Thermodynamics & Statistical Physics

Chapter 9. Ensemble theory

Yuan-Chuan Zou
zouyc@hust.edu.cn

School of Physics, Huazhong University of Science and Technology

December 30, 2013

Table of contents

9.1 Phase space and Liouville's theorem

9.1 Phase space and Liouville's theorem

- Chapters 6,7,8 are not suitable to interacting particles.

9.1 Phase space and Liouville's theorem

- Chapters 6,7,8 are not suitable to interacting particles. Because of potential energy, any movement of any particle changes states of other particles.

9.1 Phase space and Liouville's theorem

- Chapters 6,7,8 are not suitable to interacting particles. Because of potential energy, any movement of any particle changes states of other particles. No fixed energy or momentum for a particle, varying with time.

9.1 Phase space and Liouville's theorem

- Chapters 6,7,8 are not suitable to interacting particles. Because of potential energy, any movement of any particle changes states of other particles. No fixed energy or momentum for a particle, varying with time.
- Particle can not be separated from the system.

9.1 Phase space and Liouville's theorem

- Chapters 6,7,8 are not suitable to interacting particles. Because of potential energy, any movement of any particle changes states of other particles. No fixed energy or momentum for a particle, varying with time.
- Particle can not be separated from the system.
- Use state of system instead of state of particles.

9.1 Phase space and Liouville's theorem

- Chapters 6,7,8 are not suitable to interacting particles. Because of potential energy, any movement of any particle changes states of other particles. No fixed energy or momentum for a particle, varying with time.
- Particle can not be separated from the system.
- Use state of system instead of state of particles.
- Ensemble theory,

9.1 Phase space and Liouville's theorem

- Chapters 6,7,8 are not suitable to interacting particles. Because of potential energy, any movement of any particle changes states of other particles. No fixed energy or momentum for a particle, varying with time.
- Particle can not be separated from the system.
- Use state of system instead of state of particles.
- Ensemble theory, by using Hamiltonian.

9.1 Phase space and Liouville's theorem

- Chapters 6,7,8 are not suitable to interacting particles. Because of potential energy, any movement of any particle changes states of other particles. No fixed energy or momentum for a particle, varying with time.
- Particle can not be separated from the system.
- Use state of system instead of state of particles.
- Ensemble theory, by using Hamiltonian.
- Consider N particles system, each one with r freedom.

9.1 Phase space and Liouville's theorem

- Chapters 6,7,8 are not suitable to interacting particles. Because of potential energy, any movement of any particle changes states of other particles. No fixed energy or momentum for a particle, varying with time.
- Particle can not be separated from the system.
- Use state of system instead of state of particles.
- Ensemble theory, by using Hamiltonian.
- Consider N particles system, each one with r freedom.
- For a particle j, it has: $(q_{j1}, ...q_{jr}; p_{j1}, ...p_{jr})$.

9.1 Phase space and Liouville's theorem

- Chapters 6,7,8 are not suitable to interacting particles. Because of potential energy, any movement of any particle changes states of other particles. No fixed energy or momentum for a particle, varying with time.
- Particle can not be separated from the system.
- Use state of system instead of state of particles.
- Ensemble theory, by using Hamiltonian.
- Consider N particles system, each one with r freedom.
- For a particle j, it has: $(q_{j1}, ...q_{jr}; p_{j1}, ...p_{jr})$.
- For the system, to describe the micro-state, using the **phase-space point**:

  $(q_{11}, ...q_{1r}, ...q_{N1}, ...q_{Nr}; p_{11}, ...p_{1r}, ...p_{N1}, ...p_{Nr})$

Phase space and Liouville's theorem

- There are $2Nr$ quantities in $(q_{11},...q_{1r},...q_{N1},...q_{Nr};p_{11},...p_{1r},...p_{N1},...p_{Nr})$.

Phase space and Liouville's theorem

- There are $2Nr$ quantities in $(q_{11}, ...q_{1r}, ...q_{N1}, ...q_{Nr}; p_{11}, ...p_{1r}, ...p_{N1}, ...p_{Nr})$. The change of any quantity means the change of the state of the system, and means the movement of the phase-space point.

Phase space and Liouville's theorem

- There are $2Nr$ quantities in $(q_{11}, ...q_{1r}, ...q_{N1}, ...q_{Nr}; p_{11}, ...p_{1r}, ...p_{N1}, ...p_{Nr})$. The change of any quantity means the change of the state of the system, and means the movement of the phase-space point.
- Define $f = Nr$, simplifies the phase-space point: $(q_1, ...q_f; p_1, ...p_f)$.

Phase space and Liouville's theorem

- There are $2Nr$ quantities in $(q_{11}, ...q_{1r}, ...q_{N1}, ...q_{Nr}; p_{11}, ...p_{1r}, ...p_{N1}, ...p_{Nr})$. The change of any quantity means the change of the state of the system, and means the movement of the phase-space point.
- Define $f = Nr$, simplifies the phase-space point: $(q_1, ...q_f; p_1, ...p_f)$.
- Any movement of the particles obeys Hamiltonian canonical equation: $\dot{q}_i = \frac{\partial H}{\partial p_i}, \dot{p}_i = -\frac{\partial H}{\partial q_i}$, $i = 1, 2, ...f$.

Phase space and Liouville's theorem

- There are $2Nr$ quantities in $(q_{11}, ...q_{1r}, ...q_{N1}, ...q_{Nr}; p_{11}, ...p_{1r}, ...p_{N1}, ...p_{Nr})$. The change of any quantity means the change of the state of the system, and means the movement of the phase-space point.
- Define $f = Nr$, simplifies the phase-space point: $(q_1, ...q_f; p_1, ...p_f)$.
- Any movement of the particles obeys Hamiltonian canonical equation: $\dot{q}_i = \frac{\partial H}{\partial p_i}, \dot{p}_i = -\frac{\partial H}{\partial q_i}$, $i = 1, 2, ...f$.
- $(\dot{q}_i, \dot{p}_i)$ determines the trajectory of the phase-space point.

Phase space and Liouville's theorem

- Consider a lot of ($\mathcal{N}$) identical systems, with different initial state. Let them develop.

Phase space and Liouville's theorem

- Consider a lot of ($\mathcal{N}$) identical systems, with different initial state. Let them develop.
- At a certain time t, one can count the number of points at any given volume $\mathrm{d}\Omega = \mathrm{d}q_1 ... \mathrm{d}q_f \mathrm{d}p_1 ... \mathrm{d}p_f$,

Phase space and Liouville's theorem

- Consider a lot of ($\mathcal{N}$) identical systems, with different initial state. Let them develop.
- At a certain time t, one can count the number of points at any given volume $\mathrm{d}\Omega = \mathrm{d}q_1 ... \mathrm{d}q_f \mathrm{d}p_1 ... \mathrm{d}p_f$, the number is $\rho(q_1, ...q_f, p_1, ...p_f, t)\mathrm{d}\Omega$,

Phase space and Liouville's theorem

- Consider a lot of ($\mathcal{N}$) identical systems, with different initial state. Let them develop.
- At a certain time t, one can count the number of points at any given volume $\mathrm{d}\Omega = \mathrm{d}q_1 ... \mathrm{d}q_f \mathrm{d}p_1 ... \mathrm{d}p_f$, the number is $\rho(q_1, ...q_f, p_1, ...p_f, t)\mathrm{d}\Omega$, where ρ is the number density of points, or number of density of micro-states.

Phase space and Liouville's theorem

- Consider a lot of ($\mathcal{N}$) identical systems, with different initial state. Let them develop.
- At a certain time t, one can count the number of points at any given volume $\mathrm{d}\Omega = \mathrm{d}q_1 ... \mathrm{d}q_f \mathrm{d}p_1 ... \mathrm{d}p_f$, the number is $\rho(q_1, ...q_f, p_1, ...p_f, t)\mathrm{d}\Omega$, where ρ is the number density of points, or number of density of micro-states. Obviously, $\mathcal{N} = \int \rho \mathrm{d}\Omega$.

Phase space and Liouville's theorem

- Consider a lot of ($\mathcal{N}$) identical systems, with different initial state. Let them develop.
- At a certain time t, one can count the number of points at any given volume $\mathrm{d}\Omega = \mathrm{d}q_1...\mathrm{d}q_f\mathrm{d}p_1...\mathrm{d}p_f$, the number is $\rho(q_1, ...q_f, p_1, ...p_f, t)\mathrm{d}\Omega$, where ρ is the number density of points, or number of density of micro-states. Obviously, $\mathcal{N} = \int \rho \mathrm{d}\Omega$.
- The behavior of ρ depends on t: $\rho(q + \mathrm{d}q, p + \mathrm{d}p, t + \mathrm{d}t)$

Phase space and Liouville's theorem

- Consider a lot of ($\mathcal{N}$) identical systems, with different initial state. Let them develop.
- At a certain time t, one can count the number of points at any given volume $\mathrm{d}\Omega = \mathrm{d}q_1 ... \mathrm{d}q_f \mathrm{d}p_1 ... \mathrm{d}p_f$, the number is $\rho(q_1, ...q_f, p_1, ...p_f, t)\mathrm{d}\Omega$, where ρ is the number density of points, or number of density of micro-states. Obviously, $\mathcal{N} = \int \rho \mathrm{d}\Omega$.
- The behavior of ρ depends on t:
$$\rho(q + \mathrm{d}q, p + \mathrm{d}p, t + \mathrm{d}t)$$
$$= \rho(q, p, t) + \frac{\partial \rho}{\partial q_1}\mathrm{d}q_1 + ... + \frac{\partial \rho}{\partial p_f}\mathrm{d}p_f + \frac{\partial \rho}{\partial t}\mathrm{d}t$$

Phase space and Liouville's theorem

- Consider a lot of $(\mathcal{N})$ identical systems, with different initial state. Let them develop.
- At a certain time t, one can count the number of points at any given volume $\mathrm{d}\Omega = \mathrm{d}q_1 ... \mathrm{d}q_f \mathrm{d}p_1 ... \mathrm{d}p_f$, the number is $\rho(q_1, ...q_f, p_1, ...p_f, t)\mathrm{d}\Omega$, where ρ is the number density of points, or number of density of micro-states. Obviously, $\mathcal{N} = \int \rho \mathrm{d}\Omega$.
- The behavior of ρ depends on t:
  $\rho(q + \mathrm{d}q, p + \mathrm{d}p, t + \mathrm{d}t)$
  $= \rho(q, p, t) + \frac{\partial \rho}{\partial q_1}\mathrm{d}q_1 + ... + \frac{\partial \rho}{\partial p_f}\mathrm{d}p_f + \frac{\partial \rho}{\partial t}\mathrm{d}t$
  $= \rho(t) + (\frac{\partial \rho}{\partial t} + \frac{\partial \rho}{\partial q_1}\dot{q}_1 + ... + \frac{\partial \rho}{\partial p_f}\dot{p}_f)\mathrm{d}t.$

Phase space and Liouville's theorem

- $\rho(q + \mathrm{d}q, p + \mathrm{d}p, t + \mathrm{d}t)$
  $= \rho(t) + (\frac{\partial \rho}{\partial t} + \frac{\partial \rho}{\partial q_1}\dot{q}_1 + ... + \frac{\partial \rho}{\partial p_f}\dot{p}_f)\mathrm{d}t$

Phase space and Liouville's theorem

- $\rho(q + \mathrm{d}q, p + \mathrm{d}p, t + \mathrm{d}t)$
  $= \rho(t) + (\frac{\partial \rho}{\partial t} + \frac{\partial \rho}{\partial q_1}\dot{q}_1 + ... + \frac{\partial \rho}{\partial p_f}\dot{p}_f)\mathrm{d}t$
  $= \rho(t) + [\frac{\partial \rho}{\partial t} + \sum(\frac{\partial \rho}{\partial q_i}\dot{q}_i + \frac{\partial \rho}{\partial p_i}\dot{p}_i)]\mathrm{d}t$

Phase space and Liouville's theorem

- $\rho(q + \mathrm{d}q, p + \mathrm{d}p, t + \mathrm{d}t)$
  $= \rho(t) + (\frac{\partial \rho}{\partial t} + \frac{\partial \rho}{\partial q_1}\dot{q}_1 + ... + \frac{\partial \rho}{\partial p_f}\dot{p}_f)\mathrm{d}t$
  $= \rho(t) + [\frac{\partial \rho}{\partial t} + \sum(\frac{\partial \rho}{\partial q_i}\dot{q}_i + \frac{\partial \rho}{\partial p_i}\dot{p}_i)]\mathrm{d}t$
- $\frac{\mathrm{d}\rho}{\mathrm{d}t} = \frac{\partial \rho}{\partial t} + \sum(\frac{\partial \rho}{\partial q_i}\dot{q}_i + \frac{\partial \rho}{\partial p_i}\dot{p}_i)$.

Phase space and Liouville's theorem

- $\rho(q+\mathrm{d}q, p+\mathrm{d}p, t+\mathrm{d}t)$
  $= \rho(t) + (\frac{\partial\rho}{\partial t} + \frac{\partial\rho}{\partial q_1}\dot{q}_1 + ... + \frac{\partial\rho}{\partial p_f}\dot{p}_f)\mathrm{d}t$
  $= \rho(t) + [\frac{\partial\rho}{\partial t} + \sum(\frac{\partial\rho}{\partial q_i}\dot{q}_i + \frac{\partial\rho}{\partial p_i}\dot{p}_i)]\mathrm{d}t$
- $\frac{\mathrm{d}\rho}{\mathrm{d}t} = \frac{\partial\rho}{\partial t} + \sum(\frac{\partial\rho}{\partial q_i}\dot{q}_i + \frac{\partial\rho}{\partial p_i}\dot{p}_i)$.
- Provable: $\frac{\mathrm{d}\rho}{\mathrm{d}t} = 0$.

Phase space and Liouville's theorem

- $\rho(q+\mathrm{d}q, p+\mathrm{d}p, t+\mathrm{d}t)$
  $=\rho(t)+(\frac{\partial\rho}{\partial t}+\frac{\partial\rho}{\partial q_1}\dot{q}_1+...+\frac{\partial\rho}{\partial p_f}\dot{p}_f)\mathrm{d}t$
  $=\rho(t)+[\frac{\partial\rho}{\partial t}+\sum(\frac{\partial\rho}{\partial q_i}\dot{q}_i+\frac{\partial\rho}{\partial p_i}\dot{p}_i)]\mathrm{d}t$
- $\frac{\mathrm{d}\rho}{\mathrm{d}t}=\frac{\partial\rho}{\partial t}+\sum(\frac{\partial\rho}{\partial q_i}\dot{q}_i+\frac{\partial\rho}{\partial p_i}\dot{p}_i)$.
- Provable: $\frac{\mathrm{d}\rho}{\mathrm{d}t}=0$.
- Consider a fixed volume element:
  $\mathrm{d}\Omega=\mathrm{d}q_1...\mathrm{d}q_f\mathrm{d}p_1...\mathrm{d}p_f$.

Phase space and Liouville's theorem

- $\rho(q+\mathrm{d}q, p+\mathrm{d}p, t+\mathrm{d}t)$
  $= \rho(t) + (\frac{\partial\rho}{\partial t} + \frac{\partial\rho}{\partial q_1}\dot{q}_1 + ... + \frac{\partial\rho}{\partial p_f}\dot{p}_f)\mathrm{d}t$
  $= \rho(t) + [\frac{\partial\rho}{\partial t} + \sum(\frac{\partial\rho}{\partial q_i}\dot{q}_i + \frac{\partial\rho}{\partial p_i}\dot{p}_i)]\mathrm{d}t$
- $\frac{\mathrm{d}\rho}{\mathrm{d}t} = \frac{\partial\rho}{\partial t} + \sum(\frac{\partial\rho}{\partial q_i}\dot{q}_i + \frac{\partial\rho}{\partial p_i}\dot{p}_i)$.
- Provable: $\frac{\mathrm{d}\rho}{\mathrm{d}t} = 0$.
- Consider a fixed volume element:
  $\mathrm{d}\Omega = \mathrm{d}q_1...\mathrm{d}q_f\mathrm{d}p_1...\mathrm{d}p_f$.
  At time t, the number of phase-space points: $\rho\mathrm{d}\Omega$;

Phase space and Liouville's theorem

- $\rho(q + \mathrm{d}q, p + \mathrm{d}p, t + \mathrm{d}t)$
  $= \rho(t) + (\frac{\partial\rho}{\partial t} + \frac{\partial\rho}{\partial q_1}\dot{q}_1 + ... + \frac{\partial\rho}{\partial p_f}\dot{p}_f)\mathrm{d}t$
  $= \rho(t) + [\frac{\partial\rho}{\partial t} + \sum(\frac{\partial\rho}{\partial q_i}\dot{q}_i + \frac{\partial\rho}{\partial p_i}\dot{p}_i)]\mathrm{d}t$
- $\frac{\mathrm{d}\rho}{\mathrm{d}t} = \frac{\partial\rho}{\partial t} + \sum(\frac{\partial\rho}{\partial q_i}\dot{q}_i + \frac{\partial\rho}{\partial p_i}\dot{p}_i)$.
- Provable: $\frac{\mathrm{d}\rho}{\mathrm{d}t} = 0$.
- Consider a fixed volume element:
  $\mathrm{d}\Omega = \mathrm{d}q_1...\mathrm{d}q_f\mathrm{d}p_1...\mathrm{d}p_f$.
  At time t, the number of phase-space points: $\rho\mathrm{d}\Omega$;
  at time $t + \mathrm{d}t$, the number: $(\rho + \frac{\partial\rho}{\partial t}\mathrm{d}t)\mathrm{d}\Omega$.

Phase space and Liouville's theorem

- $\rho(q+\mathrm{d}q, p+\mathrm{d}p, t+\mathrm{d}t)$
  $= \rho(t) + (\frac{\partial\rho}{\partial t} + \frac{\partial\rho}{\partial q_1}\dot{q}_1 + ... + \frac{\partial\rho}{\partial p_f}\dot{p}_f)\mathrm{d}t$
  $= \rho(t) + [\frac{\partial\rho}{\partial t} + \sum(\frac{\partial\rho}{\partial q_i}\dot{q}_i + \frac{\partial\rho}{\partial p_i}\dot{p}_i)]\mathrm{d}t$
- $\frac{\mathrm{d}\rho}{\mathrm{d}t} = \frac{\partial\rho}{\partial t} + \sum(\frac{\partial\rho}{\partial q_i}\dot{q}_i + \frac{\partial\rho}{\partial p_i}\dot{p}_i)$.
- Provable: $\frac{\mathrm{d}\rho}{\mathrm{d}t} = 0$.
- Consider a fixed volume element:
  $\mathrm{d}\Omega = \mathrm{d}q_1...\mathrm{d}q_f\mathrm{d}p_1...\mathrm{d}p_f$.
  At time t, the number of phase-space points: $\rho\mathrm{d}\Omega$;
  at time $t+\mathrm{d}t$, the number: $(\rho + \frac{\partial\rho}{\partial t}\mathrm{d}t)\mathrm{d}\Omega$.
- The variance of the number comes from the flowing in and out through the surfaces of the volume element.

Phase space and Liouville's theorem

- Consider a pair of surfaces $q_i = q_i$ and $q_i = q_i + \mathrm{d}q_i$ as an example.

Phase space and Liouville's theorem

- Consider a pair of surfaces $q_i = q_i$ and $q_i = q_i + \mathrm{d}q_i$ as an example.
- $\dot{q}_i$ is the velocity of flowing in; the surface $\mathrm{d}A = \mathrm{d}q_1 ... \mathrm{d}q_{i-1} \mathrm{d}q_{i+1} ... \mathrm{d}q_f \mathrm{d}p_1 ... \mathrm{d}p_f$.

Phase space and Liouville's theorem

- Consider a pair of surfaces $q_i = q_i$ and $q_i = q_i + \mathrm{d}q_i$ as an example.
- $\dot{q}_i$ is the velocity of flowing in; the surface $\mathrm{d}A = \mathrm{d}q_1 ... \mathrm{d}q_{i-1} \mathrm{d}q_{i+1} ... \mathrm{d}q_f \mathrm{d}p_1 ... \mathrm{d}p_f$.
- The number of points flowing in through the surface: $\rho \dot{q}_i \mathrm{d}t \mathrm{d}A$;

Phase space and Liouville's theorem

- Consider a pair of surfaces $q_i = q_i$ and $q_i = q_i + \mathrm{d}q_i$ as an example.
- $\dot{q}_i$ is the velocity of flowing in; the surface $\mathrm{d}A = \mathrm{d}q_1 ... \mathrm{d}q_{i-1} \mathrm{d}q_{i+1} ... \mathrm{d}q_f \mathrm{d}p_1 ... \mathrm{d}p_f$.
- The number of points flowing in through the surface: $\rho \dot{q}_i \mathrm{d}t \mathrm{d}A$;
  similar, the number flowing out through the contrary surface: $(\rho \dot{q}_i)_{q_i + \mathrm{d}q_i} \mathrm{d}t \mathrm{d}A$

Phase space and Liouville's theorem

- Consider a pair of surfaces $q_i = q_i$ and $q_i = q_i + \mathrm{d}q_i$ as an example.
- $\dot{q}_i$ is the velocity of flowing in; the surface $\mathrm{d}A = \mathrm{d}q_1 ... \mathrm{d}q_{i-1} \mathrm{d}q_{i+1} ... \mathrm{d}q_f \mathrm{d}p_1 ... \mathrm{d}p_f$.
- The number of points flowing in through the surface: $\rho \dot{q}_i \mathrm{d}t \mathrm{d}A$;

  similar, the number flowing out through the contrary surface: $(\rho \dot{q}_i)_{q_i + \mathrm{d}q_i} \mathrm{d}t \mathrm{d}A = [(\rho \dot{q}_i)_{q_i} + \frac{\partial(\rho \dot{q}_i)}{\partial q_i} \mathrm{d}q_i] \mathrm{d}t \mathrm{d}A$.

Phase space and Liouville's theorem

- Consider a pair of surfaces $q_i = q_i$ and $q_i = q_i + \mathrm{d}q_i$ as an example.
- $\dot{q}_i$ is the velocity of flowing in; the surface $\mathrm{d}A = \mathrm{d}q_1 ... \mathrm{d}q_{i-1}\mathrm{d}q_{i+1} ... \mathrm{d}q_f \mathrm{d}p_1 ... \mathrm{d}p_f$.
- The number of points flowing in through the surface: $\rho\dot{q}_i \mathrm{d}t\mathrm{d}A$;
  similar, the number flowing out through the contrary surface: $(\rho\dot{q}_i)_{q_i+\mathrm{d}q_i}\mathrm{d}t\mathrm{d}A = [(\rho\dot{q}_i)_{q_i} + \frac{\partial(\rho\dot{q}_i)}{\partial q_i}\mathrm{d}q_i]\mathrm{d}t\mathrm{d}A$.
- The net flowed in: $-\frac{\partial(\rho\dot{q}_i)}{\partial q_i}\mathrm{d}q_i\mathrm{d}t\mathrm{d}A$

Phase space and Liouville's theorem

- Consider a pair of surfaces $q_i = q_i$ and $q_i = q_i + \mathrm{d}q_i$ as an example.
- $\dot{q}_i$ is the velocity of flowing in; the surface $\mathrm{d}A = \mathrm{d}q_1 ... \mathrm{d}q_{i-1}\mathrm{d}q_{i+1} ... \mathrm{d}q_f \mathrm{d}p_1 ... \mathrm{d}p_f$.
- The number of points flowing in through the surface: $\rho\dot{q}_i \mathrm{d}t\mathrm{d}A$;
  similar, the number flowing out through the contrary surface: $(\rho\dot{q}_i)_{q_i+\mathrm{d}q_i}\mathrm{d}t\mathrm{d}A = [(\rho\dot{q}_i)_{q_i} + \frac{\partial(\rho\dot{q}_i)}{\partial q_i}\mathrm{d}q_i]\mathrm{d}t\mathrm{d}A$.
- The net flowed in: $-\frac{\partial(\rho\dot{q}_i)}{\partial q_i}\mathrm{d}q_i\mathrm{d}t\mathrm{d}A = -\frac{\partial(\rho\dot{q}_i)}{\partial q_i}\mathrm{d}t\mathrm{d}\Omega$.

Phase space and Liouville's theorem

- Consider a pair of surfaces $q_i = q_i$ and $q_i = q_i + \mathrm{d}q_i$ as an example.
- $\dot{q}_i$ is the velocity of flowing in; the surface $\mathrm{d}A = \mathrm{d}q_1 ... \mathrm{d}q_{i-1}\mathrm{d}q_{i+1} ... \mathrm{d}q_f \mathrm{d}p_1 ... \mathrm{d}p_f$.
- The number of points flowing in through the surface: $\rho\dot{q}_i \mathrm{d}t\mathrm{d}A$;
  similar, the number flowing out through the contrary surface: $(\rho\dot{q}_i)_{q_i+\mathrm{d}q_i}\mathrm{d}t\mathrm{d}A = [(\rho\dot{q}_i)_{q_i} + \frac{\partial(\rho\dot{q}_i)}{\partial q_i}\mathrm{d}q_i]\mathrm{d}t\mathrm{d}A$.
- The net flowed in: $-\frac{\partial(\rho\dot{q}_i)}{\partial q_i}\mathrm{d}q_i\mathrm{d}t\mathrm{d}A = -\frac{\partial(\rho\dot{q}_i)}{\partial q_i}\mathrm{d}t\mathrm{d}\Omega$.
- Similar for p_i, the net in: $-\frac{\partial(\rho\dot{p}_i)}{\partial p_i}\mathrm{d}t\mathrm{d}\Omega$.

Phase space and Liouville's theorem

- Consider a pair of surfaces $q_i = q_i$ and $q_i = q_i + \mathrm{d}q_i$ as an example.
- $\dot{q}_i$ is the velocity of flowing in; the surface $\mathrm{d}A = \mathrm{d}q_1 ... \mathrm{d}q_{i-1}\mathrm{d}q_{i+1} ... \mathrm{d}q_f \mathrm{d}p_1 ... \mathrm{d}p_f$.
- The number of points flowing in through the surface: $\rho\dot{q}_i \mathrm{d}t\mathrm{d}A$;
  similar, the number flowing out through the contrary surface: $(\rho\dot{q}_i)_{q_i+\mathrm{d}q_i}\mathrm{d}t\mathrm{d}A = [(\rho\dot{q}_i)_{q_i} + \frac{\partial(\rho\dot{q}_i)}{\partial q_i}\mathrm{d}q_i]\mathrm{d}t\mathrm{d}A$.
- The net flowed in: $-\frac{\partial(\rho\dot{q}_i)}{\partial q_i}\mathrm{d}q_i\mathrm{d}t\mathrm{d}A = -\frac{\partial(\rho\dot{q}_i)}{\partial q_i}\mathrm{d}t\mathrm{d}\Omega$.
- Similar for p_i, the net in: $-\frac{\partial(\rho\dot{p}_i)}{\partial p_i}\mathrm{d}t\mathrm{d}\Omega$.
- Sum on all surfaces: $-\sum[\frac{\partial(\rho\dot{q}_i)}{\partial q_i} + \frac{\partial(\rho\dot{p}_i)}{\partial p_i}]\mathrm{d}t\mathrm{d}\Omega$.

Phase space and Liouville's theorem

- On the other hand, the net gain in the fixed volume: $\frac{\partial\rho}{\partial t}\mathrm{d}t\mathrm{d}\Omega$.

Phase space and Liouville's theorem

- On the other hand, the net gain in the fixed volume: $\frac{\partial\rho}{\partial t}\mathrm{d}t\mathrm{d}\Omega$.
- $\therefore -\sum[\frac{\partial(\rho\dot{q}_i)}{\partial q_i}+\frac{\partial(\rho\dot{p}_i)}{\partial p_i}]\mathrm{d}t\mathrm{d}\Omega=\frac{\partial\rho}{\partial t}\mathrm{d}t\mathrm{d}\Omega$

Phase space and Liouville's theorem

- On the other hand, the net gain in the fixed volume: $\frac{\partial\rho}{\partial t}\mathrm{d}t\mathrm{d}\Omega$.
- $\therefore -\sum[\frac{\partial(\rho\dot{q}_i)}{\partial q_i}+\frac{\partial(\rho\dot{p}_i)}{\partial p_i}]\mathrm{d}t\mathrm{d}\Omega=\frac{\partial\rho}{\partial t}\mathrm{d}t\mathrm{d}\Omega$
  $\Rightarrow \frac{\partial\rho}{\partial t}=-\sum[\frac{\partial(\rho\dot{q}_i)}{\partial q_i}+\frac{\partial(\rho\dot{p}_i)}{\partial p_i}]$

Phase space and Liouville's theorem

- On the other hand, the net gain in the fixed volume: $\frac{\partial\rho}{\partial t}\mathrm{d}t\mathrm{d}\Omega$.
- $\therefore -\sum[\frac{\partial(\rho\dot{q}_i)}{\partial q_i}+\frac{\partial(\rho\dot{p}_i)}{\partial p_i}]\mathrm{d}t\mathrm{d}\Omega=\frac{\partial\rho}{\partial t}\mathrm{d}t\mathrm{d}\Omega$

$$\begin{aligned}\Rightarrow \frac{\partial\rho}{\partial t} &= -\sum[\frac{\partial(\rho\dot{q}_i)}{\partial q_i}+\frac{\partial(\rho\dot{p}_i)}{\partial p_i}] \\ &= -\sum[\frac{\partial\rho}{\partial q_i}\dot{q}_i+\frac{\partial\rho}{\partial p_i}\dot{p}_i+\rho(\frac{\partial\dot{q}_i}{\partial q_i}+\frac{\partial\dot{p}_i}{\partial p_i})].\end{aligned}$$

Phase space and Liouville's theorem

- On the other hand, the net gain in the fixed volume: $\frac{\partial\rho}{\partial t}\mathrm{d}t\mathrm{d}\Omega$.
- $\therefore -\sum[\frac{\partial(\rho\dot{q}_i)}{\partial q_i}+\frac{\partial(\rho\dot{p}_i)}{\partial p_i}]\mathrm{d}t\mathrm{d}\Omega=\frac{\partial\rho}{\partial t}\mathrm{d}t\mathrm{d}\Omega$
  $$\Rightarrow \frac{\partial\rho}{\partial t}=-\sum[\frac{\partial(\rho\dot{q}_i)}{\partial q_i}+\frac{\partial(\rho\dot{p}_i)}{\partial p_i}]$$
  $$=-\sum[\frac{\partial\rho}{\partial q_i}\dot{q}_i+\frac{\partial\rho}{\partial p_i}\dot{p}_i+\rho(\frac{\partial\dot{q}_i}{\partial q_i}+\frac{\partial\dot{p}_i}{\partial p_i})].$$
- According to $\dot{q}_i=\frac{\partial H}{\partial p_i},\dot{p}_i=-\frac{\partial H}{\partial q_i}$,

Phase space and Liouville's theorem

- On the other hand, the net gain in the fixed volume: $\frac{\partial \rho}{\partial t}\mathrm{d}t\mathrm{d}\Omega$.
- $\therefore -\sum[\frac{\partial(\rho\dot{q}_i)}{\partial q_i}+\frac{\partial(\rho\dot{p}_i)}{\partial p_i}]\mathrm{d}t\mathrm{d}\Omega = \frac{\partial \rho}{\partial t}\mathrm{d}t\mathrm{d}\Omega$
  $\Rightarrow \frac{\partial \rho}{\partial t} = -\sum[\frac{\partial(\rho\dot{q}_i)}{\partial q_i}+\frac{\partial(\rho\dot{p}_i)}{\partial p_i}]$
  $= -\sum[\frac{\partial \rho}{\partial q_i}\dot{q}_i+\frac{\partial \rho}{\partial p_i}\dot{p}_i+\rho(\frac{\partial \dot{q}_i}{\partial q_i}+\frac{\partial \dot{p}_i}{\partial p_i})]$.
- According to $\dot{q}_i = \frac{\partial H}{\partial p_i}, \dot{p}_i = -\frac{\partial H}{\partial q_i}$, we have $\frac{\partial^2 H}{\partial p_i \partial q_i} = \frac{\partial^2 H}{\partial q_i \partial p_i} \Rightarrow -\frac{\partial \dot{p}_i}{\partial p_i} = \frac{\partial \dot{q}_i}{\partial q_i}$.

