{2mkT}(p_x^2+p_y^2+p_z^2)}\mathrm{d}p_x\mathrm{d}p_y\mathrm{d}p_z =$ $e^{-\alpha}\frac{V}{h^3}(2mkT)^{\frac{3}{2}}\int e^{-\frac{p_x^2}{2mkT}}\mathrm{d}\frac{p_x}{\sqrt{2mkT}}\int e^{-\frac{p_y^2}{2mkT}}\mathrm{d}\frac{p_y}{\sqrt{2mkT}}\int e^{-\frac{p_z^2}{2mk}}$ $= e^{-\alpha}\frac{V}{h^3}(2mkT)^{\frac{3}{2}}(\sqrt{\pi})^3 \Rightarrow e^{-\alpha} = \frac{N}{V}(\frac{h^2}{2\pi mkT})^{\frac{3}{2}}$.
- $\therefore a = N(\frac{1}{2\pi mkT})^{\frac{3}{2}}e^{-\frac{1}{2mkT}(p_x^2+p_y^2+p_z^2)}\mathrm{d}p_x\mathrm{d}p_y\mathrm{d}p_z$.

Maxwell speed distribution

- Turn to velocity space: $v_x = \frac{p_x}{m}$,

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  $= n(\frac{m}{2\pi kT})^{\frac{3}{2}} e^{-\frac{m}{2kT}(v_x^2+v_y^2+v_z^2)}\mathrm{d}v_x\mathrm{d}v_y\mathrm{d}v_z$.

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- Convert to spheric polar coordinates (v, θ, φ),
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  Maxwell speed distribution. Obeys:
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Maxwell speed distribution $\boxed{f(v) = 4\pi n(\frac{m}{2kT})^{\frac{3}{2}} e^{-\frac{m}{2kT}v^2} v^2}$

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

Maxwell speed distribution

- Root-mean-square speed:

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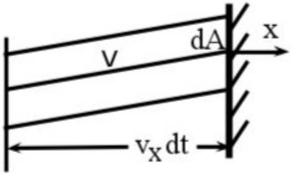
Application 1: frequency of colliding.
Γ : Number of colliding molecules on the surface in unit time unit area.



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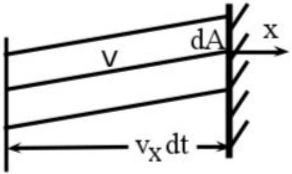

For a given velocity, (v_x, v_y, v_z), all particles inside the oblique cylinder can collide.

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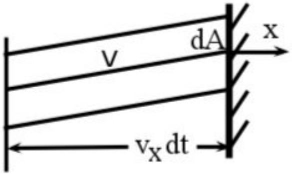

For a given velocity, (v_x, v_y, v_z), all particles inside the oblique cylinder can collide. The number is
$f(v_x, v_y, v_z)\mathrm{d}v_x\mathrm{d}v_y\mathrm{d}v_z \cdot v_x\mathrm{d}t\mathrm{d}A$.

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$$\boxed{f(v_x, v_y, v_z) = n\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{m}{2kT}(v_x^2+v_y^2+v_z^2)}}$$

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&= n\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \int_0^\infty v_x e^{-\frac{m}{2kT}v_x^2} \mathrm{d}v_x \iint_{-\infty}^{\infty} e^{-\frac{m}{2kT}(v_y^2+v_z^2)} \mathrm{d}v_y \mathrm{d}v_z \\
&= n\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \cdot \left(\frac{1}{2}\frac{2kT}{m}\right) \cdot \left(\frac{2kT}{m}\pi\right)
\end{aligned}$$

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&= n(\frac{m}{2\pi kT})^{\frac{3}{2}}\int_0^\infty v_x e^{-\frac{m}{2kT}v_x^2}\mathrm{d}v_x\iint_{-\infty}^{\infty}e^{-\frac{m}{2kT}(v_y^2+v_z^2)}\mathrm{d}v_y\mathrm{d}v_z\\
&= n(\frac{m}{2\pi kT})^{\frac{3}{2}}\cdot(\frac{1}{2}\frac{2kT}{m})\cdot(\frac{2kT}{m}\pi)\\
&= n\sqrt{\frac{kT}{2\pi m}}\end{aligned}$$

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&= n\sqrt{\frac{kT}{2\pi m}} \\
&= \frac{1}{4} n\bar{v}.
\end{aligned}$$

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  $= 2mn(\frac{m}{2\pi kT})^{\frac{3}{2}} (\frac{2kT}{m})^{\frac{3}{2}} \int_0^\infty (\frac{m}{2kT} v_x^2) e^{-\frac{m}{2kT} v_x^2} \mathrm{d}(\sqrt{\frac{m}{2kT}} v_x) \cdot$
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  $= nkT$.