Phase space and Liouville's theorem

- On the other hand, the net gain in the fixed volume: $\frac{\partial \rho}{\partial t}\mathrm{d}t\mathrm{d}\Omega$.
- $\therefore -\sum[\frac{\partial(\rho\dot{q}_i)}{\partial q_i} + \frac{\partial(\rho\dot{p}_i)}{\partial p_i}]\mathrm{d}t\mathrm{d}\Omega = \frac{\partial \rho}{\partial t}\mathrm{d}t\mathrm{d}\Omega$
  $\Rightarrow \frac{\partial \rho}{\partial t} = -\sum[\frac{\partial(\rho\dot{q}_i)}{\partial q_i} + \frac{\partial(\rho\dot{p}_i)}{\partial p_i}]$
  $= -\sum[\frac{\partial \rho}{\partial q_i}\dot{q}_i + \frac{\partial \rho}{\partial p_i}\dot{p}_i + \rho(\frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i})]$.
- According to $\dot{q}_i = \frac{\partial H}{\partial p_i}, \dot{p}_i = -\frac{\partial H}{\partial q_i}$, we have
  $\frac{\partial^2 H}{\partial p_i \partial q_i} = \frac{\partial^2 H}{\partial q_i \partial p_i} \Rightarrow -\frac{\partial \dot{p}_i}{\partial p_i} = \frac{\partial \dot{q}_i}{\partial q_i}$.
  $\therefore \frac{\partial \rho}{\partial t} + \sum(\frac{\partial \rho}{\partial q_i}\dot{q}_i + \frac{\partial \rho}{\partial p_i}\dot{p}_i) = 0$,

Phase space and Liouville's theorem

- On the other hand, the net gain in the fixed volume: $\frac{\partial\rho}{\partial t}\mathrm{d}t\mathrm{d}\Omega$.
- $\therefore -\sum[\frac{\partial(\rho\dot{q}_i)}{\partial q_i} + \frac{\partial(\rho\dot{p}_i)}{\partial p_i}]\mathrm{d}t\mathrm{d}\Omega = \frac{\partial\rho}{\partial t}\mathrm{d}t\mathrm{d}\Omega$
  $\Rightarrow \frac{\partial\rho}{\partial t} = -\sum[\frac{\partial(\rho\dot{q}_i)}{\partial q_i} + \frac{\partial(\rho\dot{p}_i)}{\partial p_i}]$
  $= -\sum[\frac{\partial\rho}{\partial q_i}\dot{q}_i + \frac{\partial\rho}{\partial p_i}\dot{p}_i + \rho(\frac{\partial\dot{q}_i}{\partial q_i} + \frac{\partial\dot{p}_i}{\partial p_i})]$.
- According to $\dot{q}_i = \frac{\partial H}{\partial p_i}, \dot{p}_i = -\frac{\partial H}{\partial q_i}$, we have
  $\frac{\partial^2 H}{\partial p_i\partial q_i} = \frac{\partial^2 H}{\partial q_i\partial p_i} \Rightarrow -\frac{\partial\dot{p}_i}{\partial p_i} = \frac{\partial\dot{q}_i}{\partial q_i}$.
  $\therefore \frac{\partial\rho}{\partial t} + \sum(\frac{\partial\rho}{\partial q_i}\dot{q}_i + \frac{\partial\rho}{\partial p_i}\dot{p}_i) = 0$, or $\frac{\mathrm{d}\rho}{\mathrm{d}t} = 0$.
  Liouville's theorem.

Phase space and Liouville's theorem

- On the other hand, the net gain in the fixed volume: $\frac{\partial\rho}{\partial t}\mathrm{d}t\mathrm{d}\Omega$.
- $\therefore -\sum[\frac{\partial(\rho\dot{q}_i)}{\partial q_i}+\frac{\partial(\rho\dot{p}_i)}{\partial p_i}]\mathrm{d}t\mathrm{d}\Omega=\frac{\partial\rho}{\partial t}\mathrm{d}t\mathrm{d}\Omega$
  $$\Rightarrow \frac{\partial\rho}{\partial t}=-\sum[\frac{\partial(\rho\dot{q}_i)}{\partial q_i}+\frac{\partial(\rho\dot{p}_i)}{\partial p_i}]$$
  $$=-\sum[\frac{\partial\rho}{\partial q_i}\dot{q}_i+\frac{\partial\rho}{\partial p_i}\dot{p}_i+\rho(\frac{\partial\dot{q}_i}{\partial q_i}+\frac{\partial\dot{p}_i}{\partial p_i})].$$
- According to $\dot{q}_i=\frac{\partial H}{\partial p_i},\dot{p}_i=-\frac{\partial H}{\partial q_i}$, we have $\frac{\partial^2 H}{\partial p_i\partial q_i}=\frac{\partial^2 H}{\partial q_i\partial p_i}\Rightarrow -\frac{\partial\dot{p}_i}{\partial p_i}=\frac{\partial\dot{q}_i}{\partial q_i}$.
  $\therefore \frac{\partial\rho}{\partial t}+\sum(\frac{\partial\rho}{\partial q_i}\dot{q}_i+\frac{\partial\rho}{\partial p_i}\dot{p}_i)=0$, or $\frac{\mathrm{d}\rho}{\mathrm{d}t}=0$.
  Liouville's theorem.
  Or $\frac{\partial\rho}{\partial t}=-\sum(\frac{\partial\rho}{\partial q_i}\frac{\partial H}{\partial p_i}-\frac{\partial\rho}{\partial p_i}\frac{\partial H}{\partial q_i})$.

Table of contents

9.2 The microcanonical ensemble

9.2 The microcanonical ensemble

- Redefine ρ (normalized): $\int \rho(q,p,t)\mathrm{d}\Omega = 1$.

9.2 The microcanonical ensemble

- Redefine ρ (normalized): $\int \rho(q,p,t)\mathrm{d}\Omega = 1$.
- Meaning: distribution function of the micro-states; probability to find the system in $\mathrm{d}\Omega$ is: $\rho(q,p,t)\mathrm{d}\Omega$.

9.2 The microcanonical ensemble

- Redefine ρ (normalized): $\int \rho(q,p,t)\mathrm{d}\Omega = 1$.
- Meaning: distribution function of the micro-states; probability to find the system in $\mathrm{d}\Omega$ is: $\rho(q,p,t)\mathrm{d}\Omega$.
- For any variable $B(q,p)$, the average value: $\bar{B}(t) = \int B(q,p)\rho(q,p,t)\mathrm{d}\Omega$.

9.2 The microcanonical ensemble

- Redefine ρ (normalized): $\int \rho(q,p,t)\mathrm{d}\Omega = 1$.
- Meaning: distribution function of the micro-states; probability to find the system in $\mathrm{d}\Omega$ is: $\rho(q,p,t)\mathrm{d}\Omega$.
- For any variable $B(q,p)$, the average value: $\bar{B}(t) = \int B(q,p)\rho(q,p,t)\mathrm{d}\Omega$.
  Meaning...

9.2 The microcanonical ensemble

- Redefine ρ (normalized): $\int \rho(q,p,t)\mathrm{d}\Omega = 1$.
- Meaning: distribution function of the micro-states; probability to find the system in $\mathrm{d}\Omega$ is: $\rho(q,p,t)\mathrm{d}\Omega$.
- For any variable $B(q,p)$, the average value:
  $\bar{B}(t) = \int B(q,p)\rho(q,p,t)\mathrm{d}\Omega$.
  Meaning...
- For quantum system, $\rho_s(t)$ represents the probability for system being state s at time t.

9.2 The microcanonical ensemble

- Redefine ρ (normalized): $\int \rho(q,p,t)\mathrm{d}\Omega = 1$.
- Meaning: distribution function of the micro-states; probability to find the system in $\mathrm{d}\Omega$ is: $\rho(q,p,t)\mathrm{d}\Omega$.
- For any variable $B(q,p)$, the average value:
  $\bar{B}(t) = \int B(q,p)\rho(q,p,t)\mathrm{d}\Omega$.
  Meaning...
- For quantum system, $\rho_s(t)$ represents the probability for system being state s at time t.
  $\sum \rho_s(t) = 1$;

9.2 The microcanonical ensemble

- Redefine ρ (normalized): $\int \rho(q,p,t)\mathrm{d}\Omega = 1$.
- Meaning: distribution function of the micro-states; probability to find the system in $\mathrm{d}\Omega$ is: $\rho(q,p,t)\mathrm{d}\Omega$.
- For any variable $B(q,p)$, the average value:
  $\bar{B}(t) = \int B(q,p)\rho(q,p,t)\mathrm{d}\Omega$.
  Meaning...
- For quantum system, $\rho_s(t)$ represents the probability for system being state s at time t.
  $\sum \rho_s(t) = 1$; $\bar{B}(t) = \sum \rho_s(t)B$.

9.2 The microcanonical ensemble

- Redefine ρ (normalized): $\int \rho(q,p,t)\mathrm{d}\Omega = 1$.
- Meaning: distribution function of the micro-states; probability to find the system in $\mathrm{d}\Omega$ is: $\rho(q,p,t)\mathrm{d}\Omega$.
- For any variable $B(q,p)$, the average value:
  $\bar{B}(t) = \int B(q,p)\rho(q,p,t)\mathrm{d}\Omega$.
  Meaning...
- For quantum system, $\rho_s(t)$ represents the probability for system being state s at time t.
  $\sum \rho_s(t) = 1$; $\bar{B}(t) = \sum \rho_s(t)B$.
- Core task: distribution function ρ.

The microcanonical ensemble

- Consider isolated system in equilibrium, with distribution function ρ.

The microcanonical ensemble

- Consider isolated system in equilibrium, with distribution function ρ.
- Equilibrium $\rightarrow \frac{\partial \rho}{\partial t} = 0$;

The microcanonical ensemble

- Consider isolated system in equilibrium, with distribution function ρ.
- Equilibrium $\to \frac{\partial \rho}{\partial t} = 0$;
  Liouville's theorem $\to \frac{\mathrm{d}\rho}{\mathrm{d}t} = 0$.

The microcanonical ensemble

- Consider isolated system in equilibrium, with distribution function ρ.
- Equilibrium $\rightarrow \frac{\partial \rho}{\partial t} = 0$;
  Liouville's theorem $\rightarrow \frac{\mathrm{d}\rho}{\mathrm{d}t} = 0$.
- A natural **assumption**: $\rho(q, p) = \mathrm{Const.}$

The microcanonical ensemble

- Consider isolated system in equilibrium, with distribution function ρ.
- Equilibrium $\rightarrow \frac{\partial \rho}{\partial t} = 0$;
  Liouville's theorem $\rightarrow \frac{\mathrm{d}\rho}{\mathrm{d}t} = 0$.
- A natural **assumption**: $\rho(q, p) = \mathrm{Const.}$
- As there is no absolute isolated system, it has more or less energy change with the environment.

The microcanonical ensemble

- Consider isolated system in equilibrium, with distribution function ρ.
- Equilibrium $\rightarrow \frac{\partial \rho}{\partial t} = 0$;
  Liouville's theorem $\rightarrow \frac{\mathrm{d}\rho}{\mathrm{d}t} = 0$.
- A natural **assumption**: $\rho(q, p) = \mathrm{Const.}$
- As there is no absolute isolated system, it has more or less energy change with the environment. Energy of the system is not an absolutely fixed value, but a range: $(E, E + \Delta E)$.

The microcanonical ensemble

- Consider isolated system in equilibrium, with distribution function ρ.
- Equilibrium $\rightarrow \frac{\partial \rho}{\partial t} = 0$;
  Liouville's theorem $\rightarrow \frac{\mathrm{d}\rho}{\mathrm{d}t} = 0$.
- A natural **assumption**: $\rho(q, p) = \mathrm{Const.}$
- As there is no absolute isolated system, it has more or less energy change with the environment. Energy of the system is not an absolutely fixed value, but a range: $(E, E + \Delta E)$.
  The assumption goes to (equal probability principle):

$$\rho(q, p) = \begin{cases} \mathrm{const.}, & E \leq H \leq E + \Delta E, \\ 0, & \mathrm{others.} \end{cases}$$

The microcanonical ensemble

- For quantum system, $\rho_s = \frac{1}{\Omega}$, where Ω is the total number of micro-states of the system.

The microcanonical ensemble

- For quantum system, $\rho_s = \frac{1}{\Omega}$, where Ω is the total number of micro-states of the system.
- Consider the classical system as the limit of quantum system, the number of micro-state of the classical system: $\Omega = \frac{1}{N!}\frac{1}{h^{Nr}} \int\limits_{E \le H(q,p) \le E+\Delta E} \mathrm{d}\Omega$.

The microcanonical ensemble

- For quantum system, $\rho_s = \frac{1}{\Omega}$, where Ω is the total number of micro-states of the system.
- Consider the classical system as the limit of quantum system, the number of micro-state of the classical system: $\Omega = \frac{1}{N!}\frac{1}{h^{Nr}} \int\limits_{E \le H(q,p) \le E+\Delta E} \mathrm{d}\Omega$.
- For multiple kinds of particles:
  $\Omega = \frac{1}{\prod N_i!}\frac{1}{h^{Nr}} \int\limits_{E \le H(q,p) \le E+\Delta E} \mathrm{d}\Omega$.

The microcanonical ensemble

- For quantum system, $\rho_s = \frac{1}{\Omega}$, where Ω is the total number of micro-states of the system.
- Consider the classical system as the limit of quantum system, the number of micro-state of the classical system: $\Omega = \frac{1}{N!}\frac{1}{h^{Nr}} \int\limits_{E \leq H(q,p) \leq E+\Delta E} \mathrm{d}\Omega$.
- For multiple kinds of particles:
  $\Omega = \frac{1}{\prod N_i!}\frac{1}{h^{Nr}} \int\limits_{E \leq H(q,p) \leq E+\Delta E} \mathrm{d}\Omega$.
- "The most probable distribution" is different from the ensemble average, in concept.

The microcanonical ensemble

- For quantum system, $\rho_s = \frac{1}{\Omega}$, where Ω is the total number of micro-states of the system.
- Consider the classical system as the limit of quantum system, the number of micro-state of the classical system: $\Omega = \frac{1}{N!}\frac{1}{h^{Nr}}\int\limits_{E\le H(q,p)\le E+\Delta E} \mathrm{d}\Omega$.
- For multiple kinds of particles:
$\Omega = \frac{1}{\prod N_i!}\frac{1}{h^{Nr}}\int\limits_{E\le H(q,p)\le E+\Delta E} \mathrm{d}\Omega$.
- "The most probable distribution" is different from the ensemble average, in concept. But if the fluctuation is small, $\frac{\bar{B^2}-(\bar{B})^2}{(\bar{B})^2} \ll 1$, both are equal.

Table of contents

9.3 Thermodynamics in microcanonical ensemble theory

9.3 Thermodynamics in microcanonical ensemble theory

- For a given system (N, E, V), the number of states: $\Omega(N, E, V)$.

9.3 Thermodynamics in microcanonical ensemble theory

- For a given system (N, E, V), the number of states: $\Omega(N, E, V)$.
- Consider an isolated system $A^{(0)}$: $(N^{(0)}, E^{(0)}, V^{(0)})$, the number of states: $\Omega^{(0)}(N^{(0)}, E^{(0)}, V^{(0)})$.

9.3 Thermodynamics in microcanonical ensemble theory

- For a given system (N, E, V), the number of states: $\Omega(N, E, V)$.
- Consider an isolated system $A^{(0)}$: $(N^{(0)}, E^{(0)}, V^{(0)})$, the number of states: $\Omega^{(0)}(N^{(0)}, E^{(0)}, V^{(0)})$.
  Divide it into two sub-systems: A_1: (N_1, E_1, V_1), A_2: (N_2, E_2, V_2), with $\Omega_1(N_1, E_1, V_1)$, $\Omega_2(N_2, E_2, V_2)$.

9.3 Thermodynamics in microcanonical ensemble theory

- For a given system (N, E, V), the number of states: $\Omega(N, E, V)$.
- Consider an isolated system $A^{(0)}$: $(N^{(0)}, E^{(0)}, V^{(0)})$, the number of states: $\Omega^{(0)}(N^{(0)}, E^{(0)}, V^{(0)})$.
  Divide it into two sub-systems: A_1: (N_1, E_1, V_1), A_2: (N_2, E_2, V_2), with $\Omega_1(N_1, E_1, V_1)$, $\Omega_2(N_2, E_2, V_2)$.
- Obviously, $N^{(0)} = N_1 + N_2$, $E^{(0)} = E_1 + E_2$, $V^{(0)} = V_1 + V_2$,

9.3 Thermodynamics in microcanonical ensemble theory

- For a given system (N, E, V), the number of states: $\Omega(N, E, V)$.
- Consider an isolated system $A^{(0)}$: $(N^{(0)}, E^{(0)}, V^{(0)})$, the number of states: $\Omega^{(0)}(N^{(0)}, E^{(0)}, V^{(0)})$.
  Divide it into two sub-systems: A_1: (N_1, E_1, V_1), A_2: (N_2, E_2, V_2), with $\Omega_1(N_1, E_1, V_1)$, $\Omega_2(N_2, E_2, V_2)$.
- Obviously, $N^{(0)} = N_1 + N_2$, $E^{(0)} = E_1 + E_2$, $V^{(0)} = V_1 + V_2$, and $\Omega^{(0)} = \Omega_1 \cdot \Omega_2$.

9.3 Thermodynamics in microcanonical ensemble theory

- For a given system (N, E, V), the number of states: $\Omega(N, E, V)$.
- Consider an isolated system $A^{(0)}$: $(N^{(0)}, E^{(0)}, V^{(0)})$, the number of states: $\Omega^{(0)}(N^{(0)}, E^{(0)}, V^{(0)})$.
  Divide it into two sub-systems: A_1: (N_1, E_1, V_1), A_2: (N_2, E_2, V_2), with $\Omega_1(N_1, E_1, V_1)$, $\Omega_2(N_2, E_2, V_2)$.
- Obviously, $N^{(0)} = N_1 + N_2$, $E^{(0)} = E_1 + E_2$, $V^{(0)} = V_1 + V_2$, and $\Omega^{(0)} = \Omega_1 \cdot \Omega_2$.
- Keep (N_1, N_2, V_1, V_2), let (E_1, E_2) vary, to see the condition to get equilibrium:

9.3 Thermodynamics in microcanonical ensemble theory

- For a given system (N, E, V), the number of states: $\Omega(N, E, V)$.
- Consider an isolated system $A^{(0)}$: $(N^{(0)}, E^{(0)}, V^{(0)})$, the number of states: $\Omega^{(0)}(N^{(0)}, E^{(0)}, V^{(0)})$.
  Divide it into two sub-systems: A_1: (N_1, E_1, V_1), A_2: (N_2, E_2, V_2), with $\Omega_1(N_1, E_1, V_1)$, $\Omega_2(N_2, E_2, V_2)$.
- Obviously, $N^{(0)} = N_1 + N_2$, $E^{(0)} = E_1 + E_2$, $V^{(0)} = V_1 + V_2$, and $\Omega^{(0)} = \Omega_1 \cdot \Omega_2$.
- Keep (N_1, N_2, V_1, V_2), let (E_1, E_2) vary, to see the condition to get equilibrium: $\frac{\partial \Omega^{(0)}}{\partial E_1} = 0$,

9.3 Thermodynamics in microcanonical ensemble theory

- For a given system (N, E, V), the number of states: $\Omega(N, E, V)$.
- Consider an isolated system $A^{(0)}$: $(N^{(0)}, E^{(0)}, V^{(0)})$, the number of states: $\Omega^{(0)}(N^{(0)}, E^{(0)}, V^{(0)})$.
  Divide it into two sub-systems: A_1: (N_1, E_1, V_1), A_2: (N_2, E_2, V_2), with $\Omega_1(N_1, E_1, V_1)$, $\Omega_2(N_2, E_2, V_2)$.
- Obviously, $N^{(0)} = N_1 + N_2$, $E^{(0)} = E_1 + E_2$, $V^{(0)} = V_1 + V_2$, and $\Omega^{(0)} = \Omega_1 \cdot \Omega_2$.
- Keep (N_1, N_2, V_1, V_2), let (E_1, E_2) vary, to see the condition to get equilibrium: $\frac{\partial \Omega^{(0)}}{\partial E_1} = 0$, i.e., with the choosing of (E_1, E_2), number of states has maximum because of the equal probability principle.

Thermodynamics in microcanonical ensemble theory

- $\dfrac{\partial \Omega^{(0)}}{\partial E_1}$

Thermodynamics in microcanonical ensemble theory

- $\dfrac{\partial \Omega^{(0)}}{\partial E_1} = \dfrac{\partial(\Omega_1 \Omega_2)}{\partial E_1}$

Thermodynamics in microcanonical ensemble theory

- $\frac{\partial \Omega^{(0)}}{\partial E_1} = \frac{\partial (\Omega_1 \Omega_2)}{\partial E_1} = \frac{\partial \Omega_1}{\partial E_1} \Omega_2 + \Omega_1 \frac{\partial \Omega_2}{\partial E_1}$

Thermodynamics in microcanonical ensemble theory

- $\frac{\partial \Omega^{(0)}}{\partial E_1} = \frac{\partial(\Omega_1 \Omega_2)}{\partial E_1} = \frac{\partial \Omega_1}{\partial E_1}\Omega_2 + \Omega_1 \frac{\partial \Omega_2}{\partial E_1} = \frac{\partial \Omega_1}{\partial E_1}\Omega_2 + \Omega_1 \frac{\partial \Omega_2}{\partial E_2}\frac{\partial E_2}{\partial E_1}$

Thermodynamics in microcanonical ensemble theory

- $\frac{\partial\Omega^{(0)}}{\partial E_1} = \frac{\partial(\Omega_1\Omega_2)}{\partial E_1} = \frac{\partial\Omega_1}{\partial E_1}\Omega_2 + \Omega_1\frac{\partial\Omega_2}{\partial E_1} = \frac{\partial\Omega_1}{\partial E_1}\Omega_2 + \Omega_1\frac{\partial\Omega_2}{\partial E_2}\frac{\partial E_2}{\partial E_1}$
  $= \frac{\partial\Omega_1}{\partial E_1}\Omega_2 - \Omega_1\frac{\partial\Omega_2}{\partial E_2}$

Thermodynamics in microcanonical ensemble theory

- $\frac{\partial\Omega^{(0)}}{\partial E_1} = \frac{\partial(\Omega_1\Omega_2)}{\partial E_1} = \frac{\partial\Omega_1}{\partial E_1}\Omega_2 + \Omega_1\frac{\partial\Omega_2}{\partial E_1} = \frac{\partial\Omega_1}{\partial E_1}\Omega_2 + \Omega_1\frac{\partial\Omega_2}{\partial E_2}\frac{\partial E_2}{\partial E_1}$
  $= \frac{\partial\Omega_1}{\partial E_1}\Omega_2 - \Omega_1\frac{\partial\Omega_2}{\partial E_2} = 0;$

Thermodynamics in microcanonical ensemble theory

- $\frac{\partial \Omega^{(0)}}{\partial E_1} = \frac{\partial(\Omega_1\Omega_2)}{\partial E_1} = \frac{\partial \Omega_1}{\partial E_1}\Omega_2 + \Omega_1\frac{\partial \Omega_2}{\partial E_1} = \frac{\partial \Omega_1}{\partial E_1}\Omega_2 + \Omega_1\frac{\partial \Omega_2}{\partial E_2}\frac{\partial E_2}{\partial E_1}$ $= \frac{\partial \Omega_1}{\partial E_1}\Omega_2 - \Omega_1\frac{\partial \Omega_2}{\partial E_2} = 0; \Rightarrow \frac{\partial \ln \Omega_1}{\partial E_1} = \frac{\partial \ln \Omega_2}{\partial E_2}.$

Thermodynamics in microcanonical ensemble theory

- $\frac{\partial \Omega^{(0)}}{\partial E_1} = \frac{\partial(\Omega_1 \Omega_2)}{\partial E_1} = \frac{\partial \Omega_1}{\partial E_1}\Omega_2 + \Omega_1 \frac{\partial \Omega_2}{\partial E_1} = \frac{\partial \Omega_1}{\partial E_1}\Omega_2 + \Omega_1 \frac{\partial \Omega_2}{\partial E_2}\frac{\partial E_2}{\partial E_1}$
  $= \frac{\partial \Omega_1}{\partial E_1}\Omega_2 - \Omega_1 \frac{\partial \Omega_2}{\partial E_2} = 0; \Rightarrow \frac{\partial \ln \Omega_1}{\partial E_1} = \frac{\partial \ln \Omega_2}{\partial E_2}.$
- More complete:
  $\left(\frac{\partial \ln \Omega_1(N_1, E_1, V_1)}{\partial E_1}\right)_{N_1, V_1} = \left(\frac{\partial \ln \Omega_2(N_2, E_2, V_2)}{\partial E_2}\right)_{N_2, V_2}.$

Thermodynamics in microcanonical ensemble theory

- $\frac{\partial\Omega^{(0)}}{\partial E_1} = \frac{\partial(\Omega_1\Omega_2)}{\partial E_1} = \frac{\partial\Omega_1}{\partial E_1}\Omega_2 + \Omega_1\frac{\partial\Omega_2}{\partial E_1} = \frac{\partial\Omega_1}{\partial E_1}\Omega_2 + \Omega_1\frac{\partial\Omega_2}{\partial E_2}\frac{\partial E_2}{\partial E_1}$
  $= \frac{\partial\Omega_1}{\partial E_1}\Omega_2 - \Omega_1\frac{\partial\Omega_2}{\partial E_2} = 0; \Rightarrow \frac{\partial\ln\Omega_1}{\partial E_1} = \frac{\partial\ln\Omega_2}{\partial E_2}$.
- More complete:
  $\left(\frac{\partial\ln\Omega_1(N_1,E_1,V_1)}{\partial E_1}\right)_{N_1,V_1} = \left(\frac{\partial\ln\Omega_2(N_2,E_2,V_2)}{\partial E_2}\right)_{N_2,V_2}$.
  Set $\beta = (\frac{\partial\ln\Omega(N,E,V)}{\partial E})_{N,V}$, $\beta_1 = \beta_2$.

Thermodynamics in microcanonical ensemble theory

- $\frac{\partial \Omega^{(0)}}{\partial E_1} = \frac{\partial(\Omega_1 \Omega_2)}{\partial E_1} = \frac{\partial \Omega_1}{\partial E_1}\Omega_2 + \Omega_1 \frac{\partial \Omega_2}{\partial E_1} = \frac{\partial \Omega_1}{\partial E_1}\Omega_2 + \Omega_1 \frac{\partial \Omega_2}{\partial E_2}\frac{\partial E_2}{\partial E_1}$ $= \frac{\partial \Omega_1}{\partial E_1}\Omega_2 - \Omega_1 \frac{\partial \Omega_2}{\partial E_2} = 0; \Rightarrow \frac{\partial \ln \Omega_1}{\partial E_1} = \frac{\partial \ln \Omega_2}{\partial E_2}.$
- More complete:
  $\left(\frac{\partial \ln \Omega_1(N_1,E_1,V_1)}{\partial E_1}\right)_{N_1,V_1} = \left(\frac{\partial \ln \Omega_2(N_2,E_2,V_2)}{\partial E_2}\right)_{N_2,V_2}.$
  Set $\beta = (\frac{\partial \ln \Omega(N,E,V)}{\partial E})_{N,V}$, $\beta_1 = \beta_2$.
- Basic function (3.2.7): $\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V + \mu \mathrm{d}N$,

Thermodynamics in microcanonical ensemble theory

- $\frac{\partial\Omega^{(0)}}{\partial E_1} = \frac{\partial(\Omega_1\Omega_2)}{\partial E_1} = \frac{\partial\Omega_1}{\partial E_1}\Omega_2 + \Omega_1\frac{\partial\Omega_2}{\partial E_1} = \frac{\partial\Omega_1}{\partial E_1}\Omega_2 + \Omega_1\frac{\partial\Omega_2}{\partial E_2}\frac{\partial E_2}{\partial E_1}$
  $= \frac{\partial\Omega_1}{\partial E_1}\Omega_2 - \Omega_1\frac{\partial\Omega_2}{\partial E_2} = 0; \Rightarrow \frac{\partial\ln\Omega_1}{\partial E_1} = \frac{\partial\ln\Omega_2}{\partial E_2}$.
- More complete:
  $\left(\frac{\partial\ln\Omega_1(N_1,E_1,V_1)}{\partial E_1}\right)_{N_1,V_1} = \left(\frac{\partial\ln\Omega_2(N_2,E_2,V_2)}{\partial E_2}\right)_{N_2,V_2}$.
  Set $\beta = (\frac{\partial\ln\Omega(N,E,V)}{\partial E})_{N,V}$, $\beta_1 = \beta_2$.
- Basic function (3.2.7): $\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V + \mu\mathrm{d}N$, for fixed (N,V), the condition for equilibrium is $T_1 = T_2$, i.e., $\frac{1}{T_1} = (\frac{\partial S_1}{\partial U_1})_{N_1,V_1} = (\frac{\partial S_2}{\partial U_2})_{N_2,V_2} = \frac{1}{T_2}$.

Thermodynamics in microcanonical ensemble theory

- $\frac{\partial\Omega^{(0)}}{\partial E_1} = \frac{\partial(\Omega_1\Omega_2)}{\partial E_1} = \frac{\partial\Omega_1}{\partial E_1}\Omega_2 + \Omega_1\frac{\partial\Omega_2}{\partial E_1} = \frac{\partial\Omega_1}{\partial E_1}\Omega_2 + \Omega_1\frac{\partial\Omega_2}{\partial E_2}\frac{\partial E_2}{\partial E_1}$ $= \frac{\partial\Omega_1}{\partial E_1}\Omega_2 - \Omega_1\frac{\partial\Omega_2}{\partial E_2} = 0; \Rightarrow \frac{\partial\ln\Omega_1}{\partial E_1} = \frac{\partial\ln\Omega_2}{\partial E_2}$.
- More complete:
  $\left(\frac{\partial\ln\Omega_1(N_1,E_1,V_1)}{\partial E_1}\right)_{N_1,V_1} = \left(\frac{\partial\ln\Omega_2(N_2,E_2,V_2)}{\partial E_2}\right)_{N_2,V_2}$.
  Set $\beta = (\frac{\partial\ln\Omega(N,E,V)}{\partial E})_{N,V}$, $\beta_1 = \beta_2$.
- Basic function (3.2.7): $\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V + \mu\mathrm{d}N$, for fixed (N, V), the condition for equilibrium is $T_1 = T_2$, i.e., $\frac{1}{T_1} = (\frac{\partial S_1}{\partial U_1})_{N_1,V_1} = (\frac{\partial S_2}{\partial U_2})_{N_2,V_2} = \frac{1}{T_2}$.
- $\therefore \beta = \frac{1}{kT}$, where k is the Boltzmann constant, which can be found by taking into an example, like ideal gas.

Thermodynamics in microcanonical ensemble theory

- $\frac{\partial\Omega^{(0)}}{\partial E_1} = \frac{\partial(\Omega_1\Omega_2)}{\partial E_1} = \frac{\partial\Omega_1}{\partial E_1}\Omega_2 + \Omega_1\frac{\partial\Omega_2}{\partial E_1} = \frac{\partial\Omega_1}{\partial E_1}\Omega_2 + \Omega_1\frac{\partial\Omega_2}{\partial E_2}\frac{\partial E_2}{\partial E_1}$
  $= \frac{\partial\Omega_1}{\partial E_1}\Omega_2 - \Omega_1\frac{\partial\Omega_2}{\partial E_2} = 0; \Rightarrow \frac{\partial\ln\Omega_1}{\partial E_1} = \frac{\partial\ln\Omega_2}{\partial E_2}$.
- More complete:
  $\left(\frac{\partial\ln\Omega_1(N_1,E_1,V_1)}{\partial E_1}\right)_{N_1,V_1} = \left(\frac{\partial\ln\Omega_2(N_2,E_2,V_2)}{\partial E_2}\right)_{N_2,V_2}$.
  Set $\beta = (\frac{\partial\ln\Omega(N,E,V)}{\partial E})_{N,V}$, $\beta_1 = \beta_2$.
- Basic function (3.2.7): $\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V + \mu\mathrm{d}N$, for fixed (N,V), the condition for equilibrium is $T_1 = T_2$, i.e., $\frac{1}{T_1} = (\frac{\partial S_1}{\partial U_1})_{N_1,V_1} = (\frac{\partial S_2}{\partial U_2})_{N_2,V_2} = \frac{1}{T_2}$.
- $\therefore \beta = \frac{1}{kT}$, where k is the Boltzmann constant, which can be found by taking into an example, like ideal gas.
- As $\frac{1}{T} = k\beta$, $S = k\ln\Omega$.

Thermodynamics in microcanonical ensemble theory

- If between sub-systems A_1, A_2, not only energy, but also particles and volume can exchange, we have:

Thermodynamics in microcanonical ensemble theory

- If between sub-systems A_1, A_2, not only energy, but also particles and volume can exchange, we have:
$(\frac{\partial \ln \Omega_1}{\partial E_1})_{N_1,V_1} = (\frac{\partial \ln \Omega_2}{\partial E_2})_{N_2,V_2} \to \beta_1 = \beta_2$,
$(\frac{\partial \ln \Omega_1}{\partial V_1})_{N_1,E_1} = (\frac{\partial \ln \Omega_2}{\partial V_2})_{N_2,E_2} \to \gamma_1 = \gamma_2$,
$(\frac{\partial \ln \Omega_1}{\partial N_1})_{E_1,V_1} = (\frac{\partial \ln \Omega_2}{\partial N_2})_{E_2,V_2} \to \alpha_1 = \alpha_2$.

Thermodynamics in microcanonical ensemble theory

- If between sub-systems A_1, A_2, not only energy, but also particles and volume can exchange, we have:
  $(\frac{\partial \ln \Omega_1}{\partial E_1})_{N_1,V_1} = (\frac{\partial \ln \Omega_2}{\partial E_2})_{N_2,V_2} \to \beta_1 = \beta_2$,
  $(\frac{\partial \ln \Omega_1}{\partial V_1})_{N_1,E_1} = (\frac{\partial \ln \Omega_2}{\partial V_2})_{N_2,E_2} \to \gamma_1 = \gamma_2$,
  $(\frac{\partial \ln \Omega_1}{\partial N_1})_{E_1,V_1} = (\frac{\partial \ln \Omega_2}{\partial N_2})_{E_2,V_2} \to \alpha_1 = \alpha_2$.
- Then the complete differential:
  $\mathrm{d} \ln \Omega = \beta \mathrm{d}E + \gamma \mathrm{d}V + \alpha \mathrm{d}N$.

Thermodynamics in microcanonical ensemble theory

- If between sub-systems A_1, A_2, not only energy, but also particles and volume can exchange, we have:
  $(\frac{\partial \ln \Omega_1}{\partial E_1})_{N_1,V_1} = (\frac{\partial \ln \Omega_2}{\partial E_2})_{N_2,V_2} \to \beta_1 = \beta_2$,
  $(\frac{\partial \ln \Omega_1}{\partial V_1})_{N_1,E_1} = (\frac{\partial \ln \Omega_2}{\partial V_2})_{N_2,E_2} \to \gamma_1 = \gamma_2$,
  $(\frac{\partial \ln \Omega_1}{\partial N_1})_{E_1,V_1} = (\frac{\partial \ln \Omega_2}{\partial N_2})_{E_2,V_2} \to \alpha_1 = \alpha_2$.
- Then the complete differential:
  $\mathrm{d} \ln \Omega = \beta \mathrm{d}E + \gamma \mathrm{d}V + \alpha \mathrm{d}N$.
  Compare with (3.2.7): $\mathrm{d}S = \frac{1}{T}\mathrm{d}U + \frac{p}{T}\mathrm{d}V - \frac{\mu}{T}\mathrm{d}N$.

Thermodynamics in microcanonical ensemble theory

- If between sub-systems A_1, A_2, not only energy, but also particles and volume can exchange, we have:
  $(\frac{\partial \ln \Omega_1}{\partial E_1})_{N_1,V_1} = (\frac{\partial \ln \Omega_2}{\partial E_2})_{N_2,V_2} \to \beta_1 = \beta_2$,
  $(\frac{\partial \ln \Omega_1}{\partial V_1})_{N_1,E_1} = (\frac{\partial \ln \Omega_2}{\partial V_2})_{N_2,E_2} \to \gamma_1 = \gamma_2$,
  $(\frac{\partial \ln \Omega_1}{\partial N_1})_{E_1,V_1} = (\frac{\partial \ln \Omega_2}{\partial N_2})_{E_2,V_2} \to \alpha_1 = \alpha_2$.
- Then the complete differential:
  $\mathrm{d}\ln\Omega = \beta \mathrm{d}E + \gamma \mathrm{d}V + \alpha \mathrm{d}N$.
  Compare with (3.2.7): $\mathrm{d}S = \frac{1}{T}\mathrm{d}U + \frac{p}{T}\mathrm{d}V - \frac{\mu}{T}\mathrm{d}N$.
  $\Rightarrow \gamma = \frac{p}{kT}$, $\alpha = -\frac{\mu}{kT}$.

Thermodynamics in microcanonical ensemble theory

- If between sub-systems A_1, A_2, not only energy, but also particles and volume can exchange, we have:
  $(\frac{\partial \ln \Omega_1}{\partial E_1})_{N_1,V_1} = (\frac{\partial \ln \Omega_2}{\partial E_2})_{N_2,V_2} \to \beta_1 = \beta_2$,
  $(\frac{\partial \ln \Omega_1}{\partial V_1})_{N_1,E_1} = (\frac{\partial \ln \Omega_2}{\partial V_2})_{N_2,E_2} \to \gamma_1 = \gamma_2$,
  $(\frac{\partial \ln \Omega_1}{\partial N_1})_{E_1,V_1} = (\frac{\partial \ln \Omega_2}{\partial N_2})_{E_2,V_2} \to \alpha_1 = \alpha_2$.
- Then the complete differential:
  $\mathrm{d}\ln\Omega = \beta \mathrm{d}E + \gamma \mathrm{d}V + \alpha \mathrm{d}N$.
  Compare with (3.2.7): $\mathrm{d}S = \frac{1}{T}\mathrm{d}U + \frac{p}{T}\mathrm{d}V - \frac{\mu}{T}\mathrm{d}N$.
  $\Rightarrow \gamma = \frac{p}{kT}$, $\alpha = -\frac{\mu}{kT}$.
- The condition for equilibrium: $T_1 = T_2$, $p_1 = p_2$, $\mu_1 = \mu_2$; also showed the meaning of α, β, and γ.

Thermodynamics in microcanonical ensemble theory

- Apply to classical ideal gas:

Thermodynamics in microcanonical ensemble theory

- Apply to classical ideal gas:
- $\mathrm{d}\Omega = \mathrm{d}q_1 ... \mathrm{d}q_f \mathrm{d}p_1 ... \mathrm{d}p_f$

Thermodynamics in microcanonical ensemble theory

- Apply to classical ideal gas:
- $\mathrm{d}\Omega = \mathrm{d}q_1 ... \mathrm{d}q_f \mathrm{d}p_1 ... \mathrm{d}p_f$
  $= \mathrm{d}q_{11} \mathrm{d}q_{12} \mathrm{d}q_{13} ... \mathrm{d}q_{N3} \mathrm{d}p_1 ... \mathrm{d}p_f,$

Thermodynamics in microcanonical ensemble theory

- Apply to classical ideal gas:
- $\mathrm{d}\Omega = \mathrm{d}q_1 ... \mathrm{d}q_f \mathrm{d}p_1 ... \mathrm{d}p_f$
  $= \mathrm{d}q_{11}\mathrm{d}q_{12}\mathrm{d}q_{13}...\mathrm{d}q_{N3}\mathrm{d}p_1...\mathrm{d}p_f$,
  $\therefore \Omega = \frac{1}{N!}\frac{1}{h^{Nr}}\int \mathrm{d}\Omega = CV^N$, where C does not depend on q.

Thermodynamics in microcanonical ensemble theory

- Apply to classical ideal gas:
- $\mathrm{d}\Omega = \mathrm{d}q_1 ... \mathrm{d}q_f \mathrm{d}p_1 ... \mathrm{d}p_f$
  $= \mathrm{d}q_{11} \mathrm{d}q_{12} \mathrm{d}q_{13} ... \mathrm{d}q_{N3} \mathrm{d}p_1 ... \mathrm{d}p_f$,
  $\therefore \Omega = \frac{1}{N!} \frac{1}{h^{Nr}} \int \mathrm{d}\Omega = CV^N$, where C does not depend on q.
- $\frac{p}{kT} = \gamma$

Thermodynamics in microcanonical ensemble theory

- Apply to classical ideal gas:
- $\mathrm{d}\Omega = \mathrm{d}q_1 \ldots \mathrm{d}q_f \mathrm{d}p_1 \ldots \mathrm{d}p_f$
  $= \mathrm{d}q_{11}\mathrm{d}q_{12}\mathrm{d}q_{13} \ldots \mathrm{d}q_{N3}\mathrm{d}p_1 \ldots \mathrm{d}p_f$,
  $\therefore \Omega = \frac{1}{N!}\frac{1}{h^{Nr}}\int \mathrm{d}\Omega = CV^N$, where C does not depend on q.
- $\frac{p}{kT} = \gamma = \frac{\partial \ln \Omega}{\partial V}$

Thermodynamics in microcanonical ensemble theory

- Apply to classical ideal gas:
- $\mathrm{d}\Omega = \mathrm{d}q_1 ... \mathrm{d}q_f \mathrm{d}p_1 ... \mathrm{d}p_f$
  $= \mathrm{d}q_{11}\mathrm{d}q_{12}\mathrm{d}q_{13} ... \mathrm{d}q_{N3}\mathrm{d}p_1 ... \mathrm{d}p_f,$
  $\therefore \Omega = \frac{1}{N!}\frac{1}{h^{Nr}}\int \mathrm{d}\Omega = CV^N$, where C does not depend on q.
- $\frac{p}{kT} = \gamma = \frac{\partial \ln \Omega}{\partial V} = \frac{\partial \ln V^N}{\partial V}$

Thermodynamics in microcanonical ensemble theory

- Apply to classical ideal gas:
- $\mathrm{d}\Omega = \mathrm{d}q_1 ... \mathrm{d}q_f \mathrm{d}p_1 ... \mathrm{d}p_f$
  $= \mathrm{d}q_{11}\mathrm{d}q_{12}\mathrm{d}q_{13}...\mathrm{d}q_{N3}\mathrm{d}p_1...\mathrm{d}p_f$,
  $\therefore \Omega = \frac{1}{N!}\frac{1}{h^{Nr}}\int \mathrm{d}\Omega = CV^N$, where C does not depend on q.
- $\frac{p}{kT} = \gamma = \frac{\partial \ln \Omega}{\partial V} = \frac{\partial \ln V^N}{\partial V} = \frac{N}{V}$.

Thermodynamics in microcanonical ensemble theory

- Apply to classical ideal gas:
- $\mathrm{d}\Omega = \mathrm{d}q_1 ... \mathrm{d}q_f \mathrm{d}p_1 ... \mathrm{d}p_f$
  $= \mathrm{d}q_{11}\mathrm{d}q_{12}\mathrm{d}q_{13} ... \mathrm{d}q_{N3}\mathrm{d}p_1 ... \mathrm{d}p_f,$
  $\therefore \Omega = \frac{1}{N!}\frac{1}{h^{Nr}}\int \mathrm{d}\Omega = CV^N$, where C does not depend on q.
- $\frac{p}{kT} = \gamma = \frac{\partial \ln \Omega}{\partial V} = \frac{\partial \ln V^N}{\partial V} = \frac{N}{V}$.
  $\Rightarrow pV = NkT$.

Thermodynamics in microcanonical ensemble theory

- Apply to classical ideal gas:
- $\mathrm{d}\Omega = \mathrm{d}q_1 ... \mathrm{d}q_f \mathrm{d}p_1 ... \mathrm{d}p_f$
  $= \mathrm{d}q_{11}\mathrm{d}q_{12}\mathrm{d}q_{13}...\mathrm{d}q_{N3}\mathrm{d}p_1...\mathrm{d}p_f,$
  $\therefore \Omega = \frac{1}{N!}\frac{1}{h^{Nr}}\int \mathrm{d}\Omega = CV^N$, where C does not depend on q.
- $\frac{p}{kT} = \gamma = \frac{\partial \ln \Omega}{\partial V} = \frac{\partial \ln V^N}{\partial V} = \frac{N}{V}$.
  $\Rightarrow pV = NkT$.
- Known EOS of ideal gas: $pV = nRT$.

Thermodynamics in microcanonical ensemble theory

- Apply to classical ideal gas:
- $\mathrm{d}\Omega = \mathrm{d}q_1 ... \mathrm{d}q_f \mathrm{d}p_1 ... \mathrm{d}p_f$
  $= \mathrm{d}q_{11} \mathrm{d}q_{12} \mathrm{d}q_{13} ... \mathrm{d}q_{N3} \mathrm{d}p_1 ... \mathrm{d}p_f$,
  $\therefore \Omega = \frac{1}{N!} \frac{1}{h^{Nr}} \int \mathrm{d}\Omega = CV^N$, where C does not depend on q.
- $\frac{p}{kT} = \gamma = \frac{\partial \ln \Omega}{\partial V} = \frac{\partial \ln V^N}{\partial V} = \frac{N}{V}$.
  $\Rightarrow pV = NkT$.
- Known EOS of ideal gas: $pV = nRT$.
- $\therefore k = \frac{R}{N_0}$ is just the Boltzmann constant.

Thermodynamics in microcanonical ensemble theory

- General procedure in microcanonical ensemble theory:

Thermodynamics in microcanonical ensemble theory

- General procedure in microcanonical ensemble theory:
- 1. $\Omega(N, E, V)$ (Ω as function of (N, E, V));

Thermodynamics in microcanonical ensemble theory

- General procedure in microcanonical ensemble theory:
- 1. $\Omega(N, E, V)$ (Ω as function of (N, E, V));
- 2. $S(N, E, V) = k \ln \Omega(N, E, V)$ (S as function of (N, E, V)),

Thermodynamics in microcanonical ensemble theory

- General procedure in microcanonical ensemble theory:
- 1. $\Omega(N, E, V)$ (Ω as function of (N, E, V));
- 2. $S(N, E, V) = k \ln \Omega(N, E, V)$ (S as function of (N, E, V)),
  $\Rightarrow E(S, V, N)$ (E as function of (S, V, N));

Thermodynamics in microcanonical ensemble theory

- General procedure in microcanonical ensemble theory:
- 1. $\Omega(N, E, V)$ (Ω as function of (N, E, V));
- 2. $S(N, E, V) = k \ln \Omega(N, E, V)$ (S as function of (N, E, V)),
  $\Rightarrow E(S, V, N)$ (E as function of (S, V, N));
- 3. $\mathrm{d}E = T\mathrm{d}S - p\mathrm{d}V + \mu \mathrm{d}N$
  $\Rightarrow T = (\frac{\partial E}{\partial S})_{V,N}, p = -(\frac{\partial E}{\partial V})_{S,N}$,

Thermodynamics in microcanonical ensemble theory

- General procedure in microcanonical ensemble theory:
- 1. $\Omega(N,E,V)$ (Ω as function of (N,E,V));
- 2. $S(N,E,V) = k\ln\Omega(N,E,V)$ (S as function of (N,E,V)),
  $\Rightarrow E(S,V,N)$ (E as function of (S,V,N));
- 3. $\mathrm{d}E = T\mathrm{d}S - p\mathrm{d}V + \mu\mathrm{d}N$
  $\Rightarrow T = (\frac{\partial E}{\partial S})_{V,N}, p = -(\frac{\partial E}{\partial V})_{S,N}$,
  $\rightarrow T(S,V,N) \rightarrow S(T,V,N) \rightarrow E(T,V,N)$

Thermodynamics in microcanonical ensemble theory

- General procedure in microcanonical ensemble theory:
- 1. $\Omega(N, E, V)$ (Ω as function of (N, E, V));
- 2. $S(N, E, V) = k \ln \Omega(N, E, V)$ (S as function of (N, E, V)),
  $\Rightarrow E(S, V, N)$ (E as function of (S, V, N));
- 3. $\mathrm{d}E = T\mathrm{d}S - p\mathrm{d}V + \mu \mathrm{d}N$
  $\Rightarrow T = (\frac{\partial E}{\partial S})_{V,N}, p = -(\frac{\partial E}{\partial V})_{S,N},$
  $\rightarrow T(S, V, N) \rightarrow S(T, V, N) \rightarrow E(T, V, N)$
  $p(S, V, N) \rightarrow p(T, V, N)$.

Application: monatomic ideal gas.

Application: monatomic ideal gas.

- Hamiltonian: $H = \sum_{i=1}^{3N} \frac{p_i^2}{2m}$.

Application: monatomic ideal gas.

- Hamiltonian: $H = \sum_{i=1}^{3N} \frac{p_i^2}{2m}$.
- $\Omega(N, E, V) = \frac{1}{N! h^{3N}} \int\limits_{(E, E+\Delta E)} \mathrm{d}q_1 \ldots \mathrm{d}q_{3N} \mathrm{d}p_1 \ldots \mathrm{d}p_{3N}$

Application: monatomic ideal gas.

- Hamiltonian: $H = \sum_{i=1}^{3N} \frac{p_i^2}{2m}$.
- $\Omega(N, E, V) = \frac{1}{N! h^{3N}} \int\limits_{(E, E+\Delta E)} \mathrm{d}q_1 ... \mathrm{d}q_{3N} \mathrm{d}p_1 ... \mathrm{d}p_{3N}$

$$= \frac{1}{N! h^{3N}} \left(\int\limits_{H \leq E+\Delta E} \mathrm{d}\Omega - \int\limits_{H \leq E} \mathrm{d}\Omega \right)$$

Application: monatomic ideal gas.

- Hamiltonian: $H = \sum_{i=1}^{3N} \frac{p_i^2}{2m}$.
- $\Omega(N, E, V) = \frac{1}{N!h^{3N}} \int\limits_{(E,E+\Delta E)} \mathrm{d}q_1 \ldots \mathrm{d}q_{3N} \mathrm{d}p_1 \ldots \mathrm{d}p_{3N}$

$$= \frac{1}{N!h^{3N}} \left(\int\limits_{H \leq E+\Delta E} \mathrm{d}\Omega - \int\limits_{H \leq E} \mathrm{d}\Omega \right)$$

Provable:

$$\int\limits_{H \leq E} \mathrm{d}\Omega = V^N \int\limits_{H \leq E} \mathrm{d}p_1 \ldots \mathrm{d}p_{3N} = V^N \cdot \frac{(2\pi m E)^{\frac{3}{2}N}}{(\frac{3}{2}N)!};$$

Application: monatomic ideal gas.

- Hamiltonian: $H = \sum_{i=1}^{3N} \frac{p_i^2}{2m}$.
- $\Omega(N, E, V) = \frac{1}{N!h^{3N}} \int\limits_{(E,E+\Delta E)} \mathrm{d}q_1 \ldots \mathrm{d}q_{3N} \mathrm{d}p_1 \ldots \mathrm{d}p_{3N}$

  $= \frac{1}{N!h^{3N}} \left(\int\limits_{H \leq E+\Delta E} \mathrm{d}\Omega - \int\limits_{H \leq E} \mathrm{d}\Omega \right)$

  Provable:

  $\int\limits_{H \leq E} \mathrm{d}\Omega = V^N \int\limits_{H \leq E} \mathrm{d}p_1 \ldots \mathrm{d}p_{3N} = V^N \cdot \frac{(2\pi m E)^{\frac{3}{2}N}}{(\frac{3}{2}N)!}$;
- $\Omega(N, E, V) = (\frac{V}{h^3})^N \cdot \frac{(2\pi m)^{\frac{3}{2}N}}{N!(\frac{3}{2}N)!} \left[(E + \Delta E)^{\frac{3}{2}N} - E^{\frac{3}{2}N} \right]$

Application: monatomic ideal gas.

- Hamiltonian: $H = \sum_{i=1}^{3N} \frac{p_i^2}{2m}$.
- $\Omega(N, E, V) = \frac{1}{N! h^{3N}} \int\limits_{(E, E+\Delta E)} \mathrm{d}q_1 \ldots \mathrm{d}q_{3N} \mathrm{d}p_1 \ldots \mathrm{d}p_{3N}$

  $= \frac{1}{N! h^{3N}} \left(\int\limits_{H \le E + \Delta E} \mathrm{d}\Omega - \int\limits_{H \le E} \mathrm{d}\Omega \right)$

  Provable:

  $\int\limits_{H \le E} \mathrm{d}\Omega = V^N \int\limits_{H \le E} \mathrm{d}p_1 \ldots \mathrm{d}p_{3N} = V^N \cdot \frac{(2\pi m E)^{\frac{3}{2}N}}{(\frac{3}{2}N)!}$;
- $\Omega(N, E, V) = (\frac{V}{h^3})^N \cdot \frac{(2\pi m)^{\frac{3}{2}N}}{N! (\frac{3}{2}N)!} \left[(E + \Delta E)^{\frac{3}{2}N} - E^{\frac{3}{2}N} \right]$

  $\simeq \frac{3}{2} N \cdot (\frac{V}{h^3})^N \cdot \frac{(2\pi m E)^{\frac{3}{2}N}}{N! (\frac{3}{2}N)!} \frac{\Delta E}{E}$.

Application: monatomic ideal gas. Prove...

- Prove: $\sigma(E) \equiv \int\limits_{H\leq E} \mathrm{d}p_1 ... \mathrm{d}p_{3N} = \frac{(2\pi m E)^{\frac{3}{2}N}}{(\frac{3}{2}N)!}$.

Application: monatomic ideal gas. Prove...

- Prove: $\sigma(E) \equiv \int\limits_{H \leq E} \mathrm{d}p_1 ... \mathrm{d}p_{3N} = \frac{(2\pi m E)^{\frac{3}{2}N}}{(\frac{3}{2}N)!}$.
- First: $p_i = \sqrt{2mE} x_i \Rightarrow \sigma(E) = (2mE)^{\frac{3}{2}N} \int\limits_{\sum x_i^2 \leq 1} \mathrm{d}x_1 ... \mathrm{d}x_{3N} \equiv K(2mE)^{\frac{3}{2}N}$...(a)

Application: monatomic ideal gas. Prove...

- Prove: $\sigma(E) \equiv \int\limits_{H \leq E} \mathrm{d}p_1 ... \mathrm{d}p_{3N} = \frac{(2\pi m E)^{\frac{3}{2}N}}{(\frac{3}{2}N)!}$.
- First: $p_i = \sqrt{2mE} x_i \Rightarrow \sigma(E) = (2mE)^{\frac{3}{2}N} \int\limits_{\sum x_i^2 \leq 1} \mathrm{d}x_1 ... \mathrm{d}x_{3N} \equiv K(2mE)^{\frac{3}{2}N}$...(a)
- Second, calculate $A \equiv \int_{-\infty}^{+\infty} e^{-\beta H} \mathrm{d}p_1 ... \mathrm{d}p_{3N}$.

Application: monatomic ideal gas. Prove...

- Prove: $\sigma(E) \equiv \int\limits_{H\leq E} \mathrm{d}p_1 ... \mathrm{d}p_{3N} = \frac{(2\pi mE)^{\frac{3}{2}N}}{(\frac{3}{2}N)!}$.
- First: $p_i = \sqrt{2mE}x_i \Rightarrow \sigma(E) = (2mE)^{\frac{3}{2}N} \int\limits_{\sum x_i^2 \leq 1} \mathrm{d}x_1 ... \mathrm{d}x_{3N} \equiv K(2mE)^{\frac{3}{2}N}$...(a)
- Second, calculate $A \equiv \int_{-\infty}^{+\infty} e^{-\beta H} \mathrm{d}p_1 ... \mathrm{d}p_{3N}$.
- Method 1. $A = \int_{-\infty}^{+\infty} e^{-\beta \sum \frac{p_i^2}{2m}} \mathrm{d}p_1 ... \mathrm{d}p_{3N}$

Application: monatomic ideal gas. Prove...

- Prove: $\sigma(E) \equiv \int\limits_{H\leq E} \mathrm{d}p_1 ... \mathrm{d}p_{3N} = \frac{(2\pi mE)^{\frac{3}{2}N}}{(\frac{3}{2}N)!}$.
- First: $p_i = \sqrt{2mE}x_i \Rightarrow \sigma(E) =$ $(2mE)^{\frac{3}{2}N} \int\limits_{\sum x_i^2 \leq 1} \mathrm{d}x_1 ... \mathrm{d}x_{3N} \equiv K(2mE)^{\frac{3}{2}N}$...(a)
- Second, calculate $A \equiv \int_{-\infty}^{+\infty} e^{-\beta H} \mathrm{d}p_1 ... \mathrm{d}p_{3N}$.
- Method 1. $A = \int_{-\infty}^{+\infty} e^{-\beta \sum \frac{p_i^2}{2m}} \mathrm{d}p_1 ... \mathrm{d}p_{3N}$ $= \prod_{i=1}^{3N} \int_{-\infty}^{+\infty} e^{-\beta \frac{p_i^2}{2m}} \mathrm{d}p_i$

Application: monatomic ideal gas. Prove...

- Prove: $\sigma(E) \equiv \int\limits_{H\leq E} \mathrm{d}p_1 ... \mathrm{d}p_{3N} = \frac{(2\pi mE)^{\frac{3}{2}N}}{(\frac{3}{2}N)!}$.
- First: $p_i = \sqrt{2mE}x_i \Rightarrow \sigma(E) = (2mE)^{\frac{3}{2}N} \int\limits_{\sum x_i^2 \leq 1} \mathrm{d}x_1 ... \mathrm{d}x_{3N} \equiv K(2mE)^{\frac{3}{2}N}$...(a)
- Second, calculate $A \equiv \int_{-\infty}^{+\infty} e^{-\beta H} \mathrm{d}p_1 ... \mathrm{d}p_{3N}$.
- Method 1. $A = \int_{-\infty}^{+\infty} e^{-\beta \sum \frac{p_i^2}{2m}} \mathrm{d}p_1 ... \mathrm{d}p_{3N}$ $= \prod_{i=1}^{3N} \int_{-\infty}^{+\infty} e^{-\beta \frac{p_i^2}{2m}} \mathrm{d}p_i = \prod_{i=1}^{3N} (\frac{2m}{\beta})^{\frac{1}{2}} \int_{-\infty}^{+\infty} e^{-\beta \frac{p_i^2}{2m}} \mathrm{d}(\frac{\beta}{2m})^{\frac{1}{2}} p_i$

Application: monatomic ideal gas. Prove...