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  Same as eq (7.2.5).

Table of contents

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

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  $= \int_{-\infty}^{\infty}\frac{1}{2}a_1 p_1^2 e^{-\beta\frac{1}{2}a_1 p_1^2}\mathrm{d}p_1 \cdot \frac{1}{Z_1}\int e^{-\beta(\varepsilon - \frac{1}{2}a_1 p_1^2)}\frac{\mathrm{d}q_1 ... \mathrm{d}q_r \mathrm{d}p_2 ... \mathrm{d}p_r}{h_0^r}$

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

Energy equipartition theorem

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

Energy equipartition theorem

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

Application 1. Monatomic molecules

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- $\varepsilon = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2)$

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- $\varepsilon = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2)$
  $\Rightarrow \bar{\varepsilon} = \frac{3}{2}kT$ (3 quadratic terms).

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

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- Using the periodic boundary condition:

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- In spheric polar coordinate, isotropic radiation, together with the polarization:
  $\Delta n_x \Delta n_y \Delta n_z = 2\frac{V}{(2\pi)^3} k^2 \mathrm{d}k \cdot 4\pi = 2\frac{V}{(2\pi)^3} (\frac{\omega}{c})^2 \mathrm{d}\frac{\omega}{c} \cdot 4\pi$
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- As for each vibration $\bar{\varepsilon} = kT$, the internal energy
  $U_\omega \mathrm{d}\omega = \frac{V}{\pi^2 c^3} kT \omega^2 \mathrm{d}\omega$.

Application 4. Equilibrium radiation

- $k_x = \frac{2\pi}{L} n_x$, $n_x = 0, \pm 1, \pm 2, \ldots$
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  Exactly the black body radiation formula!

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

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

Internal energy and heat capacity of the ideal gas

- Partition function: $Z_1^r = \sum_{l=0}^{\infty}(2l+1)e^{-\frac{l(l+1)\hbar^2}{2IkT}}$.
- Define typical temperature θ_r: $k\theta_r = \frac{\hbar^2}{2I}$.
- $Z_1^r = \sum_{l=0}^{\infty}(2l+1)e^{-\frac{l(l+1)\theta_r}{T}}$.
- If $\theta_r/T \ll 1$, ε^r is approximately continuous. Set $x = l(l+1)\frac{\theta_r}{T}$, then $\mathrm{d}x = (2l+1)\frac{\theta_r}{T}\Delta l$.
  $Z_1^r = \int_0^{\infty}(2l+1)e^{-x}\frac{\mathrm{d}x}{(2l+1)(\theta_r/T)} = \frac{T}{\theta_r}\int_0^{\infty} e^{-x}\mathrm{d}x = \frac{T}{\theta_r}$
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- $C_V^r = Nk$.
- At normal temperature (Table 7.5), $\frac{\theta_r}{T} \ll 1$ holds.

Internal energy and heat capacity of the ideal gas

- iii.2. Diatomic molecule with the same nuclei. H_2 as an example.

Internal energy and heat capacity of the ideal gas

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- Orthohydrogen: $Z_{1o}^r = \sum_{l=1,3...} (2l+1)e^{-\frac{l(l+1)\theta_r}{T}}$;

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- $U^r = U_o^r + U_p^r$

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  Parahydrogen: $Z_{1p}^r = \sum_{l=0,2\ldots}(2l+1)e^{-\frac{l(l+1)\theta_r}{T}}$.
- $U^r = U_o^r + U_p^r = -\frac{3}{4}N\frac{\partial}{\partial\beta}\ln Z_{1o}^r - \frac{1}{4}N\frac{\partial}{\partial\beta}\ln Z_{1p}^r$.