- Prove: $\sigma(E) \equiv \int\limits_{H\le E} \mathrm{d}p_1 ... \mathrm{d}p_{3N} = \frac{(2\pi mE)^{\frac{3}{2}N}}{(\frac{3}{2}N)!}$.
- First: $p_i = \sqrt{2mE}x_i \Rightarrow \sigma(E) = (2mE)^{\frac{3}{2}N} \int\limits_{\sum x_i^2 \le 1} \mathrm{d}x_1 ... \mathrm{d}x_{3N} \equiv K(2mE)^{\frac{3}{2}N}$...(a)
- Second, calculate $A \equiv \int_{-\infty}^{+\infty} e^{-\beta H} \mathrm{d}p_1 ... \mathrm{d}p_{3N}$.
- Method 1. $A = \int_{-\infty}^{+\infty} e^{-\beta \sum \frac{p_i^2}{2m}} \mathrm{d}p_1 ... \mathrm{d}p_{3N}$ $= \prod\limits_{i=1}^{3N} \int_{-\infty}^{+\infty} e^{-\beta \frac{p_i^2}{2m}} \mathrm{d}p_i = \prod\limits_{i=1}^{3N} (\frac{2m}{\beta})^{\frac{1}{2}} \int_{-\infty}^{+\infty} e^{-\beta \frac{p_i^2}{2m}} \mathrm{d}(\frac{\beta}{2m})^{\frac{1}{2}} p_i$ $= (\frac{2\pi m}{\beta})^{\frac{3}{2}N}$...(b)

Application: monatomic ideal gas. $\boxed{A = (\frac{2\pi m}{\beta})^{\frac{3}{2}N} \ldots \text{(b)}}$,

$$\boxed{\sigma(E) \equiv \int_{H \leq E} \mathrm{d}p_1 \ldots \mathrm{d}p_{3N} = K(2mE)^{\frac{3}{2}N} \ldots \text{(a)}}$$

- Method 2. $A \equiv \int_{-\infty}^{+\infty} e^{-\beta E} \mathrm{d}p_1 \ldots \mathrm{d}p_{3N}$

Application: monatomic ideal gas. $\boxed{A = (\frac{2\pi m}{\beta})^{\frac{3}{2}N} \text{...(b)}}$,

$$\boxed{\sigma(E) \equiv \int_{H \leq E} \mathrm{d}p_1 \dots \mathrm{d}p_{3N} = K(2mE)^{\frac{3}{2}N} \text{...(a)}}$$

- Method 2. $A \equiv \int_{-\infty}^{+\infty} e^{-\beta E} \mathrm{d}p_1 \dots \mathrm{d}p_{3N} = \int e^{-\beta E} \mathrm{d}\sigma(E)$

Application: monatomic ideal gas. $\boxed{A = (\frac{2\pi m}{\beta})^{\frac{3}{2}N} \text{...(b)}}$,

$\boxed{\sigma(E) \equiv \int_{H\leq E} \mathrm{d}p_1 \ldots \mathrm{d}p_{3N} = K(2mE)^{\frac{3}{2}N} \text{...(a)}}$

- Method 2. $A \equiv \int_{-\infty}^{+\infty} e^{-\beta E} \mathrm{d}p_1 \ldots \mathrm{d}p_{3N} = \int e^{-\beta E} \mathrm{d}\sigma(E)$ $= \int_0^{+\infty} e^{-\beta E} \frac{\mathrm{d}\sigma(E)}{\mathrm{d}E} \mathrm{d}E$

Application: monatomic ideal gas. $\boxed{A = (\frac{2\pi m}{\beta})^{\frac{3}{2}N} \ldots\text{(b)}}$,

$\boxed{\sigma(E) \equiv \int_{H\leq E} \mathrm{d}p_1 \ldots \mathrm{d}p_{3N} = K(2mE)^{\frac{3}{2}N} \ldots\text{(a)}}$

- Method 2. $A \equiv \int_{-\infty}^{+\infty} e^{-\beta E} \mathrm{d}p_1 \ldots \mathrm{d}p_{3N} = \int e^{-\beta E} \mathrm{d}\sigma(E)$
  $= \int_0^{+\infty} e^{-\beta E} \frac{\mathrm{d}\sigma(E)}{\mathrm{d}E} \mathrm{d}E$
  $= K \cdot (2m)^{\frac{3}{2}N} \cdot \frac{3}{2}N \cdot \int_0^{\infty} e^{-\beta E} E^{\frac{3}{2}N-1} \mathrm{d}E$

Application: monatomic ideal gas. $\boxed{A = (\frac{2\pi m}{\beta})^{\frac{3}{2}N} \text{...(b)}}$,

$\boxed{\sigma(E) \equiv \int_{H \leq E} \mathrm{d}p_1 \ldots \mathrm{d}p_{3N} = K(2mE)^{\frac{3}{2}N} \text{...(a)}}$

- Method 2. $A \equiv \int_{-\infty}^{+\infty} e^{-\beta E} \mathrm{d}p_1 \ldots \mathrm{d}p_{3N} = \int e^{-\beta E} \mathrm{d}\sigma(E)$
  $= \int_0^{+\infty} e^{-\beta E} \frac{\mathrm{d}\sigma(E)}{\mathrm{d}E} \mathrm{d}E$
  $= K \cdot (2m)^{\frac{3}{2}N} \cdot \frac{3}{2}N \cdot \int_0^{\infty} e^{-\beta E} E^{\frac{3}{2}N-1} \mathrm{d}E$
  $= K \cdot (2m)^{\frac{3}{2}N} \cdot \frac{3}{2}N \cdot \frac{1}{\beta} \left(-\int_0^{\infty} E^{\frac{3}{2}N-1} \mathrm{d}e^{-\beta E} \right)$

Application: monatomic ideal gas. $\boxed{A = (\frac{2\pi m}{\beta})^{\frac{3}{2}N} \text{...(b)}}$,

$\boxed{\sigma(E) \equiv \int_{H \leq E} \mathrm{d}p_1 \ldots \mathrm{d}p_{3N} = K(2mE)^{\frac{3}{2}N} \text{...(a)}}$

- Method 2. $A \equiv \int_{-\infty}^{+\infty} e^{-\beta E} \mathrm{d}p_1 \ldots \mathrm{d}p_{3N} = \int e^{-\beta E} \mathrm{d}\sigma(E)$
$= \int_0^{+\infty} e^{-\beta E} \frac{\mathrm{d}\sigma(E)}{\mathrm{d}E} \mathrm{d}E$
$= K \cdot (2m)^{\frac{3}{2}N} \cdot \frac{3}{2}N \cdot \int_0^{\infty} e^{-\beta E} E^{\frac{3}{2}N-1} \mathrm{d}E$
$= K \cdot (2m)^{\frac{3}{2}N} \cdot \frac{3}{2}N \cdot \frac{1}{\beta} \left(-\int_0^{\infty} E^{\frac{3}{2}N-1} \mathrm{d}e^{-\beta E} \right)$
$= K \cdot (2m)^{\frac{3}{2}N} \cdot \frac{3}{2}N \cdot (\frac{3}{2}N - 1) \cdot \frac{1}{\beta} \int_0^{\infty} e^{-\beta E} E^{\frac{3}{2}N-2} \mathrm{d}E$

Application: monatomic ideal gas. $\boxed{A = (\frac{2\pi m}{\beta})^{\frac{3}{2}N} \text{...(b)}}$,

$$\boxed{\sigma(E) \equiv \int_{H\le E} \mathrm{d}p_1 \ldots \mathrm{d}p_{3N} = K(2mE)^{\frac{3}{2}N} \text{...(a)}}$$

- Method 2. $A \equiv \int_{-\infty}^{+\infty} e^{-\beta E} \mathrm{d}p_1 \ldots \mathrm{d}p_{3N} = \int e^{-\beta E} \mathrm{d}\sigma(E)$
  $= \int_0^{+\infty} e^{-\beta E} \frac{\mathrm{d}\sigma(E)}{\mathrm{d}E} \mathrm{d}E$
  $= K \cdot (2m)^{\frac{3}{2}N} \cdot \frac{3}{2}N \cdot \int_0^{\infty} e^{-\beta E} E^{\frac{3}{2}N-1} \mathrm{d}E$
  $= K \cdot (2m)^{\frac{3}{2}N} \cdot \frac{3}{2}N \cdot \frac{1}{\beta} \left(-\int_0^{\infty} E^{\frac{3}{2}N-1} \mathrm{d}e^{-\beta E} \right)$
  $= K \cdot (2m)^{\frac{3}{2}N} \cdot \frac{3}{2}N \cdot (\frac{3}{2}N - 1) \cdot \frac{1}{\beta} \int_0^{\infty} e^{-\beta E} E^{\frac{3}{2}N-2} \mathrm{d}E \ldots$

Application: monatomic ideal gas. $\boxed{A = (\frac{2\pi m}{\beta})^{\frac{3}{2}N}\text{...(b)}}$,

$$\boxed{\sigma(E) \equiv \int_{H\leq E} \mathrm{d}p_1 \ldots \mathrm{d}p_{3N} = K(2mE)^{\frac{3}{2}N}\text{...(a)}}$$

- Method 2. $A \equiv \int_{-\infty}^{+\infty} e^{-\beta E} \mathrm{d}p_1 \ldots \mathrm{d}p_{3N} = \int e^{-\beta E} \mathrm{d}\sigma(E)$
$= \int_0^{+\infty} e^{-\beta E} \frac{\mathrm{d}\sigma(E)}{\mathrm{d}E} \mathrm{d}E$
$= K \cdot (2m)^{\frac{3}{2}N} \cdot \frac{3}{2}N \cdot \int_0^{\infty} e^{-\beta E} E^{\frac{3}{2}N-1} \mathrm{d}E$
$= K \cdot (2m)^{\frac{3}{2}N} \cdot \frac{3}{2}N \cdot \frac{1}{\beta} \left(-\int_0^{\infty} E^{\frac{3}{2}N-1} \mathrm{d}e^{-\beta E} \right)$
$= K \cdot (2m)^{\frac{3}{2}N} \cdot \frac{3}{2}N \cdot (\frac{3}{2}N - 1) \cdot \frac{1}{\beta} \int_0^{\infty} e^{-\beta E} E^{\frac{3}{2}N-2} \mathrm{d}E \ldots$
$= K \cdot (\frac{2m}{\beta})^{\frac{3}{2}N} (\frac{3}{2}N)!$...(c)

Application: monatomic ideal gas. $\boxed{A = (\frac{2\pi m}{\beta})^{\frac{3}{2}N} ...\text{(b)}}$,

$$\boxed{\sigma(E) \equiv \int_{H \le E} \mathrm{d}p_1 ... \mathrm{d}p_{3N} = K(2mE)^{\frac{3}{2}N} ...\text{(a)}}$$

- Method 2. $A \equiv \int_{-\infty}^{+\infty} e^{-\beta E} \mathrm{d}p_1 ... \mathrm{d}p_{3N} = \int e^{-\beta E} \mathrm{d}\sigma(E)$
$= \int_0^{+\infty} e^{-\beta E} \frac{\mathrm{d}\sigma(E)}{\mathrm{d}E} \mathrm{d}E$
$= K \cdot (2m)^{\frac{3}{2}N} \cdot \frac{3}{2}N \cdot \int_0^{\infty} e^{-\beta E} E^{\frac{3}{2}N-1} \mathrm{d}E$
$= K \cdot (2m)^{\frac{3}{2}N} \cdot \frac{3}{2}N \cdot \frac{1}{\beta} \left(-\int_0^{\infty} E^{\frac{3}{2}N-1} \mathrm{d}e^{-\beta E} \right)$
$= K \cdot (2m)^{\frac{3}{2}N} \cdot \frac{3}{2}N \cdot (\frac{3}{2}N - 1) \cdot \frac{1}{\beta} \int_0^{\infty} e^{-\beta E} E^{\frac{3}{2}N-2} \mathrm{d}E$ ...
$= K \cdot (\frac{2m}{\beta})^{\frac{3}{2}N} (\frac{3}{2}N)! ...\text{(c)}$
- (b)=(c) $\Rightarrow K = \frac{\pi^{\frac{3}{2}N}}{(\frac{3}{2}N)!}$,

Application: monatomic ideal gas. $\boxed{A = (\frac{2\pi m}{\beta})^{\frac{3}{2}N} \text{...(b)}}$,

$$\boxed{\sigma(E) \equiv \int_{H \le E} \mathrm{d}p_1 \ldots \mathrm{d}p_{3N} = K(2mE)^{\frac{3}{2}N} \text{...(a)}}$$

- Method 2. $A \equiv \int_{-\infty}^{+\infty} e^{-\beta E} \mathrm{d}p_1 \ldots \mathrm{d}p_{3N} = \int e^{-\beta E} \mathrm{d}\sigma(E)$
  $= \int_0^{+\infty} e^{-\beta E} \frac{\mathrm{d}\sigma(E)}{\mathrm{d}E} \mathrm{d}E$
  $= K \cdot (2m)^{\frac{3}{2}N} \cdot \frac{3}{2}N \cdot \int_0^{\infty} e^{-\beta E} E^{\frac{3}{2}N-1} \mathrm{d}E$
  $= K \cdot (2m)^{\frac{3}{2}N} \cdot \frac{3}{2}N \cdot \frac{1}{\beta} \left(-\int_0^{\infty} E^{\frac{3}{2}N-1} \mathrm{d}e^{-\beta E} \right)$
  $= K \cdot (2m)^{\frac{3}{2}N} \cdot \frac{3}{2}N \cdot (\frac{3}{2}N - 1) \cdot \frac{1}{\beta} \int_0^{\infty} e^{-\beta E} E^{\frac{3}{2}N-2} \mathrm{d}E \ldots$
  $= K \cdot (\frac{2m}{\beta})^{\frac{3}{2}N} (\frac{3}{2}N)! \text{...(c)}$
- (b)=(c) $\Rightarrow K = \frac{\pi^{\frac{3}{2}N}}{(\frac{3}{2}N)!}$,
- $\therefore \sigma(E) = \frac{(2\pi m E)^{\frac{3}{2}N}}{(\frac{3}{2}N)!}$. $\square$

Application: monatomic ideal gas.

$$\boxed{\Omega(N,E,V) \simeq \frac{3}{2}N \cdot \left(\frac{V}{h^3}\right)^N \cdot \frac{(2\pi m E)^{\frac{3}{2}N}}{N!(\frac{3}{2}N)!}\frac{\Delta E}{E}.}$$

Application: monatomic ideal gas.

$$\boxed{\Omega(N, E, V) \simeq \frac{3}{2}N \cdot \left(\frac{V}{h^3}\right)^N \cdot \frac{(2\pi m E)^{\frac{3}{2}N}}{N!(\frac{3}{2}N)!}\frac{\Delta E}{E}.}$$

- Entropy: $S = k \ln \Omega$

Application: monatomic ideal gas.

$$\boxed{\Omega(N,E,V) \simeq \frac{3}{2}N \cdot (\frac{V}{h^3})^N \cdot \frac{(2\pi m E)^{\frac{3}{2}N}}{N!(\frac{3}{2}N)!}\frac{\Delta E}{E}.}$$

- Entropy: $S = k\ln\Omega = k\ln[(\frac{V}{h^3})^N \cdot \frac{(2\pi m E)^{\frac{3}{2}N}}{N!(\frac{3}{2}N-1)!}\frac{\Delta E}{E}]$

Application: monatomic ideal gas.

$$\boxed{\Omega(N,E,V) \simeq \frac{3}{2}N \cdot (\frac{V}{h^3})^N \cdot \frac{(2\pi mE)^{\frac{3}{2}N}}{N!(\frac{3}{2}N)!}\frac{\Delta E}{E}.}$$

- Entropy: $S = k\ln\Omega = k\ln[(\frac{V}{h^3})^N \cdot \frac{(2\pi mE)^{\frac{3}{2}N}}{N!(\frac{3}{2}N-1)!}\frac{\Delta E}{E}]$
  $\simeq Nk\ln[(\frac{V}{h^3})(2\pi mE)^{\frac{3}{2}}] - k[\ln N! + \ln(\frac{3}{2}N)!] + k\ln\frac{\Delta E}{E}$

Application: monatomic ideal gas.

$$\boxed{\Omega(N,E,V) \simeq \frac{3}{2}N \cdot \left(\frac{V}{h^3}\right)^N \cdot \frac{(2\pi mE)^{\frac{3}{2}N}}{N!(\frac{3}{2}N)!}\frac{\Delta E}{E}.}$$

- Entropy: $S = k\ln\Omega = k\ln[(\frac{V}{h^3})^N \cdot \frac{(2\pi mE)^{\frac{3}{2}N}}{N!(\frac{3}{2}N-1)!}\frac{\Delta E}{E}]$
  $\simeq Nk\ln[(\frac{V}{h^3})(2\pi mE)^{\frac{3}{2}}] - k[\ln N! + \ln(\frac{3}{2}N)!] + k\ln\frac{\Delta E}{E}$
  $= Nk\ln[(\frac{V}{h^3})(2\pi mE)^{\frac{3}{2}}] - k[N(\ln N - 1) +$
  $\frac{3}{2}N(\ln\frac{3}{2}N - 1)] + k\ln\frac{\Delta E}{E}$

Application: monatomic ideal gas.

$$\boxed{\Omega(N,E,V) \simeq \frac{3}{2}N \cdot \left(\frac{V}{h^3}\right)^N \cdot \frac{(2\pi mE)^{\frac{3}{2}N}}{N!(\frac{3}{2}N)!}\frac{\Delta E}{E}.}$$

- Entropy: $S = k\ln\Omega = k\ln[(\frac{V}{h^3})^N \cdot \frac{(2\pi mE)^{\frac{3}{2}N}}{N!(\frac{3}{2}N-1)!}\frac{\Delta E}{E}]$
  $\simeq Nk\ln[(\frac{V}{h^3})(2\pi mE)^{\frac{3}{2}}] - k[\ln N! + \ln(\frac{3}{2}N)!] + k\ln\frac{\Delta E}{E}$
  $= Nk\ln[(\frac{V}{h^3})(2\pi mE)^{\frac{3}{2}}] - k[N(\ln N - 1) +$
  $\frac{3}{2}N(\ln\frac{3}{2}N - 1)] + k\ln\frac{\Delta E}{E}$
  $= Nk\ln[(\frac{V}{h^3})(2\pi mE)^{\frac{3}{2}}] - Nk\ln N + Nk -$
  $\frac{3}{2}Nk\ln(\frac{3}{2}N) + \frac{3}{2}Nk + k\ln\frac{\Delta E}{E}$

Application: monatomic ideal gas.

$$\boxed{\Omega(N,E,V) \simeq \frac{3}{2}N \cdot (\frac{V}{h^3})^N \cdot \frac{(2\pi mE)^{\frac{3}{2}N}}{N!(\frac{3}{2}N)!}\frac{\Delta E}{E}.}$$

- Entropy: $S = k\ln\Omega = k\ln[(\frac{V}{h^3})^N \cdot \frac{(2\pi mE)^{\frac{3}{2}N}}{N!(\frac{3}{2}N-1)!}\frac{\Delta E}{E}]$

  $\simeq Nk\ln[(\frac{V}{h^3})(2\pi mE)^{\frac{3}{2}}] - k[\ln N! + \ln(\frac{3}{2}N)!] + k\ln\frac{\Delta E}{E}$

  $= Nk\ln[(\frac{V}{h^3})(2\pi mE)^{\frac{3}{2}}] - k[N(\ln N - 1) +$
  $\frac{3}{2}N(\ln\frac{3}{2}N - 1)] + k\ln\frac{\Delta E}{E}$

  $= Nk\ln[(\frac{V}{h^3})(2\pi mE)^{\frac{3}{2}}] - Nk\ln N + Nk -$
  $\frac{3}{2}Nk\ln(\frac{3}{2}N) + \frac{3}{2}Nk + k\ln\frac{\Delta E}{E}$

  $= Nk\ln[(\frac{V}{h^3N})(\frac{4\pi mE}{3N})^{\frac{3}{2}}] + \frac{5}{2}Nk + k\ln\frac{\Delta E}{E}$

Application: monatomic ideal gas.

$$\boxed{\Omega(N,E,V) \simeq \frac{3}{2}N \cdot \left(\frac{V}{h^3}\right)^N \cdot \frac{(2\pi mE)^{\frac{3}{2}N}}{N!(\frac{3}{2}N)!}\frac{\Delta E}{E}.}$$

- Entropy: $S = k\ln\Omega = k\ln[(\frac{V}{h^3})^N \cdot \frac{(2\pi mE)^{\frac{3}{2}N}}{N!(\frac{3}{2}N-1)!}\frac{\Delta E}{E}]$
  $\simeq Nk\ln[(\frac{V}{h^3})(2\pi mE)^{\frac{3}{2}}] - k[\ln N! + \ln(\frac{3}{2}N)!] + k\ln\frac{\Delta E}{E}$
  $= Nk\ln[(\frac{V}{h^3})(2\pi mE)^{\frac{3}{2}}] - k[N(\ln N - 1) + \frac{3}{2}N(\ln\frac{3}{2}N - 1)] + k\ln\frac{\Delta E}{E}$
  $= Nk\ln[(\frac{V}{h^3})(2\pi mE)^{\frac{3}{2}}] - Nk\ln N + Nk - \frac{3}{2}Nk\ln(\frac{3}{2}N) + \frac{3}{2}Nk + k\ln\frac{\Delta E}{E}$
  $= Nk\ln[(\frac{V}{h^3N})(\frac{4\pi mE}{3N})^{\frac{3}{2}}] + \frac{5}{2}Nk + k\ln\frac{\Delta E}{E}$
  $\simeq Nk\ln[(\frac{V}{h^3N})(\frac{4\pi mE}{3N})^{\frac{3}{2}}] + \frac{5}{2}Nk.$

Application: monatomic ideal gas.

$$\boxed{S = Nk\ln[(\frac{V}{h^3N})(\frac{4\pi mE}{3N})^{\frac{3}{2}}] + \frac{5}{2}Nk}$$

- $\Rightarrow E(N,S,V) = \dfrac{3h^2N^{\frac{5}{3}}}{4\pi mV^{\frac{2}{3}}}e^{(\frac{2S}{3Nk}-\frac{5}{3})}$.

Application: monatomic ideal gas.

$$\boxed{S = Nk\ln[(\frac{V}{h^3N})(\frac{4\pi mE}{3N})^{\frac{3}{2}}] + \frac{5}{2}Nk}$$

- $\Rightarrow E(N,S,V) = \frac{3h^2N^{\frac{5}{3}}}{4\pi mV^{\frac{2}{3}}}e^{(\frac{2S}{3Nk}-\frac{5}{3})}$.
  $T = (\frac{\partial E}{\partial S})_{N,V} = \frac{2}{3}\frac{E}{Nk}$

Application: monatomic ideal gas.

$$\boxed{S = Nk\ln[(\frac{V}{h^3N})(\frac{4\pi mE}{3N})^{\frac{3}{2}}] + \frac{5}{2}Nk}$$

- $\Rightarrow E(N,S,V) = \frac{3h^2N^{\frac{5}{3}}}{4\pi mV^{\frac{2}{3}}}e^{(\frac{2S}{3Nk}-\frac{5}{3})}$.
  $T = (\frac{\partial E}{\partial S})_{N,V} = \frac{2}{3}\frac{E}{Nk} \Rightarrow E = \frac{3}{2}NkT$

Application: monatomic ideal gas.

$$\boxed{S = Nk\ln[(\frac{V}{h^3N})(\frac{4\pi mE}{3N})^{\frac{3}{2}}] + \frac{5}{2}Nk}$$

- $\Rightarrow E(N,S,V) = \frac{3h^2N^{\frac{5}{3}}}{4\pi mV^{\frac{2}{3}}}e^{(\frac{2S}{3Nk}-\frac{5}{3})}$.
  $T = (\frac{\partial E}{\partial S})_{N,V} = \frac{2}{3}\frac{E}{Nk} \Rightarrow E = \frac{3}{2}NkT$
  $p = -(\frac{\partial E}{\partial V})_{N,S} = \frac{2}{3}\frac{E}{V}$

Application: monatomic ideal gas.

$$\boxed{S = Nk\ln[(\frac{V}{h^3N})(\frac{4\pi mE}{3N})^{\frac{3}{2}}] + \frac{5}{2}Nk}$$

- $\Rightarrow E(N,S,V) = \frac{3h^2N^{\frac{5}{3}}}{4\pi mV^{\frac{2}{3}}}e^{(\frac{2S}{3Nk}-\frac{5}{3})}$.
  $T = (\frac{\partial E}{\partial S})_{N,V} = \frac{2}{3}\frac{E}{Nk} \Rightarrow E = \frac{3}{2}NkT$
  $p = -(\frac{\partial E}{\partial V})_{N,S} = \frac{2}{3}\frac{E}{V}$
- $\Rightarrow pV = NkT$,

Application: monatomic ideal gas.

$$\boxed{S = Nk\ln[(\frac{V}{h^3N})(\frac{4\pi mE}{3N})^{\frac{3}{2}}] + \frac{5}{2}Nk}$$

- $\Rightarrow E(N,S,V) = \frac{3h^2N^{\frac{5}{3}}}{4\pi mV^{\frac{2}{3}}}e^{(\frac{2S}{3Nk}-\frac{5}{3})}$.
  $T = (\frac{\partial E}{\partial S})_{N,V} = \frac{2}{3}\frac{E}{Nk} \Rightarrow E = \frac{3}{2}NkT$
  $p = -(\frac{\partial E}{\partial V})_{N,S} = \frac{2}{3}\frac{E}{V}$
- $\Rightarrow pV = NkT$,
  $S = Nk\ln[\frac{V}{N}(\frac{2\pi mkT}{h^2})^{\frac{3}{2}}] + \frac{5}{2}Nk$. Same as eq. (7.6.2).

Table of contents

9.4 Canonical ensemble

9.4 Canonical ensemble

- Object: system contacting with a thermal reservoir.

9.4 Canonical ensemble

- Object: system contacting with a thermal reservoir. Exists energy exchanges. Keep temperature T.

9.4 Canonical ensemble

- Object: system contacting with a thermal reservoir. Exists energy exchanges. Keep temperature T.
- System has fixed (N, V, T).

9.4 Canonical ensemble

- Object: system contacting with a thermal reservoir. Exists energy exchanges. Keep temperature T.
- System has fixed (N, V, T).
- Consider the combined system (labelled '0') contains both the 'system' and the reservoir (labelled 'r'), which is an isolated system.

9.4 Canonical ensemble

- Object: system contacting with a thermal reservoir. Exists energy exchanges. Keep temperature T.
- System has fixed (N, V, T).
- Consider the combined system (labelled '0') contains both the 'system' and the reservoir (labelled 'r'), which is an isolated system. Back to the microcanonical ensemble.

9.4 Canonical ensemble

- Object: system contacting with a thermal reservoir. Exists energy exchanges. Keep temperature T.
- System has fixed (N, V, T).
- Consider the combined system (labelled '0') contains both the 'system' and the reservoir (labelled 'r'), which is an isolated system. Back to the microcanonical ensemble.
- Set the energy of system E, of reservoir E_r, and of the whole system $E^{(0)}$.

9.4 Canonical ensemble

- Object: system contacting with a thermal reservoir. Exists energy exchanges. Keep temperature T.
- System has fixed (N, V, T).
- Consider the combined system (labelled '0') contains both the 'system' and the reservoir (labelled 'r'), which is an isolated system. Back to the microcanonical ensemble.
- Set the energy of system E, of reservoir E_r, and of the whole system $E^{(0)}$.
- $E + E_r = E^{(0)}$.

9.4 Canonical ensemble

- Object: system contacting with a thermal reservoir. Exists energy exchanges. Keep temperature T.
- System has fixed (N, V, T).
- Consider the combined system (labelled '0') contains both the 'system' and the reservoir (labelled 'r'), which is an isolated system. Back to the microcanonical ensemble.
- Set the energy of system E, of reservoir E_r, and of the whole system $E^{(0)}$.
- $E + E_r = E^{(0)}$.
- Consider the probability for the system at state s.

Canonical ensemble

- As state s, there exists energy E_s. Reservoir can be any state with energy $E_r = E^{(0)} - E_s$. Total number of these states: $\Omega_r(E^{(0)} - E_s)$. For the combined system being isolated system, obeys microcanonical ensemble's the principle of equal a priori probabilities.

Canonical ensemble

- As state s, there exists energy E_s. Reservoir can be any state with energy $E_r = E^{(0)} - E_s$. Total number of these states: $\Omega_r(E^{(0)} - E_s)$. For the combined system being isolated system, obeys microcanonical ensemble's the principle of equal a priori probabilities. I.e., $\rho_s \propto \Omega_r(E^{(0)} - E_s)$.

Canonical ensemble

- As state s, there exists energy E_s. Reservoir can be any state with energy $E_r = E^{(0)} - E_s$. Total number of these states: $\Omega_r(E^{(0)} - E_s)$. For the combined system being isolated system, obeys microcanonical ensemble's the principle of equal a priori probabilities. I.e., $\rho_s \propto \Omega_r(E^{(0)} - E_s)$.
- Use $\ln \Omega$ for convenience.

Canonical ensemble

- As state s, there exists energy E_s. Reservoir can be any state with energy $E_r = E^{(0)} - E_s$. Total number of these states: $\Omega_r(E^{(0)} - E_s)$. For the combined system being isolated system, obeys microcanonical ensemble's the principle of equal a priori probabilities. I.e., $\rho_s \propto \Omega_r(E^{(0)} - E_s)$.
- Use $\ln \Omega$ for convenience.
- As $E_s \ll E^{(0)}$,
  $\ln \Omega_r(E^{(0)} - E_s) \simeq \ln \Omega_r(E^{(0)}) + (\frac{\partial \ln \Omega_r}{\partial E_r})_{E_r = E^{(0)}} \cdot (-E_s)$

Canonical ensemble

- As state s, there exists energy E_s. Reservoir can be any state with energy $E_r = E^{(0)} - E_s$. Total number of these states: $\Omega_r(E^{(0)} - E_s)$. For the combined system being isolated system, obeys microcanonical ensemble's the principle of equal a priori probabilities. I.e., $\rho_s \propto \Omega_r(E^{(0)} - E_s)$.
- Use $\ln \Omega$ for convenience.
- As $E_s \ll E^{(0)}$,
  $\ln \Omega_r(E^{(0)} - E_s) \simeq \ln \Omega_r(E^{(0)}) + (\frac{\partial \ln \Omega_r}{\partial E_r})_{E_r = E^{(0)}} \cdot (-E_s)$
  $= \ln \Omega_r(E^{(0)}) - \beta E_s$. Notice (9.3.5).

Canonical ensemble

- As state s, there exists energy E_s. Reservoir can be any state with energy $E_r = E^{(0)} - E_s$. Total number of these states: $\Omega_r(E^{(0)} - E_s)$. For the combined system being isolated system, obeys microcanonical ensemble's the principle of equal a priori probabilities. I.e., $\rho_s \propto \Omega_r(E^{(0)} - E_s)$.
- Use $\ln \Omega$ for convenience.
- As $E_s \ll E^{(0)}$,
  $\ln \Omega_r(E^{(0)} - E_s) \simeq \ln \Omega_r(E^{(0)}) + (\frac{\partial \ln \Omega_r}{\partial E_r})_{E_r = E^{(0)}} \cdot (-E_s)$
  $= \ln \Omega_r(E^{(0)}) - \beta E_s$. Notice (9.3.5).
- $\therefore \rho_s \propto e^{\ln \Omega_r(E^{(0)}) - \beta E_s} \propto e^{-\beta E_s}$,
  where $\ln \Omega_r(E^{(0)}) =$ Const.

Canonical ensemble

- Introduce a normalization factor: $\rho_s = \frac{1}{Z} e^{-\beta E_s}$,

Canonical ensemble

- Introduce a normalization factor: $\rho_s = \frac{1}{Z} e^{-\beta E_s}$, where $Z = \sum_s e^{-\beta E_s}$ is called partition function.

Canonical ensemble

- Introduce a normalization factor: $\rho_s = \frac{1}{Z} e^{-\beta E_s}$, where $Z = \sum\limits_s e^{-\beta E_s}$ is called partition function.
- Considering the degeneracy Ω_l at energy level E_l, then the probability at E_l is:
  $\rho_l = \Omega_l \cdot \frac{1}{Z} e^{-\beta E_l}$,
  the partition function can also be written as
  $Z = \sum\limits_l \Omega_l e^{-\beta E_l}$.

Canonical ensemble

- Introduce a normalization factor: $\rho_s = \frac{1}{Z} e^{-\beta E_s}$, where $Z = \sum_s e^{-\beta E_s}$ is called partition function.
- Considering the degeneracy Ω_l at energy level E_l, then the probability at E_l is:
  $\rho_l = \Omega_l \cdot \frac{1}{Z} e^{-\beta E_l}$,
  the partition function can also be written as
  $Z = \sum_l \Omega_l e^{-\beta E_l}$.
- For continuous (classical) case:
  $\rho(q,p)\mathrm{d}\Omega = \frac{1}{N!h^{Nr}} \frac{e^{-\beta E(q,p)}}{Z} \mathrm{d}\Omega$,
  where $Z = \frac{1}{N!h^{Nr}} \int e^{-\beta E(q,p)} \mathrm{d}\Omega$.

Table of contents

9.5 Thermodynamics in canonical ensemble

9.5 Thermodynamics in canonical ensemble

- Internal energy is the average energy for all possible micro-states:

9.5 Thermodynamics in canonical ensemble

- Internal energy is the average energy for all possible micro-states: $U = \bar{E}$

9.5 Thermodynamics in canonical ensemble

- Internal energy is the average energy for all possible micro-states: $U = \bar{E} = \sum E_s \rho_s$

9.5 Thermodynamics in canonical ensemble

- Internal energy is the average energy for all possible micro-states: $U = \bar{E} = \sum E_s \rho_s = \sum \frac{1}{Z} E_s e^{-\beta E_s}$

9.5 Thermodynamics in canonical ensemble

- Internal energy is the average energy for all possible micro-states: $U = \bar{E} = \sum E_s \rho_s = \sum \frac{1}{Z} E_s e^{-\beta E_s}$
$= \frac{1}{Z}(-\frac{\partial}{\partial \beta}) \sum e^{-\beta E_s}$

9.5 Thermodynamics in canonical ensemble

- Internal energy is the average energy for all possible micro-states: $U = \bar{E} = \sum E_s \rho_s = \sum \frac{1}{Z} E_s e^{-\beta E_s}$ $= \frac{1}{Z}(-\frac{\partial}{\partial \beta}) \sum e^{-\beta E_s} = \frac{1}{Z}(-\frac{\partial}{\partial \beta}) Z$

9.5 Thermodynamics in canonical ensemble

- Internal energy is the average energy for all possible micro-states: $U = \bar{E} = \sum E_s \rho_s = \sum \frac{1}{Z} E_s e^{-\beta E_s}$
$= \frac{1}{Z}(-\frac{\partial}{\partial\beta}) \sum e^{-\beta E_s} = \frac{1}{Z}(-\frac{\partial}{\partial\beta}) Z = -\frac{\partial}{\partial\beta} \ln Z.$

9.5 Thermodynamics in canonical ensemble

- Internal energy is the average energy for all possible micro-states: $U = \bar{E} = \sum E_s \rho_s = \sum \frac{1}{Z} E_s e^{-\beta E_s}$ $= \frac{1}{Z}(-\frac{\partial}{\partial \beta}) \sum e^{-\beta E_s} = \frac{1}{Z}(-\frac{\partial}{\partial \beta}) Z = -\frac{\partial}{\partial \beta} \ln Z$.
- Generalized force is the average of $\frac{\partial E_s}{\partial y}$:

9.5 Thermodynamics in canonical ensemble

- Internal energy is the average energy for all possible micro-states: $U = \bar{E} = \sum E_s \rho_s = \sum \frac{1}{Z} E_s e^{-\beta E_s}$ $= \frac{1}{Z}(-\frac{\partial}{\partial \beta}) \sum e^{-\beta E_s} = \frac{1}{Z}(-\frac{\partial}{\partial \beta}) Z = -\frac{\partial}{\partial \beta} \ln Z$.
- Generalized force is the average of $\frac{\partial E_s}{\partial y}$: $Y = \frac{1}{Z} \sum \frac{\partial E_s}{\partial y} e^{-\beta E_s}$

9.5 Thermodynamics in canonical ensemble

- Internal energy is the average energy for all possible micro-states: $U = \bar{E} = \sum E_s \rho_s = \sum \frac{1}{Z} E_s e^{-\beta E_s}$ $= \frac{1}{Z}(-\frac{\partial}{\partial \beta}) \sum e^{-\beta E_s} = \frac{1}{Z}(-\frac{\partial}{\partial \beta}) Z = -\frac{\partial}{\partial \beta} \ln Z.$
- Generalized force is the average of $\frac{\partial E_s}{\partial y}$: $Y = \frac{1}{Z} \sum \frac{\partial E_s}{\partial y} e^{-\beta E_s} = \frac{1}{Z}(-\frac{1}{\beta}\frac{\partial}{\partial y}) \sum e^{-\beta E_s}$

9.5 Thermodynamics in canonical ensemble

- Internal energy is the average energy for all possible micro-states: $U = \bar{E} = \sum E_s \rho_s = \sum \frac{1}{Z} E_s e^{-\beta E_s}$ $= \frac{1}{Z}(-\frac{\partial}{\partial \beta}) \sum e^{-\beta E_s} = \frac{1}{Z}(-\frac{\partial}{\partial \beta}) Z = -\frac{\partial}{\partial \beta} \ln Z$.
- Generalized force is the average of $\frac{\partial E_s}{\partial y}$: $Y = \frac{1}{Z} \sum \frac{\partial E_s}{\partial y} e^{-\beta E_s} = \frac{1}{Z}(-\frac{1}{\beta}\frac{\partial}{\partial y}) \sum e^{-\beta E_s}$ $= -\frac{1}{\beta}\frac{\partial}{\partial y} \ln Z$.

9.5 Thermodynamics in canonical ensemble

- Internal energy is the average energy for all possible micro-states: $U = \bar{E} = \sum E_s \rho_s = \sum \frac{1}{Z} E_s e^{-\beta E_s}$ $= \frac{1}{Z}(-\frac{\partial}{\partial \beta}) \sum e^{-\beta E_s} = \frac{1}{Z}(-\frac{\partial}{\partial \beta}) Z = -\frac{\partial}{\partial \beta} \ln Z$.
- Generalized force is the average of $\frac{\partial E_s}{\partial y}$:
  $Y = \frac{1}{Z} \sum \frac{\partial E_s}{\partial y} e^{-\beta E_s} = \frac{1}{Z}(-\frac{1}{\beta}\frac{\partial}{\partial y}) \sum e^{-\beta E_s}$
  $= -\frac{1}{\beta}\frac{\partial}{\partial y} \ln Z$.
- Similar to §7.1 and §8.1, the entropy:
  $S = k(\ln Z - \beta \frac{\partial}{\partial \beta} \ln Z)$.

9.5 Thermodynamics in canonical ensemble

- Internal energy is the average energy for all possible micro-states: $U = \bar{E} = \sum E_s \rho_s = \sum \frac{1}{Z} E_s e^{-\beta E_s}$
$= \frac{1}{Z}(-\frac{\partial}{\partial\beta}) \sum e^{-\beta E_s} = \frac{1}{Z}(-\frac{\partial}{\partial\beta}) Z = -\frac{\partial}{\partial\beta} \ln Z.$
- Generalized force is the average of $\frac{\partial E_s}{\partial y}$:
$Y = \frac{1}{Z} \sum \frac{\partial E_s}{\partial y} e^{-\beta E_s} = \frac{1}{Z}(-\frac{1}{\beta}\frac{\partial}{\partial y}) \sum e^{-\beta E_s}$
$= -\frac{1}{\beta}\frac{\partial}{\partial y} \ln Z.$
- Similar to §7.1 and §8.1, the entropy:
$S = k(\ln Z - \beta \frac{\partial}{\partial\beta} \ln Z).$
- Free energy: $F = U - TS =$
$-\frac{\partial}{\partial\beta} \ln Z - kT(\ln Z - \beta \frac{\partial}{\partial\beta} \ln Z) = -kT \ln Z,$

9.5 Thermodynamics in canonical ensemble

- Internal energy is the average energy for all possible micro-states: $U = \bar{E} = \sum E_s \rho_s = \sum \frac{1}{Z} E_s e^{-\beta E_s}$ $= \frac{1}{Z}(-\frac{\partial}{\partial\beta}) \sum e^{-\beta E_s} = \frac{1}{Z}(-\frac{\partial}{\partial\beta}) Z = -\frac{\partial}{\partial\beta} \ln Z$.
- Generalized force is the average of $\frac{\partial E_s}{\partial y}$: $Y = \frac{1}{Z} \sum \frac{\partial E_s}{\partial y} e^{-\beta E_s} = \frac{1}{Z}(-\frac{1}{\beta}\frac{\partial}{\partial y}) \sum e^{-\beta E_s}$ $= -\frac{1}{\beta}\frac{\partial}{\partial y} \ln Z$.
- Similar to §7.1 and §8.1, the entropy: $S = k(\ln Z - \beta \frac{\partial}{\partial\beta} \ln Z)$.
- Free energy: $F = U - TS =$ $-\frac{\partial}{\partial\beta} \ln Z - kT(\ln Z - \beta\frac{\partial}{\partial\beta} \ln Z) = -kT \ln Z$, is characteristic function for (N, V, T).

Fluctuation

Fluctuation

- $\overline{(E-\bar{E})^2}$

Fluctuation

- $\overline{(E-\bar{E})^2} = \sum \rho_s (E_s - \bar{E})^2$

Fluctuation

- $\overline{(E-\bar{E})^2} = \sum \rho_s (E_s - \bar{E})^2$
  $= \sum \rho_s (E_s^2 - 2\bar{E}E_s + \bar{E}^2)$

Fluctuation

- $\overline{(E-\bar{E})^2} = \sum \rho_s (E_s - \bar{E})^2$
  $= \sum \rho_s (E_s^2 - 2\bar{E}E_s + \bar{E}^2)$
  $= \sum E_s^2 \rho_s - 2\bar{E} \sum \rho_s E_s + \bar{E}^2$

Fluctuation

- $\overline{(E-\bar{E})^2} = \sum \rho_s (E_s - \bar{E})^2$
  $= \sum \rho_s (E_s^2 - 2\bar{E}E_s + \bar{E}^2)$
  $= \sum E_s^2 \rho_s - 2\bar{E} \sum \rho_s E_s + \bar{E}^2 = \sum E_s^2 \rho_s - \bar{E}^2$

Fluctuation

- $\overline{(E-\bar{E})^2} = \sum \rho_s (E_s - \bar{E})^2$
  $= \sum \rho_s (E_s^2 - 2\bar{E}E_s + \bar{E}^2)$
  $= \sum E_s^2 \rho_s - 2\bar{E} \sum \rho_s E_s + \bar{E}^2 = \sum E_s^2 \rho_s - \bar{E}^2$
  $= \overline{E^2} - \bar{E}^2;$

Fluctuation

- $\overline{(E-\bar{E})^2} = \sum \rho_s (E_s - \bar{E})^2$
  $= \sum \rho_s (E_s^2 - 2\bar{E}E_s + \bar{E}^2)$
  $= \sum E_s^2 \rho_s - 2\bar{E} \sum \rho_s E_s + \bar{E}^2 = \sum E_s^2 \rho_s - \bar{E}^2$
  $= \overline{E^2} - \bar{E}^2;$
- $\frac{\partial \bar{E}}{\partial \beta}$

Fluctuation

- $\overline{(E-\bar{E})^2} = \sum \rho_s (E_s - \bar{E})^2$
  $= \sum \rho_s (E_s^2 - 2\bar{E}E_s + \bar{E}^2)$
  $= \sum E_s^2 \rho_s - 2\bar{E} \sum \rho_s E_s + \bar{E}^2 = \sum E_s^2 \rho_s - \bar{E}^2$
  $= \overline{E^2} - \bar{E}^2$;
- $\frac{\partial \bar{E}}{\partial \beta} = \frac{\partial \sum E_s \rho_s}{\partial \beta}$

Fluctuation

- $\overline{(E-\bar{E})^2} = \sum \rho_s (E_s - \bar{E})^2$
  $= \sum \rho_s (E_s^2 - 2\bar{E}E_s + \bar{E}^2)$
  $= \sum E_s^2 \rho_s - 2\bar{E}\sum \rho_s E_s + \bar{E}^2 = \sum E_s^2 \rho_s - \bar{E}^2$
  $= \overline{E^2} - \bar{E}^2;$
- $\frac{\partial \bar{E}}{\partial \beta} = \frac{\partial \sum E_s \rho_s}{\partial \beta} = \frac{\partial}{\partial \beta} \frac{\sum E_s e^{-\beta E_s}}{Z}$

Fluctuation

- $\overline{(E-\bar{E})^2} = \sum \rho_s (E_s - \bar{E})^2$
  $= \sum \rho_s (E_s^2 - 2\bar{E}E_s + \bar{E}^2)$
  $= \sum E_s^2 \rho_s - 2\bar{E} \sum \rho_s E_s + \bar{E}^2 = \sum E_s^2 \rho_s - \bar{E}^2$
  $= \overline{E^2} - \bar{E}^2;$
- $\frac{\partial \bar{E}}{\partial \beta} = \frac{\partial \sum E_s \rho_s}{\partial \beta} = \frac{\partial}{\partial \beta} \frac{\sum E_s e^{-\beta E_s}}{Z} = \frac{\partial}{\partial \beta} \frac{\sum E_s e^{-\beta E_s}}{\sum e^{-\beta E_s}}$

Fluctuation

- $\overline{(E-\bar{E})^2} = \sum \rho_s (E_s - \bar{E})^2$
  $= \sum \rho_s (E_s^2 - 2\bar{E}E_s + \bar{E}^2)$
  $= \sum E_s^2 \rho_s - 2\bar{E}\sum \rho_s E_s + \bar{E}^2 = \sum E_s^2 \rho_s - \bar{E}^2$
  $= \overline{E^2} - \bar{E}^2;$
- $\frac{\partial \bar{E}}{\partial \beta} = \frac{\partial \sum E_s \rho_s}{\partial \beta} = \frac{\partial}{\partial \beta}\frac{\sum E_s e^{-\beta E_s}}{Z} = \frac{\partial}{\partial \beta}\frac{\sum E_s e^{-\beta E_s}}{\sum e^{-\beta E_s}}$
  $= -\frac{\sum E_s^2 e^{-\beta E_s}}{\sum e^{-\beta E_s}} + \frac{(\sum E_s e^{-\beta E_s})^2}{(\sum e^{-\beta E_s})^2}$

Fluctuation

- $\overline{(E-\bar{E})^2} = \sum \rho_s (E_s - \bar{E})^2$
$= \sum \rho_s (E_s^2 - 2\bar{E}E_s + \bar{E}^2)$
$= \sum E_s^2 \rho_s - 2\bar{E} \sum \rho_s E_s + \bar{E}^2 = \sum E_s^2 \rho_s - \bar{E}^2$
$= \overline{E^2} - \bar{E}^2;$
- $\frac{\partial \bar{E}}{\partial \beta} = \frac{\partial \sum E_s \rho_s}{\partial \beta} = \frac{\partial}{\partial \beta} \frac{\sum E_s e^{-\beta E_s}}{Z} = \frac{\partial}{\partial \beta} \frac{\sum E_s e^{-\beta E_s}}{\sum e^{-\beta E_s}}$
$= -\frac{\sum E_s^2 e^{-\beta E_s}}{\sum e^{-\beta E_s}} + \frac{(\sum E_s e^{-\beta E_s})^2}{(\sum e^{-\beta E_s})^2} = -(\overline{E^2} - \bar{E}^2);$

Fluctuation

- $\overline{(E-\bar{E})^2} = \sum \rho_s (E_s - \bar{E})^2$
  $= \sum \rho_s (E_s^2 - 2\bar{E}E_s + \bar{E}^2)$
  $= \sum E_s^2 \rho_s - 2\bar{E} \sum \rho_s E_s + \bar{E}^2 = \sum E_s^2 \rho_s - \bar{E}^2$
  $= \overline{E^2} - \bar{E}^2;$
- $\frac{\partial \bar{E}}{\partial \beta} = \frac{\partial \sum E_s \rho_s}{\partial \beta} = \frac{\partial}{\partial \beta} \frac{\sum E_s e^{-\beta E_s}}{Z} = \frac{\partial}{\partial \beta} \frac{\sum E_s e^{-\beta E_s}}{\sum e^{-\beta E_s}}$
  $= -\frac{\sum E_s^2 e^{-\beta E_s}}{\sum e^{-\beta E_s}} + \frac{(\sum E_s e^{-\beta E_s})^2}{(\sum e^{-\beta E_s})^2} = -(\overline{E^2} - \bar{E}^2);$
- $\therefore \overline{(E-\bar{E})^2} = -\frac{\partial \bar{E}}{\partial \beta}$

Fluctuation

- $\overline{(E-\bar{E})^2} = \sum \rho_s (E_s - \bar{E})^2$
$= \sum \rho_s (E_s^2 - 2\bar{E}E_s + \bar{E}^2)$
$= \sum E_s^2 \rho_s - 2\bar{E} \sum \rho_s E_s + \bar{E}^2 = \sum E_s^2 \rho_s - \bar{E}^2$
$= \overline{E^2} - \bar{E}^2;$
- $\frac{\partial \bar{E}}{\partial \beta} = \frac{\partial \sum E_s \rho_s}{\partial \beta} = \frac{\partial}{\partial \beta} \frac{\sum E_s e^{-\beta E_s}}{Z} = \frac{\partial}{\partial \beta} \frac{\sum E_s e^{-\beta E_s}}{\sum e^{-\beta E_s}}$
$= -\frac{\sum E_s^2 e^{-\beta E_s}}{\sum e^{-\beta E_s}} + \frac{(\sum E_s e^{-\beta E_s})^2}{(\sum e^{-\beta E_s})^2} = -(\overline{E^2} - \bar{E}^2);$
- $\therefore \overline{(E-\bar{E})^2} = -\frac{\partial \bar{E}}{\partial \beta} = kT^2 \frac{\partial \bar{E}}{\partial T}$

Fluctuation

- $\overline{(E-\bar{E})^2} = \sum \rho_s (E_s - \bar{E})^2$
$= \sum \rho_s (E_s^2 - 2\bar{E}E_s + \bar{E}^2)$
$= \sum E_s^2 \rho_s - 2\bar{E} \sum \rho_s E_s + \bar{E}^2 = \sum E_s^2 \rho_s - \bar{E}^2$
$= \overline{E^2} - \bar{E}^2;$
- $\frac{\partial \bar{E}}{\partial \beta} = \frac{\partial \sum E_s \rho_s}{\partial \beta} = \frac{\partial}{\partial \beta} \frac{\sum E_s e^{-\beta E_s}}{Z} = \frac{\partial}{\partial \beta} \frac{\sum E_s e^{-\beta E_s}}{\sum e^{-\beta E_s}}$
$= -\frac{\sum E_s^2 e^{-\beta E_s}}{\sum e^{-\beta E_s}} + \frac{(\sum E_s e^{-\beta E_s})^2}{(\sum e^{-\beta E_s})^2} = -(\overline{E^2} - \bar{E}^2);$
- $\therefore \overline{(E-\bar{E})^2} = -\frac{\partial \bar{E}}{\partial \beta} = kT^2 \frac{\partial \bar{E}}{\partial T} = kT^2 \frac{\partial U}{\partial T}$

Fluctuation

- $\overline{(E-\bar{E})^2} = \sum \rho_s (E_s - \bar{E})^2$
  $= \sum \rho_s (E_s^2 - 2\bar{E}E_s + \bar{E}^2)$
  $= \sum E_s^2 \rho_s - 2\bar{E}\sum \rho_s E_s + \bar{E}^2 = \sum E_s^2 \rho_s - \bar{E}^2$
  $= \overline{E^2} - \bar{E}^2;$
- $\frac{\partial \bar{E}}{\partial \beta} = \frac{\partial \sum E_s \rho_s}{\partial \beta} = \frac{\partial}{\partial \beta} \frac{\sum E_s e^{-\beta E_s}}{Z} = \frac{\partial}{\partial \beta} \frac{\sum E_s e^{-\beta E_s}}{\sum e^{-\beta E_s}}$
  $= -\frac{\sum E_s^2 e^{-\beta E_s}}{\sum e^{-\beta E_s}} + \frac{(\sum E_s e^{-\beta E_s})^2}{(\sum e^{-\beta E_s})^2} = -(\overline{E^2} - \bar{E}^2);$
- $\therefore \overline{(E-\bar{E})^2} = -\frac{\partial \bar{E}}{\partial \beta} = kT^2 \frac{\partial \bar{E}}{\partial T} = kT^2 \frac{\partial U}{\partial T} = kT^2 C_V.$

Fluctuation

- $\overline{(E-\bar{E})^2} = \sum \rho_s (E_s - \bar{E})^2$
  $= \sum \rho_s (E_s^2 - 2\bar{E}E_s + \bar{E}^2)$
  $= \sum E_s^2 \rho_s - 2\bar{E} \sum \rho_s E_s + \bar{E}^2 = \sum E_s^2 \rho_s - \bar{E}^2$
  $= \overline{E^2} - \bar{E}^2;$
- $\frac{\partial \bar{E}}{\partial \beta} = \frac{\partial \sum E_s \rho_s}{\partial \beta} = \frac{\partial}{\partial \beta} \frac{\sum E_s e^{-\beta E_s}}{Z} = \frac{\partial}{\partial \beta} \frac{\sum E_s e^{-\beta E_s}}{\sum e^{-\beta E_s}}$
  $= -\frac{\sum E_s^2 e^{-\beta E_s}}{\sum e^{-\beta E_s}} + \frac{(\sum E_s e^{-\beta E_s})^2}{(\sum e^{-\beta E_s})^2} = -(\overline{E^2} - \bar{E}^2);$
- $\therefore \overline{(E-\bar{E})^2} = -\frac{\partial \bar{E}}{\partial \beta} = kT^2 \frac{\partial \bar{E}}{\partial T} = kT^2 \frac{\partial U}{\partial T} = kT^2 C_V.$
- Relative fluctuation: $\frac{\overline{(E-\bar{E})^2}}{\bar{E}^2} = \frac{kT^2 C_V}{\bar{E}^2}$

Fluctuation

- $\overline{(E-\bar{E})^2} = \sum \rho_s (E_s - \bar{E})^2$
  $= \sum \rho_s (E_s^2 - 2\bar{E}E_s + \bar{E}^2)$
  $= \sum E_s^2 \rho_s - 2\bar{E}\sum \rho_s E_s + \bar{E}^2 = \sum E_s^2 \rho_s - \bar{E}^2$
  $= \overline{E^2} - \bar{E}^2;$
- $\frac{\partial \bar{E}}{\partial \beta} = \frac{\partial \sum E_s \rho_s}{\partial \beta} = \frac{\partial}{\partial \beta}\frac{\sum E_s e^{-\beta E_s}}{Z} = \frac{\partial}{\partial \beta}\frac{\sum E_s e^{-\beta E_s}}{\sum e^{-\beta E_s}}$
  $= -\frac{\sum E_s^2 e^{-\beta E_s}}{\sum e^{-\beta E_s}} + \frac{(\sum E_s e^{-\beta E_s})^2}{(\sum e^{-\beta E_s})^2} = -(\overline{E^2} - \bar{E}^2);$
- $\therefore \overline{(E-\bar{E})^2} = -\frac{\partial \bar{E}}{\partial \beta} = kT^2 \frac{\partial \bar{E}}{\partial T} = kT^2 \frac{\partial U}{\partial T} = kT^2 C_V.$
- Relative fluctuation: $\frac{\overline{(E-\bar{E})^2}}{\bar{E}^2} = \frac{kT^2 C_V}{\bar{E}^2} \propto \frac{1}{N}.$

Fluctuation

- $$\overline{(E-\bar{E})^2} = \sum \rho_s (E_s - \bar{E})^2$$
  $$= \sum \rho_s (E_s^2 - 2\bar{E}E_s + \bar{E}^2)$$
  $$= \sum E_s^2 \rho_s - 2\bar{E}\sum \rho_s E_s + \bar{E}^2 = \sum E_s^2 \rho_s - \bar{E}^2$$
  $$= \overline{E^2} - \bar{E}^2;$$
- $$\frac{\partial \bar{E}}{\partial \beta} = \frac{\partial \sum E_s \rho_s}{\partial \beta} = \frac{\partial}{\partial \beta}\frac{\sum E_s e^{-\beta E_s}}{Z} = \frac{\partial}{\partial \beta}\frac{\sum E_s e^{-\beta E_s}}{\sum e^{-\beta E_s}}$$
  $$= -\frac{\sum E_s^2 e^{-\beta E_s}}{\sum e^{-\beta E_s}} + \frac{(\sum E_s e^{-\beta E_s})^2}{(\sum e^{-\beta E_s})^2} = -(\overline{E^2} - \bar{E}^2);$$
- $$\therefore \overline{(E-\bar{E})^2} = -\frac{\partial \bar{E}}{\partial \beta} = kT^2 \frac{\partial \bar{E}}{\partial T} = kT^2 \frac{\partial U}{\partial T} = kT^2 C_V.$$
- Relative fluctuation: $\frac{\overline{(E-\bar{E})^2}}{\bar{E}^2} = \frac{kT^2 C_V}{\bar{E}^2} \propto \frac{1}{N}$.
  For $N \gg 1$, the relative fluctuation $\to 0$;

Fluctuation

- $\overline{(E-\bar{E})^2} = \sum \rho_s (E_s - \bar{E})^2$
  $= \sum \rho_s (E_s^2 - 2\bar{E}E_s + \bar{E}^2)$
  $= \sum E_s^2 \rho_s - 2\bar{E}\sum \rho_s E_s + \bar{E}^2 = \sum E_s^2 \rho_s - \bar{E}^2$
  $= \overline{E^2} - \bar{E}^2$;
- $\frac{\partial \bar{E}}{\partial \beta} = \frac{\partial \sum E_s \rho_s}{\partial \beta} = \frac{\partial}{\partial \beta} \frac{\sum E_s e^{-\beta E_s}}{Z} = \frac{\partial}{\partial \beta} \frac{\sum E_s e^{-\beta E_s}}{\sum e^{-\beta E_s}}$
  $= -\frac{\sum E_s^2 e^{-\beta E_s}}{\sum e^{-\beta E_s}} + \frac{(\sum E_s e^{-\beta E_s})^2}{(\sum e^{-\beta E_s})^2} = -(\overline{E^2} - \bar{E}^2)$;
- $\therefore \overline{(E-\bar{E})^2} = -\frac{\partial \bar{E}}{\partial \beta} = kT^2 \frac{\partial \bar{E}}{\partial T} = kT^2 \frac{\partial U}{\partial T} = kT^2 C_V$.
- Relative fluctuation: $\frac{\overline{(E-\bar{E})^2}}{\bar{E}^2} = \frac{kT^2 C_V}{\bar{E}^2} \propto \frac{1}{N}$.
  For $N \gg 1$, the relative fluctuation $\to 0$; back to microcanonical ensemble (equivalent).

Table of contents

9.6 EOS of real gas – 1st application.

9.6 EOS of real gas – 1st application.

- Boltzmann, Bose, Fermi statistics can only deal with ideal gas (nearly no interaction).

9.6 EOS of real gas – 1st application.

- Boltzmann, Bose, Fermi statistics can only deal with ideal gas (nearly no interaction). Ensemble theory is suitable for real gas.

9.6 EOS of real gas – 1st application.

- Boltzmann, Bose, Fermi statistics can only deal with ideal gas (nearly no interaction). Ensemble theory is suitable for real gas.
- 1st step: partition function,
  $Z = \frac{1}{N!h^{3N}} \int e^{-\beta E} \mathrm{d}q_1 ... \mathrm{d}q_{3N} \mathrm{d}p_1 ... \mathrm{d}p_{3N}$;

9.6 EOS of real gas – 1st application.

- Boltzmann, Bose, Fermi statistics can only deal with ideal gas (nearly no interaction). Ensemble theory is suitable for real gas.
- 1st step: partition function, $Z = \frac{1}{N!h^{3N}} \int e^{-\beta E} \mathrm{d}q_1 ... \mathrm{d}q_{3N} \mathrm{d}p_1 ... \mathrm{d}p_{3N}$;
- 2nd step: thermal quantities, like $p = \frac{1}{\beta} \frac{\partial}{\partial V} \ln Z$.

9.6 EOS of real gas – 1st application.

- Boltzmann, Bose, Fermi statistics can only deal with ideal gas (nearly no interaction). Ensemble theory is suitable for real gas.
- 1st step: partition function,
  $Z = \frac{1}{N!h^{3N}} \int e^{-\beta E} \mathrm{d}q_1 ... \mathrm{d}q_{3N} \mathrm{d}p_1 ... \mathrm{d}p_{3N}$;
- 2nd step: thermal quantities, like $p = \frac{1}{\beta}\frac{\partial}{\partial V} \ln Z$.
- E (kinetic energy and potential energy):

9.6 EOS of real gas – 1st application.

- Boltzmann, Bose, Fermi statistics can only deal with ideal gas (nearly no interaction). Ensemble theory is suitable for real gas.
- 1st step: partition function,
  $Z = \frac{1}{N!h^{3N}} \int e^{-\beta E} \mathrm{d}q_1 ... \mathrm{d}q_{3N} \mathrm{d}p_1 ... \mathrm{d}p_{3N}$;
- 2nd step: thermal quantities, like $p = \frac{1}{\beta}\frac{\partial}{\partial V} \ln Z$.
- E (kinetic energy and potential energy):
  $E = \sum_{i=1}^{N} \frac{\overrightarrow{p_i}^2}{2m} + \sum_{i<j} \phi(\overrightarrow{r_{ij}})$.

EOS of real gas $\boxed{Z = \frac{1}{N!h^{3N}} \int e^{-\beta E} \mathrm{d}q_1 ... \mathrm{d}q_{3N} \mathrm{d}p_1 ... \mathrm{d}p_{3N}}$

- Kinetic term of E:

$$\int e^{-\beta \sum\limits_{i=1}^{N} \frac{\vec{p_i}^2}{2m}} \mathrm{d}p_1 ... \mathrm{d}p_{3N}$$

EOS of real gas $\boxed{Z = \frac{1}{N!h^{3N}} \int e^{-\beta E} \mathrm{d}q_1 ... \mathrm{d}q_{3N} \mathrm{d}p_1 ... \mathrm{d}p_{3N}}$

- Kinetic term of E:

$$\int e^{-\beta \sum\limits_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m}} \mathrm{d}p_1 ... \mathrm{d}p_{3N} = \int e^{-\beta \sum\limits_{i=1}^{3N} \frac{p_i^2}{2m}} \mathrm{d}p_1 ... \mathrm{d}p_{3N}$$

EOS of real gas $\boxed{Z = \frac{1}{N!h^{3N}} \int e^{-\beta E} \mathrm{d}q_1 \ldots \mathrm{d}q_{3N} \mathrm{d}p_1 \ldots \mathrm{d}p_{3N}}$

- Kinetic term of E:

$$\int e^{-\beta \sum\limits_{i=1}^{N} \frac{\vec{p_i}^2}{2m}} \mathrm{d}p_1 \ldots \mathrm{d}p_{3N} = \int e^{-\beta \sum\limits_{i=1}^{3N} \frac{p_i^2}{2m}} \mathrm{d}p_1 \ldots \mathrm{d}p_{3N}$$

$$= \prod_{i=1}^{3N} \int e^{-\beta \frac{p_i^2}{2m}} \mathrm{d}p_i$$

EOS of real gas $\boxed{Z = \frac{1}{N!h^{3N}} \int e^{-\beta E} \mathrm{d}q_1 ... \mathrm{d}q_{3N} \mathrm{d}p_1 ... \mathrm{d}p_{3N}}$

- Kinetic term of E:

$$\int e^{-\beta \sum\limits_{i=1}^{N} \frac{\vec{p_i}^2}{2m}} \mathrm{d}p_1 ... \mathrm{d}p_{3N} = \int e^{-\beta \sum\limits_{i=1}^{3N} \frac{p_i^2}{2m}} \mathrm{d}p_1 ... \mathrm{d}p_{3N}$$

$$= \prod_{i=1}^{3N} \int e^{-\beta \frac{p_i^2}{2m}} \mathrm{d}p_i = \left(\frac{2\pi m}{\beta}\right)^{\frac{3}{2}N}.$$

EOS of real gas $\boxed{Z = \frac{1}{N!h^{3N}} \int e^{-\beta E} \mathrm{d}q_1 \ldots \mathrm{d}q_{3N} \mathrm{d}p_1 \ldots \mathrm{d}p_{3N}}$

- Kinetic term of E:

$$\int e^{-\beta \sum\limits_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m}} \mathrm{d}p_1 \ldots \mathrm{d}p_{3N} = \int e^{-\beta \sum\limits_{i=1}^{3N} \frac{p_i^2}{2m}} \mathrm{d}p_1 \ldots \mathrm{d}p_{3N}$$
$$= \prod_{i=1}^{3N} \int e^{-\beta \frac{p_i^2}{2m}} \mathrm{d}p_i = \left(\frac{2\pi m}{\beta}\right)^{\frac{3}{2}N}.$$

- Potential part: $Q \equiv \int e^{-\beta \sum\limits_{i<j} \phi(\vec{r}_{ij})} \mathrm{d}q_1 \ldots \mathrm{d}q_{3N}$

EOS of real gas $\boxed{Z = \frac{1}{N!h^{3N}} \int e^{-\beta E} \mathrm{d}q_1 ... \mathrm{d}q_{3N} \mathrm{d}p_1 ... \mathrm{d}p_{3N}}$

- Kinetic term of E:
  $\int e^{-\beta \sum\limits_{i=1}^{N} \frac{\vec{p_i}^2}{2m}} \mathrm{d}p_1 ... \mathrm{d}p_{3N} = \int e^{-\beta \sum\limits_{i=1}^{3N} \frac{p_i^2}{2m}} \mathrm{d}p_1 ... \mathrm{d}p_{3N}$
  $= \prod\limits_{i=1}^{3N} \int e^{-\beta \frac{p_i^2}{2m}} \mathrm{d}p_i = (\frac{2\pi m}{\beta})^{\frac{3}{2}N}$.
- Potential part: $Q \equiv \int e^{-\beta \sum\limits_{i<j} \phi(\vec{r}_{ij})} \mathrm{d}q_1 ... \mathrm{d}q_{3N}$
  $= \int e^{-\beta \sum\limits_{i<j} \phi(\vec{r}_{ij})} \mathrm{d}\tau_1 ... \mathrm{d}\tau_N$.