Internal energy and heat capacity of the ideal gas

- iii.2. Diatomic molecule with the same nuclei. H_2 as an example.
- At normal temperature, there are $3/4$ orthohydrogen (l odd) and $1/4$ parahydrogen (l even).
- Orthohydrogen: $Z_{1o}^r = \sum\limits_{l=1,3\ldots} (2l+1)e^{-\frac{l(l+1)\theta_r}{T}}$;

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- If $\theta_r \ll T$, the hydrogen molecule is in high l state,

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- Orthohydrogen: $Z_{1o}^r = \sum_{l=1,3\ldots} (2l+1)e^{-\frac{l(l+1)\theta_r}{T}}$;

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- $U^r = U_o^r + U_p^r = -\frac{3}{4}N\frac{\partial}{\partial\beta}\ln Z_{1o}^r - \frac{1}{4}N\frac{\partial}{\partial\beta}\ln Z_{1p}^r$.
- If $\theta_r \ll T$, the hydrogen molecule is in high l state, $l \sim l+1$, then $\sum_{l=0,2\ldots}^{\infty} \ldots \simeq \sum_{l=1,3\ldots}^{\infty} \ldots \simeq \frac{1}{2}\sum_{l=0,1\ldots}^{\infty} \ldots$

Internal energy and heat capacity of the ideal gas

- $Z_{1o}^r \simeq Z_{1p}^r \simeq \frac{1}{2} \sum_{l=0,1\ldots} (2l+1) e^{-\frac{l(l+1)\theta_r}{T}}$

Internal energy and heat capacity of the ideal gas

- $Z_{1o}^r \simeq Z_{1p}^r \simeq \frac{1}{2} \sum_{l=0,1\ldots} (2l+1) e^{-\frac{l(l+1)\theta_r}{T}}$
  $\simeq \frac{1}{2} \int_0^\infty (2l+1) e^{-x} \frac{\mathrm{d}x}{(2l+1)(\theta_r/T)}$

Internal energy and heat capacity of the ideal gas

- $Z^r_{1o} \simeq Z^r_{1p} \simeq \frac{1}{2} \sum_{l=0,1\ldots} (2l+1) e^{-\frac{l(l+1)\theta_r}{T}}$
  $\simeq \frac{1}{2} \int_0^\infty (2l+1) e^{-x} \frac{\mathrm{d}x}{(2l+1)(\theta_r/T)} = \frac{1}{2}\frac{T}{\theta_r}$

Internal energy and heat capacity of the ideal gas

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Internal energy and heat capacity of the ideal gas

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Internal energy and heat capacity of the ideal gas

- $Z_{1o}^{r} \simeq Z_{1p}^{r} \simeq \frac{1}{2} \sum_{l=0,1\dots} (2l+1) e^{-\frac{l(l+1)\theta_r}{T}}$
  $\simeq \frac{1}{2} \int_0^\infty (2l+1) e^{-x} \frac{\mathrm{d}x}{(2l+1)(\theta_r/T)} = \frac{1}{2} \frac{T}{\theta_r} = \frac{I}{\beta \hbar^2}$.
- $U^r = -\frac{3}{4} N \frac{\partial}{\partial \beta} \ln Z_{1o}^{r} - \frac{1}{4} N \frac{\partial}{\partial \beta} \ln Z_{1p}^{r} \simeq -N \frac{\partial}{\partial \beta} \ln Z_{1o}^{r}$

Internal energy and heat capacity of the ideal gas

- $Z_{1o}^r \simeq Z_{1p}^r \simeq \frac{1}{2} \sum\limits_{l=0,1...} (2l+1) e^{-\frac{l(l+1)\theta_r}{T}}$
  $\simeq \frac{1}{2} \int_0^\infty (2l+1) e^{-x} \frac{\mathrm{d}x}{(2l+1)(\theta_r/T)} = \frac{1}{2} \frac{T}{\theta_r} = \frac{I}{\beta \hbar^2}$.
- $U^r = -\frac{3}{4} N \frac{\partial}{\partial \beta} \ln Z_{1o}^r - \frac{1}{4} N \frac{\partial}{\partial \beta} \ln Z_{1p}^r \simeq -N \frac{\partial}{\partial \beta} \ln Z_{1o}^r$
  $= -N \frac{\partial}{\partial \beta} \ln \frac{I}{\beta \hbar^2}$