EOS of real gas $\boxed{Z = \frac{1}{N!h^{3N}} \int e^{-\beta E} \mathrm{d}q_1 ... \mathrm{d}q_{3N} \mathrm{d}p_1 ... \mathrm{d}p_{3N}}$

- Kinetic term of E:
$$\int e^{-\beta \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m}} \mathrm{d}p_1 ... \mathrm{d}p_{3N} = \int e^{-\beta \sum_{i=1}^{3N} \frac{p_i^2}{2m}} \mathrm{d}p_1 ... \mathrm{d}p_{3N}$$
$$= \prod_{i=1}^{3N} \int e^{-\beta \frac{p_i^2}{2m}} \mathrm{d}p_i = \left(\frac{2\pi m}{\beta}\right)^{\frac{3}{2}N}.$$
- Potential part: $Q \equiv \int e^{-\beta \sum_{i<j} \phi(\vec{r}_{ij})} \mathrm{d}q_1 ... \mathrm{d}q_{3N}$
$$= \int e^{-\beta \sum_{i<j} \phi(\vec{r}_{ij})} \mathrm{d}\tau_1 ... \mathrm{d}\tau_N.$$
- Then the partition function: $Z = \frac{1}{N!} \left(\frac{2\pi m}{\beta h^2}\right)^{\frac{3}{2}N} Q.$

EOS of real gas $Z = \frac{1}{N!h^{3N}} \int e^{-\beta E} \mathrm{d}q_1 ... \mathrm{d}q_{3N} \mathrm{d}p_1 ... \mathrm{d}p_{3N}$

- Kinetic term of E:
  $\int e^{-\beta \sum\limits_{i=1}^{N} \frac{\vec{p_i}^2}{2m}} \mathrm{d}p_1 ... \mathrm{d}p_{3N} = \int e^{-\beta \sum\limits_{i=1}^{3N} \frac{p_i^2}{2m}} \mathrm{d}p_1 ... \mathrm{d}p_{3N}$
  $= \prod\limits_{i=1}^{3N} \int e^{-\beta \frac{p_i^2}{2m}} \mathrm{d}p_i = (\frac{2\pi m}{\beta})^{\frac{3}{2}N}$.
- Potential part: $Q \equiv \int e^{-\beta \sum\limits_{i<j} \phi(\vec{r}_{ij})} \mathrm{d}q_1 ... \mathrm{d}q_{3N}$
  $= \int e^{-\beta \sum\limits_{i<j} \phi(\vec{r}_{ij})} \mathrm{d}\tau_1 ... \mathrm{d}\tau_N$.
- Then the partition function: $Z = \frac{1}{N!} (\frac{2\pi m}{\beta h^2})^{\frac{3}{2}N} Q$.
- Key: Q.

EOS of real gas $\boxed{Q = \int e^{-\beta \sum\limits_{i<j} \phi(\overrightarrow{r}_{ij})} \mathrm{d}\tau_1 ... \mathrm{d}\tau_N}$

- Define $f_{ij} = e^{-\beta\phi(\overrightarrow{r}_{ij})} - 1$,

EOS of real gas $\boxed{Q = \int e^{-\beta \sum\limits_{i<j} \phi(\overrightarrow{r}_{ij})} \mathrm{d}\tau_1 ... \mathrm{d}\tau_N}$

- Define $f_{ij} = e^{-\beta\phi(\overrightarrow{r}_{ij})} - 1$,
- If $\overrightarrow{r}_{ij}$ is out of the interacting range, $\phi(\overrightarrow{r}_{ij}) = 0$, then $f_{ij} = 0$.

EOS of real gas $\boxed{Q = \int e^{-\beta \sum\limits_{i<j} \phi(\overrightarrow{r}_{ij})} \mathrm{d}\tau_1 ... \mathrm{d}\tau_N}$

- Define $f_{ij} = e^{-\beta\phi(\overrightarrow{r}_{ij})} - 1$,
- If $\overrightarrow{r}_{ij}$ is out of the interacting range, $\phi(\overrightarrow{r}_{ij}) = 0$, then $f_{ij} = 0$. Only the nearby neighbours are interacting.

EOS of real gas $\boxed{Q = \int e^{-\beta \sum\limits_{i<j} \phi(\overrightarrow{r}_{ij})} \mathrm{d}\tau_1 ... \mathrm{d}\tau_N}$

- Define $f_{ij} = e^{-\beta\phi(\overrightarrow{r}_{ij})} - 1$,
- If $\overrightarrow{r}_{ij}$ is out of the interacting range, $\phi(\overrightarrow{r}_{ij}) = 0$, then $f_{ij} = 0$. Only the nearby neighbours are interacting.
- $Q = \int \prod\limits_{i<j} (1 + f_{ij}) \mathrm{d}\tau_1 ... \mathrm{d}\tau_N$

EOS of real gas $\boxed{Q = \int e^{-\beta \sum\limits_{i<j} \phi(\vec{r}_{ij})} \mathrm{d}\tau_1 \ldots \mathrm{d}\tau_N}$

- Define $f_{ij} = e^{-\beta\phi(\vec{r}_{ij})} - 1$,
- If $\vec{r}_{ij}$ is out of the interacting range, $\phi(\vec{r}_{ij}) = 0$, then $f_{ij} = 0$. Only the nearby neighbours are interacting.
- $Q = \int \prod\limits_{i<j} (1 + f_{ij}) \mathrm{d}\tau_1 \ldots \mathrm{d}\tau_N$
  $= \int (1 + \sum\limits_{i<j} f_{ij} + \sum\limits_{i<j} \sum\limits_{i'<j'} f_{ij} f_{i'j'} + \ldots) \mathrm{d}\tau_1 \ldots \mathrm{d}\tau_N.$

EOS of real gas $Q = \int e^{-\beta \sum\limits_{i<j} \phi(\overrightarrow{r}_{ij})} \mathrm{d}\tau_1 ... \mathrm{d}\tau_N$

- Define $f_{ij} = e^{-\beta\phi(\overrightarrow{r}_{ij})} - 1$,
- If $\overrightarrow{r}_{ij}$ is out of the interacting range, $\phi(\overrightarrow{r}_{ij}) = 0$, then $f_{ij} = 0$. Only the nearby neighbours are interacting.
- $Q = \int \prod\limits_{i<j}(1 + f_{ij})\mathrm{d}\tau_1 ... \mathrm{d}\tau_N$
  $= \int (1 + \sum\limits_{i<j} f_{ij} + \sum\limits_{i<j} \sum\limits_{i'<j'} f_{ij} f_{i'j'} + ...)\mathrm{d}\tau_1 ... \mathrm{d}\tau_N$.
- If just keep "1", no potential, it goes back to ideal gas. $Q = V^N$.

EOS of real gas $\boxed{Q = \int e^{-\beta \sum\limits_{i<j} \phi(\vec{r}_{ij})} \mathrm{d}\tau_1 \ldots \mathrm{d}\tau_N}$

- Define $f_{ij} = e^{-\beta\phi(\vec{r}_{ij})} - 1$,
- If $\vec{r}_{ij}$ is out of the interacting range, $\phi(\vec{r}_{ij}) = 0$, then $f_{ij} = 0$. Only the nearby neighbours are interacting.
- $Q = \int \prod\limits_{i<j} (1 + f_{ij}) \mathrm{d}\tau_1 \ldots \mathrm{d}\tau_N$
  $= \int (1 + \sum\limits_{i<j} f_{ij} + \sum\limits_{i<j} \sum\limits_{i'<j'} f_{ij} f_{i'j'} + \ldots) \mathrm{d}\tau_1 \ldots \mathrm{d}\tau_N$.
- If just keep "1", no potential, it goes back to ideal gas. $Q = V^N$.
  Then $Z = \frac{1}{N!}(\frac{2\pi m}{\beta h^2})^{\frac{3}{2}N} V^N$.

EOS of real gas $\boxed{Q = \int e^{-\beta \sum\limits_{i<j} \phi(\vec{r}_{ij})} \mathrm{d}\tau_1 \ldots \mathrm{d}\tau_N}$

- Define $f_{ij} = e^{-\beta\phi(\vec{r}_{ij})} - 1$,
- If $\vec{r}_{ij}$ is out of the interacting range, $\phi(\vec{r}_{ij}) = 0$, then $f_{ij} = 0$. Only the nearby neighbours are interacting.
- $Q = \int \prod\limits_{i<j}(1 + f_{ij})\mathrm{d}\tau_1 \ldots \mathrm{d}\tau_N$
  $= \int (1 + \sum\limits_{i<j} f_{ij} + \sum\limits_{i<j} \sum\limits_{i'<j'} f_{ij} f_{i'j'} + \ldots)\mathrm{d}\tau_1 \ldots \mathrm{d}\tau_N$.
- If just keep "1", no potential, it goes back to ideal gas. $Q = V^N$.
  Then $Z = \frac{1}{N!}(\frac{2\pi m}{\beta h^2})^{\frac{3}{2}N} V^N$.
  $p = \frac{1}{\beta}\frac{\partial}{\partial V} \ln Z$

EOS of real gas $\boxed{Q = \int e^{-\beta \sum\limits_{i<j} \phi(\vec{r}_{ij})} \mathrm{d}\tau_1 ... \mathrm{d}\tau_N}$

- Define $f_{ij} = e^{-\beta\phi(\vec{r}_{ij})} - 1$,
- If $\vec{r}_{ij}$ is out of the interacting range, $\phi(\vec{r}_{ij}) = 0$, then $f_{ij} = 0$. Only the nearby neighbours are interacting.
- $Q = \int \prod\limits_{i<j}(1 + f_{ij})\mathrm{d}\tau_1 ... \mathrm{d}\tau_N$
  $= \int (1 + \sum\limits_{i<j} f_{ij} + \sum\limits_{i<j} \sum\limits_{i'<j'} f_{ij} f_{i'j'} + ...)\mathrm{d}\tau_1 ... \mathrm{d}\tau_N$.
- If just keep "1", no potential, it goes back to ideal gas. $Q = V^N$.
  Then $Z = \frac{1}{N!}(\frac{2\pi m}{\beta h^2})^{\frac{3}{2}N} V^N$.
  $p = \frac{1}{\beta}\frac{\partial}{\partial V}\ln Z = \frac{1}{\beta}\frac{\partial \ln(CV^N)}{\partial V}$

EOS of real gas $\boxed{Q = \int e^{-\beta \sum\limits_{i<j} \phi(\overrightarrow{r}_{ij})} \mathrm{d}\tau_1 \ldots \mathrm{d}\tau_N}$

- Define $f_{ij} = e^{-\beta\phi(\overrightarrow{r}_{ij})} - 1$,
- If $\overrightarrow{r}_{ij}$ is out of the interacting range, $\phi(\overrightarrow{r}_{ij}) = 0$, then $f_{ij} = 0$. Only the nearby neighbours are interacting.
- $Q = \int \prod\limits_{i<j} (1 + f_{ij}) \mathrm{d}\tau_1 \ldots \mathrm{d}\tau_N$
  $= \int (1 + \sum\limits_{i<j} f_{ij} + \sum\limits_{i<j} \sum\limits_{i'<j'} f_{ij} f_{i'j'} + \ldots) \mathrm{d}\tau_1 \ldots \mathrm{d}\tau_N$.
- If just keep "1", no potential, it goes back to ideal gas. $Q = V^N$.
  Then $Z = \frac{1}{N!} (\frac{2\pi m}{\beta h^2})^{\frac{3}{2}N} V^N$.
  $p = \frac{1}{\beta} \frac{\partial}{\partial V} \ln Z = \frac{1}{\beta} \frac{\partial \ln(CV^N)}{\partial V} = \frac{1}{\beta} \frac{N}{V}$

EOS of real gas $\boxed{Q = \int e^{-\beta \sum\limits_{i<j} \phi(\vec{r}_{ij})} \mathrm{d}\tau_1 ... \mathrm{d}\tau_N}$

- Define $f_{ij} = e^{-\beta\phi(\vec{r}_{ij})} - 1$,
- If $\vec{r}_{ij}$ is out of the interacting range, $\phi(\vec{r}_{ij}) = 0$, then $f_{ij} = 0$. Only the nearby neighbours are interacting.
- $Q = \int \prod\limits_{i<j}(1 + f_{ij})\mathrm{d}\tau_1 ... \mathrm{d}\tau_N$
  $= \int (1 + \sum\limits_{i<j} f_{ij} + \sum\limits_{i<j}\sum\limits_{i'<j'} f_{ij}f_{i'j'} + ...)\mathrm{d}\tau_1 ... \mathrm{d}\tau_N$.
- If just keep "1", no potential, it goes back to ideal gas. $Q = V^N$.
  Then $Z = \frac{1}{N!}(\frac{2\pi m}{\beta h^2})^{\frac{3}{2}N} V^N$.
  $p = \frac{1}{\beta}\frac{\partial}{\partial V}\ln Z = \frac{1}{\beta}\frac{\partial \ln(CV^N)}{\partial V} = \frac{1}{\beta}\frac{N}{V} = \frac{NkT}{V}$.

EOS of real gas

- Else if the interacting is weak, i.e., $\phi(\overrightarrow{r}_{ij}) \to 0$, then $f_{ij} \to 0$.

EOS of real gas

- Else if the interacting is weak, i.e., $\phi(\overrightarrow{r}_{ij}) \to 0$, then $f_{ij} \to 0$. Only keep the first two terms:

EOS of real gas

- Else if the interacting is weak, i.e., $\phi(\overrightarrow{r}_{ij}) \to 0$, then $f_{ij} \to 0$. Only keep the first two terms:
  $Q = \int (1 + \sum\limits_{i<j} f_{ij}) \mathrm{d}\tau_1 ... \mathrm{d}\tau_N$.

EOS of real gas

- Else if the interacting is weak, i.e., $\phi(\overrightarrow{r}_{ij}) \to 0$, then $f_{ij} \to 0$. Only keep the first two terms:
  $Q = \int (1 + \sum\limits_{i<j} f_{ij}) \mathrm{d}\tau_1 ... \mathrm{d}\tau_N$.
- As there is no difference for the $\frac{1}{2}N(N-1)$ summation (neglect the boundary effect),

EOS of real gas

- Else if the interacting is weak, i.e., $\phi(\overrightarrow{r}_{ij}) \to 0$, then $f_{ij} \to 0$. Only keep the first two terms: $Q = \int (1 + \sum\limits_{i<j} f_{ij}) \mathrm{d}\tau_1 ... \mathrm{d}\tau_N$.
- As there is no difference for the $\frac{1}{2}N(N-1)$ summation (neglect the boundary effect), $\int \sum\limits_{i<j} f_{ij} \mathrm{d}\tau_1 ... \mathrm{d}\tau_N = \frac{1}{2}N(N-1) \int f_{12} \mathrm{d}\tau_1 ... \mathrm{d}\tau_N$

EOS of real gas

- Else if the interacting is weak, i.e., $\phi(\overrightarrow{r}_{ij}) \to 0$, then $f_{ij} \to 0$. Only keep the first two terms:
  $Q = \int(1 + \sum\limits_{i<j} f_{ij})\mathrm{d}\tau_1 ... \mathrm{d}\tau_N$.
- As there is no difference for the $\frac{1}{2}N(N-1)$ summation (neglect the boundary effect),
  $\int \sum\limits_{i<j} f_{ij}\mathrm{d}\tau_1 ... \mathrm{d}\tau_N = \frac{1}{2}N(N-1)\int f_{12}\mathrm{d}\tau_1 ... \mathrm{d}\tau_N$
  $= \frac{1}{2}N(N-1)V^{N-2}\int f_{12}\mathrm{d}\tau_1\mathrm{d}\tau_2$.

EOS of real gas

- Else if the interacting is weak, i.e., $\phi(\overrightarrow{r}_{ij}) \to 0$, then $f_{ij} \to 0$. Only keep the first two terms: $Q = \int (1 + \sum\limits_{i<j} f_{ij}) \mathrm{d}\tau_1 ... \mathrm{d}\tau_N$.
- As there is no difference for the $\frac{1}{2}N(N-1)$ summation (neglect the boundary effect), $\int \sum\limits_{i<j} f_{ij} \mathrm{d}\tau_1 ... \mathrm{d}\tau_N = \frac{1}{2}N(N-1) \int f_{12} \mathrm{d}\tau_1 ... \mathrm{d}\tau_N$ $= \frac{1}{2}N(N-1)V^{N-2} \int f_{12} \mathrm{d}\tau_1 \mathrm{d}\tau_2$.
- Integration does not depend on molecule 1's position,

EOS of real gas

- Else if the interacting is weak, i.e., $\phi(\overrightarrow{r}_{ij}) \to 0$, then $f_{ij} \to 0$. Only keep the first two terms:
  $Q = \int (1 + \sum\limits_{i<j} f_{ij}) \mathrm{d}\tau_1 ... \mathrm{d}\tau_N$.
- As there is no difference for the $\frac{1}{2}N(N-1)$ summation (neglect the boundary effect),
  $\int \sum\limits_{i<j} f_{ij} \mathrm{d}\tau_1 ... \mathrm{d}\tau_N = \frac{1}{2}N(N-1) \int f_{12} \mathrm{d}\tau_1 ... \mathrm{d}\tau_N$
  $= \frac{1}{2}N(N-1)V^{N-2} \int f_{12} \mathrm{d}\tau_1 \mathrm{d}\tau_2$.
- Integration does not depend on molecule 1's position,
  $\int f_{12} \mathrm{d}\tau_1 \mathrm{d}\tau_2 = V \int f_{12} \mathrm{d}\tau_2 = V \int f_{12} \mathrm{d}\overrightarrow{r}$.

EOS of real gas

- Else if the interacting is weak, i.e., $\phi(\overrightarrow{r}_{ij}) \to 0$, then $f_{ij} \to 0$. Only keep the first two terms:
  $Q = \int (1 + \sum\limits_{i<j} f_{ij}) \mathrm{d}\tau_1 ... \mathrm{d}\tau_N$.
- As there is no difference for the $\frac{1}{2}N(N-1)$ summation (neglect the boundary effect),
  $\int \sum\limits_{i<j} f_{ij} \mathrm{d}\tau_1 ... \mathrm{d}\tau_N = \frac{1}{2}N(N-1) \int f_{12} \mathrm{d}\tau_1 ... \mathrm{d}\tau_N$
  $= \frac{1}{2}N(N-1)V^{N-2} \int f_{12} \mathrm{d}\tau_1 \mathrm{d}\tau_2$.
- Integration does not depend on molecule 1's position,
  $\int f_{12} \mathrm{d}\tau_1 \mathrm{d}\tau_2 = V \int f_{12} \mathrm{d}\tau_2 = V \int f_{12} \mathrm{d}\overrightarrow{r}$.
- $Q = V^N + \frac{1}{2}N(N-1)V^{N-1} \int f_{12} \mathrm{d}\overrightarrow{r}$

EOS of real gas

- Else if the interacting is weak, i.e., $\phi(\overrightarrow{r}_{ij}) \to 0$, then $f_{ij} \to 0$. Only keep the first two terms:
  $Q = \int (1 + \sum\limits_{i<j} f_{ij}) \mathrm{d}\tau_1 ... \mathrm{d}\tau_N$.
- As there is no difference for the $\frac{1}{2}N(N-1)$ summation (neglect the boundary effect),
  $\int \sum\limits_{i<j} f_{ij} \mathrm{d}\tau_1 ... \mathrm{d}\tau_N = \frac{1}{2}N(N-1) \int f_{12} \mathrm{d}\tau_1 ... \mathrm{d}\tau_N$
  $= \frac{1}{2}N(N-1)V^{N-2} \int f_{12} \mathrm{d}\tau_1 \mathrm{d}\tau_2$.
- Integration does not depend on molecule 1's position,
  $\int f_{12} \mathrm{d}\tau_1 \mathrm{d}\tau_2 = V \int f_{12} \mathrm{d}\tau_2 = V \int f_{12} \mathrm{d}\overrightarrow{r}$.
- $Q = V^N + \frac{1}{2}N(N-1)V^{N-1} \int f_{12} \mathrm{d}\overrightarrow{r}$
  $\simeq V^N + \frac{1}{2}N^2 V^{N-1} \int f_{12} \mathrm{d}\overrightarrow{r}$

EOS of real gas

- Else if the interacting is weak, i.e., $\phi(\overrightarrow{r}_{ij}) \to 0$, then $f_{ij} \to 0$. Only keep the first two terms:
  $Q = \int (1 + \sum\limits_{i<j} f_{ij}) \mathrm{d}\tau_1 ... \mathrm{d}\tau_N$.
- As there is no difference for the $\frac{1}{2}N(N-1)$ summation (neglect the boundary effect),
  $\int \sum\limits_{i<j} f_{ij} \mathrm{d}\tau_1 ... \mathrm{d}\tau_N = \frac{1}{2}N(N-1) \int f_{12} \mathrm{d}\tau_1 ... \mathrm{d}\tau_N$
  $= \frac{1}{2}N(N-1)V^{N-2} \int f_{12} \mathrm{d}\tau_1 \mathrm{d}\tau_2$.
- Integration does not depend on molecule 1's position,
  $\int f_{12} \mathrm{d}\tau_1 \mathrm{d}\tau_2 = V \int f_{12} \mathrm{d}\tau_2 = V \int f_{12} \mathrm{d}\overrightarrow{r}$.
- $Q = V^N + \frac{1}{2}N(N-1)V^{N-1} \int f_{12} \mathrm{d}\overrightarrow{r}$
  $\simeq V^N + \frac{1}{2}N^2 V^{N-1} \int f_{12} \mathrm{d}\overrightarrow{r} = V^N(1 + \frac{N^2}{2V} \int f_{12} \mathrm{d}\overrightarrow{r})$.

EOS of real gas $\boxed{Q = V^N(1 + \frac{N^2}{2V}\int f_{12} \mathrm{d}\overrightarrow{r})}$

- $\ln Q = N \ln V + \ln(1 + \frac{N^2}{2V}\int f_{12} \mathrm{d}\overrightarrow{r})$.

EOS of real gas $\boxed{Q = V^N(1 + \frac{N^2}{2V}\int f_{12}\mathrm{d}\overrightarrow{r})}$

- $\ln Q = N \ln V + \ln(1 + \frac{N^2}{2V}\int f_{12}\mathrm{d}\overrightarrow{r})$.
- For weak interaction,
  $\ln(1 + \frac{N^2}{2V}\int f_{12}\mathrm{d}\overrightarrow{r}) \simeq \frac{N^2}{2V}\int f_{12}\mathrm{d}\overrightarrow{r}$.

EOS of real gas $\boxed{Q = V^N(1+\frac{N^2}{2V}\int f_{12}\mathrm{d}\overrightarrow{r})}$

- $\ln Q = N\ln V + \ln(1+\frac{N^2}{2V}\int f_{12}\mathrm{d}\overrightarrow{r})$.
- For weak interaction,
  $\ln(1+\frac{N^2}{2V}\int f_{12}\mathrm{d}\overrightarrow{r}) \simeq \frac{N^2}{2V}\int f_{12}\mathrm{d}\overrightarrow{r}$.
  $\therefore \ln Q \simeq N\ln V + \frac{N^2}{2V}\int f_{12}\mathrm{d}\overrightarrow{r}$.

EOS of real gas $\boxed{Q = V^N(1 + \frac{N^2}{2V}\int f_{12}\mathrm{d}\overrightarrow{r})}$

- $\ln Q = N\ln V + \ln(1 + \frac{N^2}{2V}\int f_{12}\mathrm{d}\overrightarrow{r})$.
- For weak interaction,
  $\ln(1 + \frac{N^2}{2V}\int f_{12}\mathrm{d}\overrightarrow{r}) \simeq \frac{N^2}{2V}\int f_{12}\mathrm{d}\overrightarrow{r}$.
  $\therefore \ln Q \simeq N\ln V + \frac{N^2}{2V}\int f_{12}\mathrm{d}\overrightarrow{r}$.
- As in $Z = \frac{1}{N!}(\frac{2\pi m}{\beta h^2})^{\frac{3}{2}N}Q$, only Q depends on V,

EOS of real gas $\boxed{Q = V^N(1 + \frac{N^2}{2V}\int f_{12}\mathrm{d}\overrightarrow{r})}$

- $\ln Q = N \ln V + \ln(1 + \frac{N^2}{2V}\int f_{12}\mathrm{d}\overrightarrow{r})$.
- For weak interaction,
  $\ln(1 + \frac{N^2}{2V}\int f_{12}\mathrm{d}\overrightarrow{r}) \simeq \frac{N^2}{2V}\int f_{12}\mathrm{d}\overrightarrow{r}$.
  $\therefore \ln Q \simeq N \ln V + \frac{N^2}{2V}\int f_{12}\mathrm{d}\overrightarrow{r}$.
- As in $Z = \frac{1}{N!}(\frac{2\pi m}{\beta h^2})^{\frac{3}{2}N}Q$, only Q depends on V,
  $p = \frac{1}{\beta}\frac{\partial}{\partial V}\ln Z$

EOS of real gas $\boxed{Q = V^N(1 + \frac{N^2}{2V}\int f_{12}\mathrm{d}\overrightarrow{r})}$

- $\ln Q = N\ln V + \ln(1 + \frac{N^2}{2V}\int f_{12}\mathrm{d}\overrightarrow{r})$.
- For weak interaction,
  $\ln(1 + \frac{N^2}{2V}\int f_{12}\mathrm{d}\overrightarrow{r}) \simeq \frac{N^2}{2V}\int f_{12}\mathrm{d}\overrightarrow{r}$.
  $\therefore \ln Q \simeq N\ln V + \frac{N^2}{2V}\int f_{12}\mathrm{d}\overrightarrow{r}$.
- As in $Z = \frac{1}{N!}(\frac{2\pi m}{\beta h^2})^{\frac{3}{2}N}Q$, only Q depends on V,
  $p = \frac{1}{\beta}\frac{\partial}{\partial V}\ln Z = \frac{1}{\beta}\frac{\partial}{\partial V}\ln Q$

EOS of real gas $\boxed{Q = V^N(1 + \frac{N^2}{2V}\int f_{12}\mathrm{d}\overrightarrow{r})}$

- $\ln Q = N\ln V + \ln(1 + \frac{N^2}{2V}\int f_{12}\mathrm{d}\overrightarrow{r})$.
- For weak interaction,
  $\ln(1 + \frac{N^2}{2V}\int f_{12}\mathrm{d}\overrightarrow{r}) \simeq \frac{N^2}{2V}\int f_{12}\mathrm{d}\overrightarrow{r}$.
  $\therefore \ln Q \simeq N\ln V + \frac{N^2}{2V}\int f_{12}\mathrm{d}\overrightarrow{r}$.
- As in $Z = \frac{1}{N!}(\frac{2\pi m}{\beta h^2})^{\frac{3}{2}N}Q$, only Q depends on V,
  $p = \frac{1}{\beta}\frac{\partial}{\partial V}\ln Z = \frac{1}{\beta}\frac{\partial}{\partial V}\ln Q$
  $= \frac{1}{\beta}\frac{\partial}{\partial V}(N\ln V + \frac{N^2}{2V}\int f_{12}\mathrm{d}\overrightarrow{r})$

EOS of real gas $\boxed{Q = V^N(1 + \frac{N^2}{2V}\int f_{12}\mathrm{d}\overrightarrow{r})}$

- $\ln Q = N\ln V + \ln(1 + \frac{N^2}{2V}\int f_{12}\mathrm{d}\overrightarrow{r})$.
- For weak interaction,
  $\ln(1 + \frac{N^2}{2V}\int f_{12}\mathrm{d}\overrightarrow{r}) \simeq \frac{N^2}{2V}\int f_{12}\mathrm{d}\overrightarrow{r}$.
  $\therefore \ln Q \simeq N\ln V + \frac{N^2}{2V}\int f_{12}\mathrm{d}\overrightarrow{r}$.
- As in $Z = \frac{1}{N!}(\frac{2\pi m}{\beta h^2})^{\frac{3}{2}N}Q$, only Q depends on V,
  $p = \frac{1}{\beta}\frac{\partial}{\partial V}\ln Z = \frac{1}{\beta}\frac{\partial}{\partial V}\ln Q$
  $= \frac{1}{\beta}\frac{\partial}{\partial V}(N\ln V + \frac{N^2}{2V}\int f_{12}\mathrm{d}\overrightarrow{r}) = \frac{1}{\beta}(\frac{N}{V} - \frac{N^2}{2V^2}\int f_{12}\mathrm{d}\overrightarrow{r})$

EOS of real gas $\boxed{Q = V^N(1+\frac{N^2}{2V}\int f_{12}\mathrm{d}\overrightarrow{r})}$

- $\ln Q = N\ln V + \ln(1+\frac{N^2}{2V}\int f_{12}\mathrm{d}\overrightarrow{r})$.
- For weak interaction,
  $\ln(1+\frac{N^2}{2V}\int f_{12}\mathrm{d}\overrightarrow{r}) \simeq \frac{N^2}{2V}\int f_{12}\mathrm{d}\overrightarrow{r}$.
  $\therefore \ln Q \simeq N\ln V + \frac{N^2}{2V}\int f_{12}\mathrm{d}\overrightarrow{r}$.
- As in $Z = \frac{1}{N!}(\frac{2\pi m}{\beta h^2})^{\frac{3}{2}N}Q$, only Q depends on V,
  $p = \frac{1}{\beta}\frac{\partial}{\partial V}\ln Z = \frac{1}{\beta}\frac{\partial}{\partial V}\ln Q$
  $= \frac{1}{\beta}\frac{\partial}{\partial V}(N\ln V + \frac{N^2}{2V}\int f_{12}\mathrm{d}\overrightarrow{r}) = \frac{1}{\beta}(\frac{N}{V} - \frac{N^2}{2V^2}\int f_{12}\mathrm{d}\overrightarrow{r})$
  $= kT\frac{N}{V}[1 - \frac{N}{2V}\int f_{12}\mathrm{d}\overrightarrow{r}]$.