Internal energy and heat capacity of the ideal gas

- $Z_{1o}^r \simeq Z_{1p}^r \simeq \frac{1}{2}\sum_{l=0,1\ldots}(2l+1)e^{-\frac{l(l+1)\theta_r}{T}}$
  $\simeq \frac{1}{2}\int_0^\infty (2l+1)e^{-x}\frac{\mathrm{d}x}{(2l+1)(\theta_r/T)} = \frac{1}{2}\frac{T}{\theta_r} = \frac{I}{\beta\hbar^2}$.
- $U^r = -\frac{3}{4}N\frac{\partial}{\partial\beta}\ln Z_{1o}^r - \frac{1}{4}N\frac{\partial}{\partial\beta}\ln Z_{1p}^r \simeq -N\frac{\partial}{\partial\beta}\ln Z_{1o}^r$
  $= -N\frac{\partial}{\partial\beta}\ln\frac{I}{\beta\hbar^2} = \frac{N}{\beta}$

Internal energy and heat capacity of the ideal gas

- $Z^r_{1o} \simeq Z^r_{1p} \simeq \frac{1}{2}\sum\limits_{l=0,1\ldots}(2l+1)e^{-\frac{l(l+1)\theta_r}{T}}$
  $\simeq \frac{1}{2}\int_0^\infty (2l+1)e^{-x}\frac{\mathrm{d}x}{(2l+1)(\theta_r/T)} = \frac{1}{2}\frac{T}{\theta_r} = \frac{I}{\beta\hbar^2}$.
- $U^r = -\frac{3}{4}N\frac{\partial}{\partial\beta}\ln Z^r_{1o} - \frac{1}{4}N\frac{\partial}{\partial\beta}\ln Z^r_{1p} \simeq -N\frac{\partial}{\partial\beta}\ln Z^r_{1o}$
  $= -N\frac{\partial}{\partial\beta}\ln\frac{I}{\beta\hbar^2} = \frac{N}{\beta} = NkT$.

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- $Z^r_{1o} \simeq Z^r_{1p} \simeq \frac{1}{2} \sum_{l=0,1\ldots} (2l+1) e^{-\frac{l(l+1)\theta_r}{T}}$
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- $U^r = -\frac{3}{4} N \frac{\partial}{\partial \beta} \ln Z^r_{1o} - \frac{1}{4} N \frac{\partial}{\partial \beta} \ln Z^r_{1p} \simeq -N \frac{\partial}{\partial \beta} \ln Z^r_{1o}$
  $= -N \frac{\partial}{\partial \beta} \ln \frac{I}{\beta \hbar^2} = \frac{N}{\beta} = NkT$.
- $C^r_V = Nk$.

Internal energy and heat capacity of the ideal gas

- $Z_{1o}^r \simeq Z_{1p}^r \simeq \frac{1}{2}\sum_{l=0,1\ldots}(2l+1)e^{-\frac{l(l+1)\theta_r}{T}}$
  $\simeq \frac{1}{2}\int_0^\infty (2l+1)e^{-x}\frac{\mathrm{d}x}{(2l+1)(\theta_r/T)} = \frac{1}{2}\frac{T}{\theta_r} = \frac{I}{\beta\hbar^2}$.
- $U^r = -\frac{3}{4}N\frac{\partial}{\partial\beta}\ln Z_{1o}^r - \frac{1}{4}N\frac{\partial}{\partial\beta}\ln Z_{1p}^r \simeq -N\frac{\partial}{\partial\beta}\ln Z_{1o}^r$
  $= -N\frac{\partial}{\partial\beta}\ln\frac{I}{\beta\hbar^2} = \frac{N}{\beta} = NkT$.
- $C_V^r = Nk$.
- If $\theta_r \ll T$ does not hold, the summation is necessary.

General processes for **classical** statistics

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- Object as an example: diatomic molecules.

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- $\varepsilon = \frac{1}{2m}(p_x^2+p_y^2+p_z^2)+\frac{1}{2I}(p_\theta^2+\frac{1}{\sin^2\theta}p_\varphi^2)+\frac{1}{2m_\mu}(p_r^2+m_\mu^2\omega^2r^2)$.

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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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  $Z_1^t=\int e^{-\frac{\beta}{2m}(p_x^2+p_y^2+p_z^2)}\frac{\mathrm{d}x\mathrm{d}y\mathrm{d}z\mathrm{d}p_x\mathrm{d}p_y\mathrm{d}p_z}{h_0^3}$,

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

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

  $Z_1^v = \int e^{-\frac{\beta}{2m_\mu}(p_r^2+m_\mu^2\omega^2r^2)}\frac{\mathrm{d}p_r\mathrm{d}r}{h_0}$.

General processes for **classical** statistics

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- $Z_1 = \int \ldots \int e^{-\beta\varepsilon(q,p)}\frac{\mathrm{d}q_1 \ldots \mathrm{d}q_r \mathrm{d}p_1 \ldots \mathrm{d}p_r}{h_0^r}$,
  $Z_1^t = \int e^{-\frac{\beta}{2m}(p_x^2+p_y^2+p_z^2)}\frac{\mathrm{d}x\mathrm{d}y\mathrm{d}z\mathrm{d}p_x\mathrm{d}p_y\mathrm{d}p_z}{h_0^3}$,
  $Z_1^r = \int e^{-\frac{\beta}{2I}(p_\theta^2+\frac{1}{\sin^2\theta}p_\varphi^2)}\frac{\mathrm{d}p_\theta\mathrm{d}p_\varphi\mathrm{d}\theta\mathrm{d}\varphi}{h_0^2}$,
  $Z_1^v = \int e^{-\frac{\beta}{2m_\mu}(p_r^2+m_\mu^2\omega^2r^2)}\frac{\mathrm{d}p_r\mathrm{d}r}{h_0}$.
- Integration:

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

  $Z_1^v = \int e^{-\frac{\beta}{2m_\mu}(p_r^2+m_\mu^2\omega^2r^2)}\frac{\mathrm{d}p_r\mathrm{d}r}{h_0}$.
- Integration:

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

General processes for classical statistics

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

General processes for classical statistics

- $Z_1^r = \int e^{-\frac{\beta}{2I}\left(p_\theta^2 + \frac{1}{\sin^2\theta} p_\varphi^2\right)} \frac{\mathrm{d}p_\theta \mathrm{d}p_\varphi \mathrm{d}\theta \mathrm{d}\varphi}{h_0^2}$
  $= \frac{1}{h_0^2} \int_0^{2\pi} \mathrm{d}\varphi \int_0^{\pi} \mathrm{d}\theta \int_{-\infty}^{\infty} e^{-\frac{\beta}{2I} p_\theta^2} \mathrm{d}p_\theta \int_{-\infty}^{\infty} e^{-\frac{\beta}{2I \sin^2\theta} p_\varphi^2} \mathrm{d}p_\varphi$

General processes for classical statistics

- $Z_1^r = \int e^{-\frac{\beta}{2I}(p_\theta^2 + \frac{1}{\sin^2\theta}p_\varphi^2)} \frac{\mathrm{d}p_\theta \mathrm{d}p_\varphi \mathrm{d}\theta \mathrm{d}\varphi}{h_0^2}$
  $= \frac{1}{h_0^2}\int_0^{2\pi}\mathrm{d}\varphi \int_0^\pi \mathrm{d}\theta \int_{-\infty}^{\infty} e^{-\frac{\beta}{2I}p_\theta^2}\mathrm{d}p_\theta \int_{-\infty}^{\infty} e^{-\frac{\beta}{2I\sin^2\theta}p_\varphi^2}\mathrm{d}p_\varphi$
  $=$
  $\frac{2\pi}{h_0^2}\int_0^\pi \mathrm{d}\theta \sqrt{\frac{2I}{\beta}}\sqrt{\pi}\cdot\sqrt{\frac{2I\sin^2\theta}{\beta}}\int_{-\infty}^{\infty} e^{-\frac{\beta}{2I\sin^2\theta}p_\varphi^2}\mathrm{d}\sqrt{\frac{\beta}{2I\sin^2\theta}}p_\varphi$