EOS of real gas $\boxed{Q = V^N(1 + \frac{N^2}{2V}\int f_{12}\mathrm{d}\overrightarrow{r})}$

- $\ln Q = N\ln V + \ln(1 + \frac{N^2}{2V}\int f_{12}\mathrm{d}\overrightarrow{r})$.
- For weak interaction,
  $\ln(1 + \frac{N^2}{2V}\int f_{12}\mathrm{d}\overrightarrow{r}) \simeq \frac{N^2}{2V}\int f_{12}\mathrm{d}\overrightarrow{r}$.
  $\therefore \ln Q \simeq N\ln V + \frac{N^2}{2V}\int f_{12}\mathrm{d}\overrightarrow{r}$.
- As in $Z = \frac{1}{N!}(\frac{2\pi m}{\beta h^2})^{\frac{3}{2}N}Q$, only Q depends on V,
  $p = \frac{1}{\beta}\frac{\partial}{\partial V}\ln Z = \frac{1}{\beta}\frac{\partial}{\partial V}\ln Q$
  $= \frac{1}{\beta}\frac{\partial}{\partial V}(N\ln V + \frac{N^2}{2V}\int f_{12}\mathrm{d}\overrightarrow{r}) = \frac{1}{\beta}(\frac{N}{V} - \frac{N^2}{2V^2}\int f_{12}\mathrm{d}\overrightarrow{r})$
  $= kT\frac{N}{V}[1 - \frac{N}{2V}\int f_{12}\mathrm{d}\overrightarrow{r}]$.
- Define $B \equiv -\frac{N_A}{2}\int f_{12}\mathrm{d}\overrightarrow{r}$, then $pV = NkT(1 + \frac{nB}{V})$.

EOS of real gas $\boxed{Q = V^N(1 + \frac{N^2}{2V}\int f_{12}\mathrm{d}\overrightarrow{r})}$

- $\ln Q = N\ln V + \ln(1 + \frac{N^2}{2V}\int f_{12}\mathrm{d}\overrightarrow{r})$.
- For weak interaction,
  $\ln(1 + \frac{N^2}{2V}\int f_{12}\mathrm{d}\overrightarrow{r}) \simeq \frac{N^2}{2V}\int f_{12}\mathrm{d}\overrightarrow{r}$.
  $\therefore \ln Q \simeq N\ln V + \frac{N^2}{2V}\int f_{12}\mathrm{d}\overrightarrow{r}$.
- As in $Z = \frac{1}{N!}(\frac{2\pi m}{\beta h^2})^{\frac{3}{2}N}Q$, only Q depends on V,
  $p = \frac{1}{\beta}\frac{\partial}{\partial V}\ln Z = \frac{1}{\beta}\frac{\partial}{\partial V}\ln Q$
  $= \frac{1}{\beta}\frac{\partial}{\partial V}(N\ln V + \frac{N^2}{2V}\int f_{12}\mathrm{d}\overrightarrow{r}) = \frac{1}{\beta}(\frac{N}{V} - \frac{N^2}{2V^2}\int f_{12}\mathrm{d}\overrightarrow{r})$
  $= kT\frac{N}{V}[1 - \frac{N}{2V}\int f_{12}\mathrm{d}\overrightarrow{r}]$.
- Define $B \equiv -\frac{N_A}{2}\int f_{12}\mathrm{d}\overrightarrow{r}$, then $pV = NkT(1 + \frac{nB}{V})$.
- Key: B.

EOS of real gas $\boxed{B \equiv -\frac{N_A}{2}\int f_{12}\mathrm{d}\overrightarrow{r}}$

- Semi-empirical formula: $\phi(r) = \phi_0[(\frac{r_0}{r})^{12} - 2(\frac{r_0}{r})^6]$, fig.

EOS of real gas $\boxed{B \equiv -\frac{N_A}{2}\int f_{12} \mathrm{d}\overrightarrow{r}}$

- Semi-empirical formula: $\phi(r) = \phi_0[(\frac{r_0}{r})^{12} - 2(\frac{r_0}{r})^6]$, fig.
- Simplify:

$$\phi(r) = \infty, \qquad r < r_0,$$
$$\phi(r) = -\phi_0(\frac{r_0}{r})^6, \quad r \geq r_0.$$

EOS of real gas $\boxed{B \equiv -\frac{N_A}{2}\int f_{12}\mathrm{d}\overrightarrow{r}}$

- Semi-empirical formula: $\phi(r) = \phi_0[(\frac{r_0}{r})^{12} - 2(\frac{r_0}{r})^6]$, fig.
- Simplify:

$$\phi(r) = \infty, \qquad r < r_0,$$
$$\phi(r) = -\phi_0(\frac{r_0}{r})^6, \qquad r \geq r_0.$$

- $B = -\frac{N_A}{2}\int f_{12}\mathrm{d}\overrightarrow{r}$

EOS of real gas $\boxed{B \equiv -\frac{N_A}{2}\int f_{12}\mathrm{d}\overrightarrow{r}}$

- Semi-empirical formula: $\phi(r) = \phi_0[(\frac{r_0}{r})^{12} - 2(\frac{r_0}{r})^6]$, fig.
- Simplify:
  $\phi(r) = \infty, \qquad\qquad r < r_0,$
  $\phi(r) = -\phi_0(\frac{r_0}{r})^6, \quad r \geq r_0.$
- $B = -\frac{N_A}{2}\int f_{12}\mathrm{d}\overrightarrow{r} = -\frac{N_A}{2}\int(e^{-\beta\phi(\overrightarrow{r})} - 1)\mathrm{d}\overrightarrow{r}$

EOS of real gas $\boxed{B \equiv -\frac{N_A}{2}\int f_{12}\mathrm{d}\overrightarrow{r}}$

- Semi-empirical formula: $\phi(r) = \phi_0[(\frac{r_0}{r})^{12} - 2(\frac{r_0}{r})^6]$, fig.
- Simplify:

$$\phi(r) = \infty, \qquad r < r_0,$$
$$\phi(r) = -\phi_0(\frac{r_0}{r})^6, \quad r \geq r_0.$$

- $B = -\frac{N_A}{2}\int f_{12}\mathrm{d}\overrightarrow{r} = -\frac{N_A}{2}\int(e^{-\beta\phi(\overrightarrow{r})} - 1)\mathrm{d}\overrightarrow{r}$

$$= -2\pi N_A \int_0^\infty (e^{-\frac{\phi(r)}{kT}} - 1)r^2\mathrm{d}r$$

EOS of real gas $\boxed{B \equiv -\frac{N_A}{2}\int f_{12} \mathrm{d}\overrightarrow{r}}$

- Semi-empirical formula: $\phi(r) = \phi_0[(\frac{r_0}{r})^{12} - 2(\frac{r_0}{r})^6]$, fig.
- Simplify:

$$\phi(r) = \infty, \qquad r < r_0,$$
$$\phi(r) = -\phi_0(\frac{r_0}{r})^6, \quad r \geq r_0.$$

- $B = -\frac{N_A}{2}\int f_{12}\mathrm{d}\overrightarrow{r} = -\frac{N_A}{2}\int(e^{-\beta\phi(\overrightarrow{r})} - 1)\mathrm{d}\overrightarrow{r}$

$$= -2\pi N_A \int_0^\infty (e^{-\frac{\phi(r)}{kT}} - 1) r^2 \mathrm{d}r$$
$$= -2\pi N_A [\int_0^{r_0}(-r^2)\mathrm{d}r + \int_{r_0}^\infty (e^{\frac{\phi_0}{kT}(\frac{r_0}{r})^6} - 1) r^2 \mathrm{d}r]$$

EOS of real gas $B \equiv -\frac{N_A}{2}\int f_{12}\mathrm{d}\overrightarrow{r}$

- Semi-empirical formula: $\phi(r) = \phi_0[(\frac{r_0}{r})^{12} - 2(\frac{r_0}{r})^6]$, fig.
- Simplify:

$$\phi(r) = \infty, \qquad r < r_0,$$
$$\phi(r) = -\phi_0(\frac{r_0}{r})^6, \quad r \geq r_0.$$

- $B = -\frac{N_A}{2}\int f_{12}\mathrm{d}\overrightarrow{r} = -\frac{N_A}{2}\int(e^{-\beta\phi(\overrightarrow{r})} - 1)\mathrm{d}\overrightarrow{r}$

$$= -2\pi N_A \int_0^\infty (e^{-\frac{\phi(r)}{kT}} - 1)r^2\mathrm{d}r$$
$$= -2\pi N_A[\int_0^{r_0}(-r^2)\mathrm{d}r + \int_{r_0}^\infty (e^{\frac{\phi_0}{kT}(\frac{r_0}{r})^6} - 1)r^2\mathrm{d}r]$$
$$= 2\pi N_A[\frac{r_0^3}{3} - \int_{r_0}^\infty (e^{\frac{\phi_0}{kT}(\frac{r_0}{r})^6} - 1)r^2\mathrm{d}r].$$

EOS of real gas $\boxed{B \equiv -\frac{N_A}{2}\int f_{12}\mathrm{d}\overrightarrow{r}}$

- Semi-empirical formula: $\phi(r) = \phi_0[(\frac{r_0}{r})^{12} - 2(\frac{r_0}{r})^6]$, fig.
- Simplify:

$$\phi(r) = \infty, \qquad r < r_0,$$
$$\phi(r) = -\phi_0(\frac{r_0}{r})^6, \quad r \geq r_0.$$

- $B = -\frac{N_A}{2}\int f_{12}\mathrm{d}\overrightarrow{r} = -\frac{N_A}{2}\int(e^{-\beta\phi(\overrightarrow{r})} - 1)\mathrm{d}\overrightarrow{r}$

$$= -2\pi N_A \int_0^\infty (e^{-\frac{\phi(r)}{kT}} - 1)r^2\mathrm{d}r$$
$$= -2\pi N_A[\int_0^{r_0}(-r^2)\mathrm{d}r + \int_{r_0}^\infty (e^{\frac{\phi_0}{kT}(\frac{r_0}{r})^6} - 1)r^2\mathrm{d}r]$$
$$= 2\pi N_A[\frac{r_0^3}{3} - \int_{r_0}^\infty (e^{\frac{\phi_0}{kT}(\frac{r_0}{r})^6} - 1)r^2\mathrm{d}r].$$

- Simplify, at high temperature, molecule's kinetic energy can be greater than the potential energy ϕ_0, i.e., $\phi_0 \ll kT$,

EOS of real gas $\boxed{B \equiv -\frac{N_A}{2}\int f_{12}\mathrm{d}\overrightarrow{r}}$

- Semi-empirical formula: $\phi(r) = \phi_0[(\frac{r_0}{r})^{12} - 2(\frac{r_0}{r})^6]$, fig.
- Simplify:

  $\phi(r) = \infty, \qquad r < r_0,$

  $\phi(r) = -\phi_0(\frac{r_0}{r})^6, \quad r \geq r_0.$
- $B = -\frac{N_A}{2}\int f_{12}\mathrm{d}\overrightarrow{r} = -\frac{N_A}{2}\int(e^{-\beta\phi(\overrightarrow{r})} - 1)\mathrm{d}\overrightarrow{r}$

  $= -2\pi N_A \int_0^\infty (e^{-\frac{\phi(r)}{kT}} - 1)r^2\mathrm{d}r$

  $= -2\pi N_A[\int_0^{r_0}(-r^2)\mathrm{d}r + \int_{r_0}^\infty (e^{\frac{\phi_0}{kT}(\frac{r_0}{r})^6} - 1)r^2\mathrm{d}r]$

  $= 2\pi N_A[\frac{r_0^3}{3} - \int_{r_0}^\infty (e^{\frac{\phi_0}{kT}(\frac{r_0}{r})^6} - 1)r^2\mathrm{d}r].$
- Simplify, at high temperature, molecule's kinetic energy can be greater than the potential energy ϕ_0, i.e., $\phi_0 \ll kT$, then $e^{\frac{\phi_0}{kT}(\frac{r_0}{r})^6} \simeq 1 + \frac{\phi_0}{kT}(\frac{r_0}{r})^6$.

EOS of real gas $\boxed{B = 2\pi N_A[\frac{r_0^3}{3} - \int_{r_0}^{\infty}(e^{\frac{\phi_0}{kT}(\frac{r_0}{r})^6} - 1)r^2\mathrm{d}r]}$

- $\int_{r_0}^{\infty}(e^{\frac{\phi_0}{kT}(\frac{r_0}{r})^6} - 1)r^2\mathrm{d}r \simeq \int_{r_0}^{\infty}\frac{\phi_0}{kT}(\frac{r_0}{r})^6 r^2\mathrm{d}r$

EOS of real gas $\boxed{B = 2\pi N_A[\frac{r_0^3}{3} - \int_{r_0}^{\infty}(e^{\frac{\phi_0}{kT}(\frac{r_0}{r})^6} - 1)r^2\mathrm{d}r]}$

- $\int_{r_0}^{\infty}(e^{\frac{\phi_0}{kT}(\frac{r_0}{r})^6} - 1)r^2\mathrm{d}r \simeq \int_{r_0}^{\infty} \frac{\phi_0}{kT}(\frac{r_0}{r})^6 r^2\mathrm{d}r$
  $= \frac{\phi_0 r_0^6}{kT}\int_{r_0}^{\infty} r^{-4}\mathrm{d}r$

EOS of real gas $\boxed{B = 2\pi N_A[\frac{r_0^3}{3} - \int_{r_0}^{\infty}(e^{\frac{\phi_0}{kT}(\frac{r_0}{r})^6} - 1)r^2\mathrm{d}r]}$

- $\int_{r_0}^{\infty}(e^{\frac{\phi_0}{kT}(\frac{r_0}{r})^6} - 1)r^2\mathrm{d}r \simeq \int_{r_0}^{\infty}\frac{\phi_0}{kT}(\frac{r_0}{r})^6 r^2\mathrm{d}r$
  $= \frac{\phi_0 r_0^6}{kT}\int_{r_0}^{\infty} r^{-4}\mathrm{d}r = \frac{\phi_0 r_0^3}{3kT}$.

EOS of real gas $\boxed{B = 2\pi N_A[\frac{r_0^3}{3} - \int_{r_0}^{\infty}(e^{\frac{\phi_0}{kT}(\frac{r_0}{r})^6} - 1)r^2 \mathrm{d}r]}$

- $\int_{r_0}^{\infty}(e^{\frac{\phi_0}{kT}(\frac{r_0}{r})^6} - 1)r^2 \mathrm{d}r \simeq \int_{r_0}^{\infty} \frac{\phi_0}{kT}(\frac{r_0}{r})^6 r^2 \mathrm{d}r$
  $= \frac{\phi_0 r_0^6}{kT}\int_{r_0}^{\infty} r^{-4}\mathrm{d}r = \frac{\phi_0 r_0^3}{3kT}$.
- $\therefore B \simeq 2\pi N_A(\frac{r_0^3}{3} - \frac{\phi_0 r_0^3}{3kT})$.

EOS of real gas $\boxed{B = 2\pi N_A[\frac{r_0^3}{3} - \int_{r_0}^{\infty}(e^{\frac{\phi_0}{kT}(\frac{r_0}{r})^6} - 1)r^2\mathrm{d}r]}$

- $\int_{r_0}^{\infty}(e^{\frac{\phi_0}{kT}(\frac{r_0}{r})^6} - 1)r^2\mathrm{d}r \simeq \int_{r_0}^{\infty}\frac{\phi_0}{kT}(\frac{r_0}{r})^6 r^2\mathrm{d}r$
  $= \frac{\phi_0 r_0^6}{kT}\int_{r_0}^{\infty} r^{-4}\mathrm{d}r = \frac{\phi_0 r_0^3}{3kT}$.
- $\therefore B \simeq 2\pi N_A(\frac{r_0^3}{3} - \frac{\phi_0 r_0^3}{3kT})$.
- Define $b = \frac{2}{3}\pi N_A r_0^3$, $a = \frac{2}{3}\pi N_A^2 \phi_0 r_0^3$, then
  $B = b - \frac{a}{N_A kT}$.

EOS of real gas $\boxed{B = 2\pi N_A[\frac{r_0^3}{3} - \int_{r_0}^{\infty}(e^{\frac{\phi_0}{kT}(\frac{r_0}{r})^6} - 1)r^2\mathrm{d}r]}$

- $\int_{r_0}^{\infty}(e^{\frac{\phi_0}{kT}(\frac{r_0}{r})^6} - 1)r^2\mathrm{d}r \simeq \int_{r_0}^{\infty}\frac{\phi_0}{kT}(\frac{r_0}{r})^6 r^2\mathrm{d}r$
  $= \frac{\phi_0 r_0^6}{kT}\int_{r_0}^{\infty} r^{-4}\mathrm{d}r = \frac{\phi_0 r_0^3}{3kT}$.
- $\therefore B \simeq 2\pi N_A(\frac{r_0^3}{3} - \frac{\phi_0 r_0^3}{3kT})$.
- Define $b = \frac{2}{3}\pi N_A r_0^3$, $a = \frac{2}{3}\pi N_A^2 \phi_0 r_0^3$, then
  $B = b - \frac{a}{N_A kT}$.
- $pV = NkT(1 + \frac{nB}{V}) = NkT(1 + \frac{nb}{V}) - \frac{n^2 a}{V}$.

EOS of real gas $\boxed{B = 2\pi N_A[\frac{r_0^3}{3} - \int_{r_0}^{\infty}(e^{\frac{\phi_0}{kT}(\frac{r_0}{r})^6} - 1)r^2 \mathrm{d}r]}$

- $\int_{r_0}^{\infty}(e^{\frac{\phi_0}{kT}(\frac{r_0}{r})^6} - 1)r^2 \mathrm{d}r \simeq \int_{r_0}^{\infty} \frac{\phi_0}{kT}(\frac{r_0}{r})^6 r^2 \mathrm{d}r$
  $= \frac{\phi_0 r_0^6}{kT}\int_{r_0}^{\infty} r^{-4}\mathrm{d}r = \frac{\phi_0 r_0^3}{3kT}$.
- $\therefore B \simeq 2\pi N_A(\frac{r_0^3}{3} - \frac{\phi_0 r_0^3}{3kT})$.
- Define $b = \frac{2}{3}\pi N_A r_0^3$, $a = \frac{2}{3}\pi N_A^2 \phi_0 r_0^3$, then
  $B = b - \frac{a}{N_A kT}$.
- $pV = NkT(1 + \frac{nB}{V}) = NkT(1 + \frac{nb}{V}) - \frac{n^2 a}{V}$.
- As $\frac{nb}{V} = \frac{n}{V}\frac{2}{3}\pi N_A r_0^3 = \frac{\frac{2}{3}\pi r_0^3}{V/N} < 1$,

EOS of real gas $\boxed{B = 2\pi N_A[\frac{r_0^3}{3} - \int_{r_0}^{\infty}(e^{\frac{\phi_0}{kT}(\frac{r_0}{r})^6} - 1)r^2\mathrm{d}r]}$

- $\int_{r_0}^{\infty}(e^{\frac{\phi_0}{kT}(\frac{r_0}{r})^6} - 1)r^2\mathrm{d}r \simeq \int_{r_0}^{\infty}\frac{\phi_0}{kT}(\frac{r_0}{r})^6 r^2\mathrm{d}r$
  $= \frac{\phi_0 r_0^6}{kT}\int_{r_0}^{\infty} r^{-4}\mathrm{d}r = \frac{\phi_0 r_0^3}{3kT}$.
- $\therefore B \simeq 2\pi N_A(\frac{r_0^3}{3} - \frac{\phi_0 r_0^3}{3kT})$.
- Define $b = \frac{2}{3}\pi N_A r_0^3$, $a = \frac{2}{3}\pi N_A^2 \phi_0 r_0^3$, then
  $B = b - \frac{a}{N_A kT}$.
- $pV = NkT(1 + \frac{nB}{V}) = NkT(1 + \frac{nb}{V}) - \frac{n^2 a}{V}$.
- As $\frac{nb}{V} = \frac{n}{V}\frac{2}{3}\pi N_A r_0^3 = \frac{\frac{2}{3}\pi r_0^3}{V/N} < 1$, $1 + \frac{nb}{V} \simeq \frac{1}{1-\frac{nb}{V}}$.

EOS of real gas $\boxed{B = 2\pi N_A[\frac{r_0^3}{3} - \int_{r_0}^{\infty}(e^{\frac{\phi_0}{kT}(\frac{r_0}{r})^6} - 1)r^2\mathrm{d}r]}$

- $\int_{r_0}^{\infty}(e^{\frac{\phi_0}{kT}(\frac{r_0}{r})^6} - 1)r^2\mathrm{d}r \simeq \int_{r_0}^{\infty} \frac{\phi_0}{kT}(\frac{r_0}{r})^6 r^2\mathrm{d}r$
  $= \frac{\phi_0 r_0^6}{kT}\int_{r_0}^{\infty} r^{-4}\mathrm{d}r = \frac{\phi_0 r_0^3}{3kT}$.
- $\therefore B \simeq 2\pi N_A(\frac{r_0^3}{3} - \frac{\phi_0 r_0^3}{3kT})$.
- Define $b = \frac{2}{3}\pi N_A r_0^3$, $a = \frac{2}{3}\pi N_A^2 \phi_0 r_0^3$, then
  $B = b - \frac{a}{N_A kT}$.
- $pV = NkT(1 + \frac{nB}{V}) = NkT(1 + \frac{nb}{V}) - \frac{n^2 a}{V}$.
- As $\frac{nb}{V} = \frac{n}{V}\frac{2}{3}\pi N_A r_0^3 = \frac{\frac{2}{3}\pi r_0^3}{V/N} < 1$, $1 + \frac{nb}{V} \simeq \frac{1}{1-\frac{nb}{V}}$.
- $\Rightarrow p = \frac{NkT}{V-nb} - \frac{n^2 a}{V^2}$,

EOS of real gas $\boxed{B = 2\pi N_A[\frac{r_0^3}{3} - \int_{r_0}^{\infty}(e^{\frac{\phi_0}{kT}(\frac{r_0}{r})^6} - 1)r^2\mathrm{d}r]}$

- $\int_{r_0}^{\infty}(e^{\frac{\phi_0}{kT}(\frac{r_0}{r})^6} - 1)r^2\mathrm{d}r \simeq \int_{r_0}^{\infty}\frac{\phi_0}{kT}(\frac{r_0}{r})^6 r^2\mathrm{d}r$
  $= \frac{\phi_0 r_0^6}{kT}\int_{r_0}^{\infty} r^{-4}\mathrm{d}r = \frac{\phi_0 r_0^3}{3kT}$.
- $\therefore B \simeq 2\pi N_A(\frac{r_0^3}{3} - \frac{\phi_0 r_0^3}{3kT})$.
- Define $b = \frac{2}{3}\pi N_A r_0^3$, $a = \frac{2}{3}\pi N_A^2\phi_0 r_0^3$, then
  $B = b - \frac{a}{N_A kT}$.
- $pV = NkT(1 + \frac{nB}{V}) = NkT(1 + \frac{nb}{V}) - \frac{n^2 a}{V}$.
- As $\frac{nb}{V} = \frac{n}{V}\frac{2}{3}\pi N_A r_0^3 = \frac{\frac{2}{3}\pi r_0^3}{V/N} < 1$, $1 + \frac{nb}{V} \simeq \frac{1}{1-\frac{nb}{V}}$.
- $\Rightarrow p = \frac{NkT}{V-nb} - \frac{n^2 a}{V^2}$, or $(p + \frac{n^2 a}{V^2})(V - nb) = NkT$.
  van der Waals equation (3.5.2).

Table of contents

9.7 Thermal capacity of solid

9.7 Thermal capacity of solid

- Object: solid, atoms vibrate around the equilibrium position.

9.7 Thermal capacity of solid

- Object: solid, atoms vibrate around the equilibrium position.
- System: N atoms, $3N$ degrees of freedom.

9.7 Thermal capacity of solid

- Object: solid, atoms vibrate around the equilibrium position.
- System: N atoms, $3N$ degrees of freedom. Each one has a displacement ξ_i, and momentum p_{ξ_i}.

9.7 Thermal capacity of solid

- Object: solid, atoms vibrate around the equilibrium position.
- System: N atoms, $3N$ degrees of freedom. Each one has a displacement ξ_i, and momentum p_{ξ_i}.
- Total kinetic energy: $\sum_{i=1}^{3N} \frac{p_{\xi_i}^2}{2m}$,

9.7 Thermal capacity of solid

- Object: solid, atoms vibrate around the equilibrium position.
- System: N atoms, $3N$ degrees of freedom. Each one has a displacement ξ_i, and momentum p_{ξ_i}.
- Total kinetic energy: $\sum_{i=1}^{3N} \frac{p_{\xi_i}^2}{2m}$,

  potential energy:

  $\phi \simeq \phi_0 + \sum_i (\frac{\partial \phi}{\partial \xi_i})_0 \xi_i + \frac{1}{2} \sum_{i,j} (\frac{\partial^2 \phi}{\partial \xi_i \partial \xi_j})_0 \xi_i \xi_j$.

  (Only suitable for small displacement.)

9.7 Thermal capacity of solid

- Object: solid, atoms vibrate around the equilibrium position.
- System: N atoms, $3N$ degrees of freedom. Each one has a displacement ξ_i, and momentum p_{ξ_i}.
- Total kinetic energy: $\sum_{i=1}^{3N} \frac{p_{\xi_i}^2}{2m}$,

  potential energy:

  $\phi \simeq \phi_0 + \sum_i (\frac{\partial \phi}{\partial \xi_i})_0 \xi_i + \frac{1}{2} \sum_{i,j} (\frac{\partial^2 \phi}{\partial \xi_i \partial \xi_j})_0 \xi_i \xi_j$.

  (Only suitable for small displacement.)
- $(\frac{\partial \phi}{\partial \xi_i})_0$ is the force exerted on the atom i at the equilibrium position,

9.7 Thermal capacity of solid

- Object: solid, atoms vibrate around the equilibrium position.
- System: N atoms, $3N$ degrees of freedom. Each one has a displacement ξ_i, and momentum p_{ξ_i}.
- Total kinetic energy: $\sum_{i=1}^{3N} \frac{p_{\xi_i}^2}{2m}$,

  potential energy:

  $\phi \simeq \phi_0 + \sum_i (\frac{\partial \phi}{\partial \xi_i})_0 \xi_i + \frac{1}{2} \sum_{i,j} (\frac{\partial^2 \phi}{\partial \xi_i \partial \xi_j})_0 \xi_i \xi_j$.

  (Only suitable for small displacement.)
- $(\frac{\partial \phi}{\partial \xi_i})_0$ is the force exerted on the atom i at the equilibrium position, i.e., $(\frac{\partial \phi}{\partial \xi_i})_0 = 0$.

Total energy of solid

- Total energy $E = \sum_{i=1}^{3N} \frac{p_{\xi_i}^2}{2m} + \frac{1}{2}\sum_{i,j} a_{i,j}\xi_i\xi_j + \phi_0$.

Total energy of solid

- Total energy $E = \sum_{i=1}^{3N} \frac{p_{\xi_i}^2}{2m} + \frac{1}{2}\sum_{i,j} a_{i,j}\xi_i\xi_j + \phi_0$.
- In principle, can be transferred to:
  $E = \frac{1}{2}\sum_{i=1}^{3N}(p_i^2 + \omega_i^2 q_i^2) + \phi_0$.

Total energy of solid

- Total energy $E = \sum_{i=1}^{3N} \frac{p_{\xi_i}^2}{2m} + \frac{1}{2}\sum_{i,j} a_{i,j}\xi_i\xi_j + \phi_0$.
- In principle, can be transferred to:
  $E = \frac{1}{2}\sum_{i=1}^{3N}(p_i^2 + \omega_i^2 q_i^2) + \phi_0$.
  It can be taken as $3N$ harmonic vibrations.

Total energy of solid

- Total energy $E = \sum_{i=1}^{3N} \frac{p_{\xi_i}^2}{2m} + \frac{1}{2}\sum_{i,j} a_{i,j}\xi_i\xi_j + \phi_0$.
- In principle, can be transferred to:
  $E = \frac{1}{2}\sum_{i=1}^{3N}(p_i^2 + \omega_i^2 q_i^2) + \phi_0$.
  It can be taken as $3N$ harmonic vibrations.
- Einstein's model: suppose all the vibrations vibrate at the same frequency ω, and the energy for each one:
  $\varepsilon_n = \hbar\omega(n + \frac{1}{2})$; total $E = \sum_{i=1}^{3N} \hbar\omega(n_i + \frac{1}{2})$.

Total energy of solid

- Total energy $E = \sum_{i=1}^{3N} \frac{p_{\xi_i}^2}{2m} + \frac{1}{2}\sum_{i,j} a_{i,j}\xi_i\xi_j + \phi_0$.
- In principle, can be transferred to:
  $E = \frac{1}{2}\sum_{i=1}^{3N}(p_i^2 + \omega_i^2 q_i^2) + \phi_0$.
  It can be taken as $3N$ harmonic vibrations.
- Einstein's model: suppose all the vibrations vibrate at the same frequency ω, and the energy for each one:
  $\varepsilon_n = \hbar\omega(n+\frac{1}{2})$; total $E = \sum_{i=1}^{3N} \hbar\omega(n_i + \frac{1}{2})$.
- More generally: ω is not the same (not independent).

Total energy of solid

- Total energy $E = \sum_{i=1}^{3N} \frac{p_{\xi_i}^2}{2m} + \frac{1}{2}\sum_{i,j} a_{i,j}\xi_i\xi_j + \phi_0$.
- In principle, can be transferred to:
  $E = \frac{1}{2}\sum_{i=1}^{3N}(p_i^2 + \omega_i^2 q_i^2) + \phi_0$.
  It can be taken as $3N$ harmonic vibrations.
- Einstein's model: suppose all the vibrations vibrate at the same frequency ω, and the energy for each one:
  $\varepsilon_n = \hbar\omega(n + \frac{1}{2})$; total $E = \sum_{i=1}^{3N} \hbar\omega(n_i + \frac{1}{2})$.
- More generally: ω is not the same (not independent).
  $E = \phi_0 + \sum_{i=1}^{3N} \hbar\omega_i(n_i + \frac{1}{2})$.