General processes for classical statistics

- $Z_1^r = \int e^{-\frac{\beta}{2I}(p_\theta^2+\frac{1}{\sin^2\theta}p_\varphi^2)} \frac{\mathrm{d}p_\theta \mathrm{d}p_\varphi \mathrm{d}\theta \mathrm{d}\varphi}{h_0^2}$
$= \frac{1}{h_0^2}\int_0^{2\pi} \mathrm{d}\varphi \int_0^{\pi} \mathrm{d}\theta \int_{-\infty}^{\infty} e^{-\frac{\beta}{2I}p_\theta^2} \mathrm{d}p_\theta \int_{-\infty}^{\infty} e^{-\frac{\beta}{2I\sin^2\theta}p_\varphi^2} \mathrm{d}p_\varphi$
$=$
$\frac{2\pi}{h_0^2}\int_0^{\pi} \mathrm{d}\theta \sqrt{\frac{2I}{\beta}}\sqrt{\pi}\cdot\sqrt{\frac{2I\sin^2\theta}{\beta}} \int_{-\infty}^{\infty} e^{-\frac{\beta}{2I\sin^2\theta}p_\varphi^2} \mathrm{d}\sqrt{\frac{\beta}{2I\sin^2\theta}}p_\varphi$
$= \frac{2\pi}{h_0^2}\int_0^{\pi} \mathrm{d}\theta \sqrt{\frac{2I}{\beta}}\sqrt{\pi}\cdot\sqrt{\frac{2I\sin^2\theta}{\beta}}\sqrt{\pi}$

General processes for classical statistics

- $Z_1^r = \int e^{-\frac{\beta}{2I}(p_\theta^2 + \frac{1}{\sin^2\theta}p_\varphi^2)} \frac{\mathrm{d}p_\theta \mathrm{d}p_\varphi \mathrm{d}\theta \mathrm{d}\varphi}{h_0^2}$
  $= \frac{1}{h_0^2} \int_0^{2\pi} \mathrm{d}\varphi \int_0^\pi \mathrm{d}\theta \int_{-\infty}^\infty e^{-\frac{\beta}{2I}p_\theta^2} \mathrm{d}p_\theta \int_{-\infty}^\infty e^{-\frac{\beta}{2I\sin^2\theta}p_\varphi^2} \mathrm{d}p_\varphi$
  $=$
  $\frac{2\pi}{h_0^2} \int_0^\pi \mathrm{d}\theta \sqrt{\frac{2I}{\beta}}\sqrt{\pi} \cdot \sqrt{\frac{2I\sin^2\theta}{\beta}} \int_{-\infty}^\infty e^{-\frac{\beta}{2I\sin^2\theta}p_\varphi^2} \mathrm{d}\sqrt{\frac{\beta}{2I\sin^2\theta}} p_\varphi$
  $= \frac{2\pi}{h_0^2} \int_0^\pi \mathrm{d}\theta \sqrt{\frac{2I}{\beta}}\sqrt{\pi} \cdot \sqrt{\frac{2I\sin^2\theta}{\beta}}\sqrt{\pi}$
  $= \frac{2\pi^2}{h_0^2} \frac{2I}{\beta} \int_0^\pi \sin\theta \mathrm{d}\theta$

General processes for classical statistics

- $Z_1^r = \int e^{-\frac{\beta}{2I}(p_\theta^2+\frac{1}{\sin^2\theta}p_\varphi^2)} \frac{\mathrm{d}p_\theta \mathrm{d}p_\varphi \mathrm{d}\theta \mathrm{d}\varphi}{h_0^2}$
  $= \frac{1}{h_0^2}\int_0^{2\pi}\mathrm{d}\varphi \int_0^{\pi}\mathrm{d}\theta \int_{-\infty}^{\infty} e^{-\frac{\beta}{2I}p_\theta^2}\mathrm{d}p_\theta \int_{-\infty}^{\infty} e^{-\frac{\beta}{2I\sin^2\theta}p_\varphi^2}\mathrm{d}p_\varphi$
  $=$
  $\frac{2\pi}{h_0^2}\int_0^{\pi}\mathrm{d}\theta\sqrt{\frac{2I}{\beta}}\sqrt{\pi}\cdot\sqrt{\frac{2I\sin^2\theta}{\beta}}\int_{-\infty}^{\infty} e^{-\frac{\beta}{2I\sin^2\theta}p_\varphi^2}\mathrm{d}\sqrt{\frac{\beta}{2I\sin^2\theta}}p_\varphi$
  $= \frac{2\pi}{h_0^2}\int_0^{\pi}\mathrm{d}\theta\sqrt{\frac{2I}{\beta}}\sqrt{\pi}\cdot\sqrt{\frac{2I\sin^2\theta}{\beta}}\sqrt{\pi}$
  $= \frac{2\pi^2}{h_0^2}\frac{2I}{\beta}\int_0^{\pi}\sin\theta \mathrm{d}\theta$
  $= \frac{8\pi^2 I}{h_0^2\beta}.$

General processes for classical statistics

- $Z_1^v = \int e^{-\frac{\beta}{2m_\mu}(p_r^2+m_\mu^2\omega^2 r^2)} \frac{\mathrm{d}p_r \mathrm{d}r}{h_0}$

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$\sqrt{\frac{2}{m_\mu\omega^2\beta}}\int_{-\infty}^{\infty} e^{-\frac{\beta}{2m_\mu}m_\mu^2\omega^2r^2}\mathrm{d}\sqrt{\frac{m_\mu\omega^2\beta}{2}}r$

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  $= Nk\{\ln V + \frac{3}{2}\ln(\frac{2\pi m}{h_0^2\beta}) - \beta\frac{\partial}{\partial\beta}[\ln V + \frac{3}{2}\ln(\frac{2\pi m}{h_0^2\beta})]\}$

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- Problem 1. S depends on h_0;

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- $$\begin{aligned} S &= Nk\{\ln[V(\frac{2\pi m}{h_0^2\beta})^{3/2}] - \beta\frac{\partial}{\partial\beta}\ln[V(\frac{2\pi m}{h_0^2\beta})^{3/2}]\} \\ &= Nk\{\ln V + \frac{3}{2}\ln(\frac{2\pi m}{h_0^2\beta}) - \beta\frac{\partial}{\partial\beta}[\ln V + \frac{3}{2}\ln(\frac{2\pi m}{h_0^2\beta})]\} \\ &= Nk[\ln V + \frac{3}{2}\ln(\frac{2\pi m}{h_0^2\beta}) - 0 - \frac{3}{2}\beta\cdot(-\frac{1}{\beta})] \\ &= Nk[\ln V + \frac{3}{2}\ln(\frac{2\pi m}{h_0^2\beta}) + \frac{3}{2}] \\ &= \frac{3}{2}Nk\ln T + Nk\ln V + \frac{3}{2}Nk[1 + \ln\frac{2\pi mk}{h_0^2}]. \end{aligned}$$
- Problem 1. S depends on h_0;
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Einstein's theory on heat capacity of solid

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  $= 3N\left(\frac{1}{2}\hbar\omega + \frac{e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}\hbar\omega\right) = \frac{3}{2}N\hbar\omega + \frac{3N\hbar\omega}{e^{\beta\hbar\omega}-1}$.
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$$= nk\left[\ln(e^{2\beta\mu B} + 1) - \beta\mu B\frac{2e^{2\beta\mu B}}{e^{2\beta\mu B} + 1}\right]$$
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- $\frac{\mu B}{kT} \gg 1$, $s \simeq 0$, only one micro-state: all magnetic moments are aligned along the external field.

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- Number of spins: N, where N_+ with ε, N_- with $-\varepsilon$.
- $N = N_+ + N_-$, $E = N_+\varepsilon + N_-(-\varepsilon)$
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  $- \frac{N}{2}(1 - \frac{E}{N\varepsilon}) \ln[\frac{N}{2}(1 - \frac{E}{N\varepsilon})]\}$

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

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

Negative temperature

Eq.(1.4.7) $đW = VH\mathrm{d}B$, B generalized displacement.

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$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_B$$
$$= \frac{\partial}{\partial E}\left\{Nk\left[\ln 2 - \frac{1}{2}\left(1+\frac{E}{N\varepsilon}\right)\ln\left(1+\frac{E}{N\varepsilon}\right) - \frac{1}{2}\left(1-\frac{E}{N\varepsilon}\right)\ln\left(1-\frac{E}{N\varepsilon}\right)\right]\right\}$$

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

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

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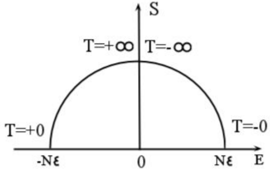

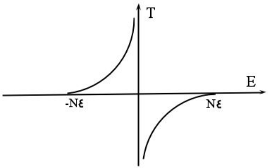

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