Partition function $\boxed{E = \phi_0 + \sum_{i=1}^{3N} \hbar\omega_i (n_i + \frac{1}{2})}$

- Partition function: $Z = \sum_s e^{-\beta E_s}$

Partition function $\boxed{E = \phi_0 + \sum_{i=1}^{3N} \hbar\omega_i(n_i + \frac{1}{2})}$

- Partition function: $Z = \sum_s e^{-\beta E_s}$

$$= e^{-\beta\phi_0} \sum_{\{n_i\}} e^{-\beta \sum_i \hbar\omega_i (n_i + \frac{1}{2})}$$

Partition function $\boxed{E = \phi_0 + \sum_{i=1}^{3N} \hbar\omega_i(n_i + \frac{1}{2})}$

- Partition function: $Z = \sum_s e^{-\beta E_s}$

$$= e^{-\beta\phi_0} \sum_{\{n_i\}} e^{-\beta \sum_i \hbar\omega_i(n_i+\frac{1}{2})} = e^{-\beta\phi_0} \sum_{\{n_i\}} \prod_i e^{-\beta\hbar\omega_i(n_i+\frac{1}{2})}$$

Partition function $\boxed{E = \phi_0 + \sum_{i=1}^{3N} \hbar\omega_i(n_i + \frac{1}{2})}$

- Partition function: $Z = \sum_s e^{-\beta E_s}$

$$= e^{-\beta\phi_0} \sum_{\{n_i\}} e^{-\beta \sum_i \hbar\omega_i(n_i+\frac{1}{2})} = e^{-\beta\phi_0} \sum_{\{n_i\}} \prod_i e^{-\beta\hbar\omega_i(n_i+\frac{1}{2})}$$

$$= e^{-\beta\phi_0} \prod_i \sum_{n_i=0}^{\infty} e^{-\beta\hbar\omega_i(n_i+\frac{1}{2})}$$

Partition function $\boxed{E = \phi_0 + \sum_{i=1}^{3N} \hbar\omega_i(n_i + \frac{1}{2})}$

- Partition function: $Z = \sum\limits_s e^{-\beta E_s}$

$$= e^{-\beta\phi_0} \sum_{\{n_i\}} e^{-\beta \sum\limits_i \hbar\omega_i(n_i+\frac{1}{2})} = e^{-\beta\phi_0} \sum_{\{n_i\}} \prod_i e^{-\beta\hbar\omega_i(n_i+\frac{1}{2})}$$

$$= e^{-\beta\phi_0} \prod_i \sum_{n_i=0}^{\infty} e^{-\beta\hbar\omega_i(n_i+\frac{1}{2})} = e^{-\beta\phi_0} \prod_i \frac{e^{-\frac{\beta\hbar\omega_i}{2}}}{1-e^{-\beta\hbar\omega_i}}.$$

Partition function $\boxed{E = \phi_0 + \sum_{i=1}^{3N} \hbar\omega_i(n_i + \frac{1}{2})}$

- Partition function: $Z = \sum_s e^{-\beta E_s}$

$$= e^{-\beta\phi_0} \sum_{\{n_i\}} e^{-\beta \sum_i \hbar\omega_i(n_i+\frac{1}{2})} = e^{-\beta\phi_0} \sum_{\{n_i\}} \prod_i e^{-\beta\hbar\omega_i(n_i+\frac{1}{2})}$$

$$= e^{-\beta\phi_0} \prod_i \sum_{n_i=0}^{\infty} e^{-\beta\hbar\omega_i(n_i+\frac{1}{2})} = e^{-\beta\phi_0} \prod_i \frac{e^{-\frac{\beta\hbar\omega_i}{2}}}{1-e^{-\beta\hbar\omega_i}}.$$

- Internal energy: $U = -\frac{\partial \ln Z}{\partial \beta}$

Partition function $\boxed{E=\phi_0+\sum_{i=1}^{3N}\hbar\omega_i(n_i+\frac{1}{2})}$

- Partition function: $Z=\sum_s e^{-\beta E_s}$

$$=e^{-\beta\phi_0}\sum_{\{n_i\}}e^{-\beta\sum_i\hbar\omega_i(n_i+\frac{1}{2})}=e^{-\beta\phi_0}\sum_{\{n_i\}}\prod_i e^{-\beta\hbar\omega_i(n_i+\frac{1}{2})}$$

$$=e^{-\beta\phi_0}\prod_i\sum_{n_i=0}^{\infty}e^{-\beta\hbar\omega_i(n_i+\frac{1}{2})}=e^{-\beta\phi_0}\prod_i\frac{e^{-\frac{\beta\hbar\omega_i}{2}}}{1-e^{-\beta\hbar\omega_i}}.$$

- Internal energy: $U=-\frac{\partial\ln Z}{\partial\beta}$

$$=\phi_0+\sum_{i=1}^{3N}\frac{1}{2}\hbar\omega_i+\sum_{i=1}^{3N}\frac{\hbar\omega_i e^{-\beta\hbar\omega_i}}{1-e^{-\beta\hbar\omega_i}}$$

Partition function $\boxed{E = \phi_0 + \sum_{i=1}^{3N} \hbar\omega_i(n_i + \frac{1}{2})}$

- Partition function: $Z = \sum_s e^{-\beta E_s}$

$$= e^{-\beta\phi_0} \sum_{\{n_i\}} e^{-\beta \sum_i \hbar\omega_i(n_i+\frac{1}{2})} = e^{-\beta\phi_0} \sum_{\{n_i\}} \prod_i e^{-\beta\hbar\omega_i(n_i+\frac{1}{2})}$$

$$= e^{-\beta\phi_0} \prod_i \sum_{n_i=0}^{\infty} e^{-\beta\hbar\omega_i(n_i+\frac{1}{2})} = e^{-\beta\phi_0} \prod_i \frac{e^{-\frac{\beta\hbar\omega_i}{2}}}{1-e^{-\beta\hbar\omega_i}}.$$

- Internal energy: $U = -\frac{\partial \ln Z}{\partial \beta}$

$$= \phi_0 + \sum_{i=1}^{3N} \frac{1}{2}\hbar\omega_i + \sum_{i=1}^{3N} \frac{\hbar\omega_i e^{-\beta\hbar\omega_i}}{1-e^{-\beta\hbar\omega_i}} \equiv U_0 + \sum_{i=1}^{3N} \frac{\hbar\omega_i}{e^{\beta\hbar\omega_i}-1}.$$

Partition function $\boxed{E = \phi_0 + \sum_{i=1}^{3N} \hbar\omega_i(n_i + \frac{1}{2})}$

- Partition function: $Z = \sum_s e^{-\beta E_s}$

$$= e^{-\beta\phi_0} \sum_{\{n_i\}} e^{-\beta \sum_i \hbar\omega_i(n_i+\frac{1}{2})} = e^{-\beta\phi_0} \sum_{\{n_i\}} \prod_i e^{-\beta\hbar\omega_i(n_i+\frac{1}{2})}$$

$$= e^{-\beta\phi_0} \prod_i \sum_{n_i=0}^{\infty} e^{-\beta\hbar\omega_i(n_i+\frac{1}{2})} = e^{-\beta\phi_0} \prod_i \frac{e^{-\frac{\beta\hbar\omega_i}{2}}}{1-e^{-\beta\hbar\omega_i}}.$$

- Internal energy: $U = -\frac{\partial \ln Z}{\partial \beta}$

$$= \phi_0 + \sum_{i=1}^{3N} \frac{1}{2}\hbar\omega_i + \sum_{i=1}^{3N} \frac{\hbar\omega_i e^{-\beta\hbar\omega_i}}{1-e^{-\beta\hbar\omega_i}} \equiv U_0 + \sum_{i=1}^{3N} \frac{\hbar\omega_i}{e^{\beta\hbar\omega_i}-1}.$$

- Simplest case: $\omega_i = \omega$,

Partition function $\boxed{E = \phi_0 + \sum_{i=1}^{3N} \hbar\omega_i (n_i + \frac{1}{2})}$

- Partition function: $Z = \sum_s e^{-\beta E_s}$

$$= e^{-\beta\phi_0} \sum_{\{n_i\}} e^{-\beta \sum_i \hbar\omega_i (n_i + \frac{1}{2})} = e^{-\beta\phi_0} \sum_{\{n_i\}} \prod_i e^{-\beta\hbar\omega_i (n_i + \frac{1}{2})}$$

$$= e^{-\beta\phi_0} \prod_i \sum_{n_i=0}^{\infty} e^{-\beta\hbar\omega_i (n_i + \frac{1}{2})} = e^{-\beta\phi_0} \prod_i \frac{e^{-\frac{\beta\hbar\omega_i}{2}}}{1 - e^{-\beta\hbar\omega_i}}.$$

- Internal energy: $U = -\frac{\partial \ln Z}{\partial \beta}$

$$= \phi_0 + \sum_{i=1}^{3N} \frac{1}{2}\hbar\omega_i + \sum_{i=1}^{3N} \frac{\hbar\omega_i e^{-\beta\hbar\omega_i}}{1 - e^{-\beta\hbar\omega_i}} \equiv U_0 + \sum_{i=1}^{3N} \frac{\hbar\omega_i}{e^{\beta\hbar\omega_i} - 1}.$$

- Simplest case: $\omega_i = \omega$, $U = \phi_0 + \frac{3}{2} N\hbar\omega + \frac{3N\hbar\omega}{e^{\beta\hbar\omega} - 1}$,

Partition function $\boxed{E = \phi_0 + \sum_{i=1}^{3N} \hbar\omega_i(n_i + \frac{1}{2})}$

- Partition function: $Z = \sum_s e^{-\beta E_s}$

$$= e^{-\beta\phi_0} \sum_{\{n_i\}} e^{-\beta \sum_i \hbar\omega_i(n_i+\frac{1}{2})} = e^{-\beta\phi_0} \sum_{\{n_i\}} \prod_i e^{-\beta\hbar\omega_i(n_i+\frac{1}{2})}$$

$$= e^{-\beta\phi_0} \prod_i \sum_{n_i=0}^{\infty} e^{-\beta\hbar\omega_i(n_i+\frac{1}{2})} = e^{-\beta\phi_0} \prod_i \frac{e^{-\frac{\beta\hbar\omega_i}{2}}}{1-e^{-\beta\hbar\omega_i}}.$$

- Internal energy: $U = -\frac{\partial \ln Z}{\partial\beta}$

$$= \phi_0 + \sum_{i=1}^{3N} \frac{1}{2}\hbar\omega_i + \sum_{i=1}^{3N} \frac{\hbar\omega_i e^{-\beta\hbar\omega_i}}{1-e^{-\beta\hbar\omega_i}} \equiv U_0 + \sum_{i=1}^{3N} \frac{\hbar\omega_i}{e^{\beta\hbar\omega_i}-1}.$$

- Simplest case: $\omega_i = \omega$, $U = \phi_0 + \frac{3}{2}N\hbar\omega + \frac{3N\hbar\omega}{e^{\beta\hbar\omega}-1}$, back to Einstein's model (7.7.3).

Debye's model $\boxed{U = U_0 + \sum_{i=1}^{3N} \frac{\hbar\omega_i}{e^{\beta\hbar\omega_i}-1}}$

Debye's model $\boxed{U = U_0 + \sum_{i=1}^{3N} \frac{\hbar\omega_i}{e^{\beta\hbar\omega_i} - 1}}$

- Take the solid as continuous elastic medium.

Debye's model $\boxed{U = U_0 + \sum_{i=1}^{3N} \frac{\hbar\omega_i}{e^{\beta\hbar\omega_i}-1}}$

- Take the solid as continuous elastic medium. $3N$ normal vibrations can produce $3N$ different fundamental waves.

Debye's model $\boxed{U = U_0 + \sum_{i=1}^{3N} \frac{\hbar\omega_i}{e^{\beta\hbar\omega_i} - 1}}$

- Take the solid as continuous elastic medium. $3N$ normal vibrations can produce $3N$ different fundamental waves.
- In elastic medium, there exists longitudinal (l) wave and transversal (t) wave (two directions),

Debye's model $\boxed{U = U_0 + \sum_{i=1}^{3N} \frac{\hbar\omega_i}{e^{\beta\hbar\omega_i} - 1}}$

- Take the solid as continuous elastic medium. $3N$ normal vibrations can produce $3N$ different fundamental waves.
- In elastic medium, there exists longitudinal (l) wave and transversal (t) wave (two directions), with dispersion relations: $\omega = c_l k$, $\omega = c_t k$, where c is the speed of sound.

Debye's model $\boxed{U = U_0 + \sum_{i=1}^{3N} \frac{\hbar\omega_i}{e^{\beta\hbar\omega_i}-1}}$

- Take the solid as continuous elastic medium. $3N$ normal vibrations can produce $3N$ different fundamental waves.
- In elastic medium, there exists longitudinal (l) wave and transversal (t) wave (two directions), with dispersion relations: $\omega = c_l k$, $\omega = c_t k$, where c is the speed of sound. For low frequencies, ω_i can be taken as continuous.

Debye's model $\boxed{U = U_0 + \sum_{i=1}^{3N} \frac{\hbar\omega_i}{e^{\beta\hbar\omega_i} - 1}}$

- Take the solid as continuous elastic medium. $3N$ normal vibrations can produce $3N$ different fundamental waves.
- In elastic medium, there exists longitudinal (l) wave and transversal (t) wave (two directions), with dispersion relations: $\omega = c_l k$, $\omega = c_t k$, where c is the speed of sound. For low frequencies, ω_i can be taken as continuous.
- The number of longitudinal normal vibrations (number of states):

Debye's model $\boxed{U = U_0 + \sum_{i=1}^{3N} \frac{\hbar\omega_i}{e^{\beta\hbar\omega_i}-1}}$

- Take the solid as continuous elastic medium. $3N$ normal vibrations can produce $3N$ different fundamental waves.
- In elastic medium, there exists longitudinal (l) wave and transversal (t) wave (two directions), with dispersion relations: $\omega = c_l k$, $\omega = c_t k$, where c is the speed of sound. For low frequencies, ω_i can be taken as continuous.
- The number of longitudinal normal vibrations (number of states): $D(p)\mathrm{d}p = \frac{V}{h^3}4\pi p^2\mathrm{d}p$

Debye's model $\boxed{U = U_0 + \sum_{i=1}^{3N} \frac{\hbar\omega_i}{e^{\beta\hbar\omega_i}-1}}$

- Take the solid as continuous elastic medium. $3N$ normal vibrations can produce $3N$ different fundamental waves.
- In elastic medium, there exists longitudinal (l) wave and transversal (t) wave (two directions), with dispersion relations: $\omega = c_l k$, $\omega = c_t k$, where c is the speed of sound. For low frequencies, ω_i can be taken as continuous.
- The number of longitudinal normal vibrations (number of states): $D(p)\mathrm{d}p = \frac{V}{h^3} 4\pi p^2 \mathrm{d}p = \frac{V}{h^3} 4\pi\hbar^3 k^2 \mathrm{d}k$

Debye's model $\boxed{U = U_0 + \sum_{i=1}^{3N} \frac{\hbar\omega_i}{e^{\beta\hbar\omega_i} - 1}}$

- Take the solid as continuous elastic medium. $3N$ normal vibrations can produce $3N$ different fundamental waves.
- In elastic medium, there exists longitudinal (l) wave and transversal (t) wave (two directions), with dispersion relations: $\omega = c_l k$, $\omega = c_t k$, where c is the speed of sound. For low frequencies, ω_i can be taken as continuous.
- The number of longitudinal normal vibrations (number of states): $D(p)\mathrm{d}p = \frac{V}{h^3}4\pi p^2\mathrm{d}p = \frac{V}{h^3}4\pi\hbar^3 k^2\mathrm{d}k$ $= \frac{V}{2\pi^2}k^2\mathrm{d}k$

Debye's model $\boxed{U = U_0 + \sum_{i=1}^{3N} \frac{\hbar\omega_i}{e^{\beta\hbar\omega_i}-1}}$

- Take the solid as continuous elastic medium. $3N$ normal vibrations can produce $3N$ different fundamental waves.
- In elastic medium, there exists longitudinal (l) wave and transversal (t) wave (two directions), with dispersion relations: $\omega = c_l k$, $\omega = c_t k$, where c is the speed of sound. For low frequencies, ω_i can be taken as continuous.
- The number of longitudinal normal vibrations (number of states): $D(p)\mathrm{d}p = \frac{V}{h^3} 4\pi p^2 \mathrm{d}p = \frac{V}{h^3} 4\pi \hbar^3 k^2 \mathrm{d}k$
$= \frac{V}{2\pi^2} k^2 \mathrm{d}k = \frac{V}{2\pi^2} \frac{1}{c_l^3} \omega^2 \mathrm{d}\omega$

Debye's model $\boxed{U = U_0 + \sum_{i=1}^{3N} \frac{\hbar\omega_i}{e^{\beta\hbar\omega_i}-1}}$

- Take the solid as continuous elastic medium. $3N$ normal vibrations can produce $3N$ different fundamental waves.
- In elastic medium, there exists longitudinal (l) wave and transversal (t) wave (two directions), with dispersion relations: $\omega = c_l k$, $\omega = c_t k$, where c is the speed of sound. For low frequencies, ω_i can be taken as continuous.
- The number of longitudinal normal vibrations (number of states): $D(p)\mathrm{d}p = \frac{V}{h^3}4\pi p^2\mathrm{d}p = \frac{V}{h^3}4\pi\hbar^3 k^2\mathrm{d}k$ $= \frac{V}{2\pi^2}k^2\mathrm{d}k = \frac{V}{2\pi^2}\frac{1}{c_l^3}\omega^2\mathrm{d}\omega \equiv D_l(\omega)\mathrm{d}\omega$.

Debye's model $\boxed{U = U_0 + \sum_{i=1}^{3N} \frac{\hbar\omega_i}{e^{\beta\hbar\omega_i}-1}}$

- Considering the two directions of transversal vibrations: $D_t(\omega)\mathrm{d}\omega = 2\frac{V}{2\pi^2}\frac{1}{c_t^3}\omega^2\mathrm{d}\omega$.

Debye's model $\boxed{U = U_0 + \sum_{i=1}^{3N} \frac{\hbar\omega_i}{e^{\beta\hbar\omega_i}-1}}$

- Considering the two directions of transversal vibrations: $D_t(\omega)\mathrm{d}\omega = 2\frac{V}{2\pi^2}\frac{1}{c_t^3}\omega^2\mathrm{d}\omega$.
- $D(\omega)\mathrm{d}\omega = \frac{V}{2\pi^2}(\frac{1}{c_l^3} + \frac{2}{c_t^3})\omega^2\mathrm{d}\omega$

Debye's model $\boxed{U = U_0 + \sum_{i=1}^{3N} \frac{\hbar\omega_i}{e^{\beta\hbar\omega_i} - 1}}$

- Considering the two directions of transversal vibrations: $D_t(\omega)\mathrm{d}\omega = 2\frac{V}{2\pi^2}\frac{1}{c_t^3}\omega^2\mathrm{d}\omega$.
- $D(\omega)\mathrm{d}\omega = \frac{V}{2\pi^2}(\frac{1}{c_l^3} + \frac{2}{c_t^3})\omega^2\mathrm{d}\omega \equiv B\omega^2\mathrm{d}\omega$, where $B = \frac{V}{2\pi^2}(\frac{1}{c_l^3} + \frac{2}{c_t^3})$.

Debye's model $\boxed{U = U_0 + \sum_{i=1}^{3N} \frac{\hbar\omega_i}{e^{\beta\hbar\omega_i} - 1}}$

- Considering the two directions of transversal vibrations: $D_t(\omega)\mathrm{d}\omega = 2\frac{V}{2\pi^2}\frac{1}{c_t^3}\omega^2\mathrm{d}\omega$.
- $D(\omega)\mathrm{d}\omega = \frac{V}{2\pi^2}(\frac{1}{c_l^3} + \frac{2}{c_t^3})\omega^2\mathrm{d}\omega \equiv B\omega^2\mathrm{d}\omega$, where $B = \frac{V}{2\pi^2}(\frac{1}{c_l^3} + \frac{2}{c_t^3})$.
- Remember the total number of states: $3N$.

Debye's model $\boxed{U = U_0 + \sum_{i=1}^{3N} \frac{\hbar\omega_i}{e^{\beta\hbar\omega_i}-1}}$

- Considering the two directions of transversal vibrations: $D_t(\omega)\mathrm{d}\omega = 2\frac{V}{2\pi^2}\frac{1}{c_t^3}\omega^2\mathrm{d}\omega$.
- $D(\omega)\mathrm{d}\omega = \frac{V}{2\pi^2}(\frac{1}{c_l^3} + \frac{2}{c_t^3})\omega^2\mathrm{d}\omega \equiv B\omega^2\mathrm{d}\omega$, where $B = \frac{V}{2\pi^2}(\frac{1}{c_l^3} + \frac{2}{c_t^3})$.
- Remember the total number of states: $3N$. $\int_0^{\omega_D} B\omega^2\mathrm{d}\omega = 3N$

Debye's model $\boxed{U = U_0 + \sum_{i=1}^{3N} \frac{\hbar\omega_i}{e^{\beta\hbar\omega_i}-1}}$

- Considering the two directions of transversal vibrations: $D_t(\omega)\mathrm{d}\omega = 2\frac{V}{2\pi^2}\frac{1}{c_t^3}\omega^2\mathrm{d}\omega$.
- $D(\omega)\mathrm{d}\omega = \frac{V}{2\pi^2}(\frac{1}{c_l^3} + \frac{2}{c_t^3})\omega^2\mathrm{d}\omega \equiv B\omega^2\mathrm{d}\omega$, where $B = \frac{V}{2\pi^2}(\frac{1}{c_l^3} + \frac{2}{c_t^3})$.
- Remember the total number of states: $3N$. $\int_0^{\omega_D} B\omega^2\mathrm{d}\omega = 3N \Rightarrow \omega_D^3 = \frac{9N}{B}$ is the maximum frequency, called Debye's frequency.

Debye's model $\boxed{U = U_0 + \sum_{i=1}^{3N} \frac{\hbar\omega_i}{e^{\beta\hbar\omega_i} - 1}}$

- Considering the two directions of transversal vibrations: $D_t(\omega)\mathrm{d}\omega = 2\frac{V}{2\pi^2}\frac{1}{c_t^3}\omega^2\mathrm{d}\omega$.
- $D(\omega)\mathrm{d}\omega = \frac{V}{2\pi^2}(\frac{1}{c_l^3} + \frac{2}{c_t^3})\omega^2\mathrm{d}\omega \equiv B\omega^2\mathrm{d}\omega$, where $B = \frac{V}{2\pi^2}(\frac{1}{c_l^3} + \frac{2}{c_t^3})$.
- Remember the total number of states: $3N$. $\int_0^{\omega_D} B\omega^2\mathrm{d}\omega = 3N \Rightarrow \omega_D^3 = \frac{9N}{B}$ is the maximum frequency, called Debye's frequency.
- Internal energy ($\sum \to \int$): $U = U_0 + \int_0^{\omega_D} \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} D(\omega)\mathrm{d}\omega$

Debye's model $\boxed{U = U_0 + \sum_{i=1}^{3N} \frac{\hbar\omega_i}{e^{\beta\hbar\omega_i} - 1}}$

- Considering the two directions of transversal vibrations: $D_t(\omega)\mathrm{d}\omega = 2\frac{V}{2\pi^2}\frac{1}{c_t^3}\omega^2\mathrm{d}\omega$.
- $D(\omega)\mathrm{d}\omega = \frac{V}{2\pi^2}(\frac{1}{c_l^3} + \frac{2}{c_t^3})\omega^2\mathrm{d}\omega \equiv B\omega^2\mathrm{d}\omega$, where $B = \frac{V}{2\pi^2}(\frac{1}{c_l^3} + \frac{2}{c_t^3})$.
- Remember the total number of states: $3N$. $\int_0^{\omega_D} B\omega^2\mathrm{d}\omega = 3N \Rightarrow \omega_D^3 = \frac{9N}{B}$ is the maximum frequency, called Debye's frequency.
- Internal energy ($\sum \to \int$): $U = U_0 + \int_0^{\omega_D} \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} D(\omega)\mathrm{d}\omega = U_0 + B\int_0^{\omega_D} \frac{\hbar\omega^3}{e^{\beta\hbar\omega} - 1}\mathrm{d}\omega$.

Debye's model $\boxed{U = U_0 + \sum_{i=1}^{3N} \frac{\hbar\omega_i}{e^{\beta\hbar\omega_i} - 1}}$

- Considering the two directions of transversal vibrations: $D_t(\omega)\mathrm{d}\omega = 2\frac{V}{2\pi^2}\frac{1}{c_t^3}\omega^2\mathrm{d}\omega$.
- $D(\omega)\mathrm{d}\omega = \frac{V}{2\pi^2}(\frac{1}{c_l^3} + \frac{2}{c_t^3})\omega^2\mathrm{d}\omega \equiv B\omega^2\mathrm{d}\omega$, where $B = \frac{V}{2\pi^2}(\frac{1}{c_l^3} + \frac{2}{c_t^3})$.
- Remember the total number of states: $3N$. $\int_0^{\omega_D} B\omega^2\mathrm{d}\omega = 3N \Rightarrow \omega_D^3 = \frac{9N}{B}$ is the maximum frequency, called Debye's frequency.
- Internal energy ($\sum \to \int$): $U = U_0 + \int_0^{\omega_D} \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} D(\omega)\mathrm{d}\omega = U_0 + B\int_0^{\omega_D} \frac{\hbar\omega^3}{e^{\beta\hbar\omega} - 1}\mathrm{d}\omega$.
- Set $y = \frac{\hbar\omega}{kT}$,

Debye's model $\boxed{U = U_0 + \sum_{i=1}^{3N} \frac{\hbar\omega_i}{e^{\beta\hbar\omega_i}-1}}$

- Considering the two directions of transversal vibrations: $D_t(\omega)\mathrm{d}\omega = 2\frac{V}{2\pi^2}\frac{1}{c_t^3}\omega^2\mathrm{d}\omega$.
- $D(\omega)\mathrm{d}\omega = \frac{V}{2\pi^2}(\frac{1}{c_l^3}+\frac{2}{c_t^3})\omega^2\mathrm{d}\omega \equiv B\omega^2\mathrm{d}\omega$, where $B = \frac{V}{2\pi^2}(\frac{1}{c_l^3}+\frac{2}{c_t^3})$.
- Remember the total number of states: $3N$. $\int_0^{\omega_D} B\omega^2\mathrm{d}\omega = 3N \Rightarrow \omega_D^3 = \frac{9N}{B}$ is the maximum frequency, called Debye's frequency.
- Internal energy ($\sum \to \int$): $U = U_0 + \int_0^{\omega_D} \frac{\hbar\omega}{e^{\beta\hbar\omega}-1}D(\omega)\mathrm{d}\omega = U_0 + B\int_0^{\omega_D}\frac{\hbar\omega^3}{e^{\beta\hbar\omega}-1}\mathrm{d}\omega$.
- Set $y = \frac{\hbar\omega}{kT}$, then $y_D = \frac{\hbar\omega_D}{kT} \equiv \frac{\theta_D}{T}$,

Debye's model $\boxed{U = U_0 + \sum_{i=1}^{3N} \frac{\hbar\omega_i}{e^{\beta\hbar\omega_i}-1}}$

- Considering the two directions of transversal vibrations: $D_t(\omega)\mathrm{d}\omega = 2\frac{V}{2\pi^2}\frac{1}{c_t^3}\omega^2\mathrm{d}\omega$.
- $D(\omega)\mathrm{d}\omega = \frac{V}{2\pi^2}(\frac{1}{c_l^3} + \frac{2}{c_t^3})\omega^2\mathrm{d}\omega \equiv B\omega^2\mathrm{d}\omega$, where $B = \frac{V}{2\pi^2}(\frac{1}{c_l^3} + \frac{2}{c_t^3})$.
- Remember the total number of states: $3N$. $\int_0^{\omega_D} B\omega^2\mathrm{d}\omega = 3N \Rightarrow \omega_D^3 = \frac{9N}{B}$ is the maximum frequency, called Debye's frequency.
- Internal energy ($\sum \to \int$): $U = U_0 + \int_0^{\omega_D} \frac{\hbar\omega}{e^{\beta\hbar\omega}-1}D(\omega)\mathrm{d}\omega = U_0 + B\int_0^{\omega_D} \frac{\hbar\omega^3}{e^{\beta\hbar\omega}-1}\mathrm{d}\omega$.
- Set $y = \frac{\hbar\omega}{kT}$, then $y_D = \frac{\hbar\omega_D}{kT} \equiv \frac{\theta_D}{T}$, where $\theta_D = \frac{\hbar\omega_D}{k}$ is called Debye's temperature.

$$\boxed{U = U_0 + B\int_0^{\omega_D} \frac{\hbar\omega^3}{e^{\beta\hbar\omega}-1}\mathrm{d}\omega}, \boxed{\omega_D^3 = \frac{9N}{B}}, \boxed{y_D = \frac{\hbar\omega_D}{kT}}$$

- $U = U_0 + B\int_0^{\frac{\hbar\omega_D}{kT}} \frac{\hbar\cdot(\frac{\hbar\omega}{kT})^3\cdot(\frac{kT}{\hbar})^3}{e^{\frac{\hbar\omega}{kT}}-1}\frac{kT}{\hbar}\mathrm{d}\frac{\hbar\omega}{kT}$

$\boxed{U = U_0 + B\int_0^{\omega_D} \frac{\hbar\omega^3}{e^{\beta\hbar\omega}-1}\mathrm{d}\omega}$, $\boxed{\omega_D^3 = \frac{9N}{B}}$, $\boxed{y_D = \frac{\hbar\omega_D}{kT}}$

- $U = U_0 + B\int_0^{\frac{\hbar\omega_D}{kT}} \frac{\hbar\cdot(\frac{\hbar\omega}{kT})^3\cdot(\frac{kT}{\hbar})^3}{e^{\frac{\hbar\omega}{kT}}-1}\frac{kT}{\hbar}\mathrm{d}\frac{\hbar\omega}{kT}$
  $= U_0 + B\hbar(\frac{kT}{\hbar})^4\int_0^{y_D} \frac{y^3}{e^y-1}\mathrm{d}y$

$$\boxed{U=U_0+B\int_0^{\omega_D}\frac{\hbar\omega^3}{e^{\beta\hbar\omega}-1}\mathrm{d}\omega},\ \boxed{\omega_D^3=\frac{9N}{B}},\ \boxed{y_D=\frac{\hbar\omega_D}{kT}}$$

- $$U=U_0+B\int_0^{\frac{\hbar\omega_D}{kT}}\frac{\hbar\cdot(\frac{\hbar\omega}{kT})^3\cdot(\frac{kT}{\hbar})^3}{e^{\frac{\hbar\omega}{kT}}-1}\frac{kT}{\hbar}\mathrm{d}\frac{\hbar\omega}{kT}$$
$$=U_0+B\hbar(\frac{kT}{\hbar})^4\int_0^{y_D}\frac{y^3}{e^y-1}\mathrm{d}y$$
$$=U_0+\frac{9N}{\omega_D^3}\frac{(kT)^4}{\hbar^3}\int_0^{y_D}\frac{y^3}{e^y-1}\mathrm{d}y$$

$\boxed{U = U_0 + B\int_0^{\omega_D} \frac{\hbar\omega^3}{e^{\beta\hbar\omega}-1}\mathrm{d}\omega}$, $\boxed{\omega_D^3 = \frac{9N}{B}}$, $\boxed{y_D = \frac{\hbar\omega_D}{kT}}$

- $U = U_0 + B\int_0^{\frac{\hbar\omega_D}{kT}} \frac{\hbar\cdot(\frac{\hbar\omega}{kT})^3\cdot(\frac{kT}{\hbar})^3}{e^{\frac{\hbar\omega}{kT}}-1}\frac{kT}{\hbar}\mathrm{d}\frac{\hbar\omega}{kT}$
  $= U_0 + B\hbar(\frac{kT}{\hbar})^4\int_0^{y_D}\frac{y^3}{e^y-1}\mathrm{d}y$
  $= U_0 + \frac{9N}{\omega_D^3}\frac{(kT)^4}{\hbar^3}\int_0^{y_D}\frac{y^3}{e^y-1}\mathrm{d}y = U_0 + \frac{9N}{y_D^3}kT\int_0^{y_D}\frac{y^3}{e^y-1}\mathrm{d}y$

$\boxed{U = U_0 + B\int_0^{\omega_D} \frac{\hbar\omega^3}{e^{\beta\hbar\omega}-1}\mathrm{d}\omega}$, $\boxed{\omega_D^3 = \frac{9N}{B}}$, $\boxed{y_D = \frac{\hbar\omega_D}{kT}}$

- $$U = U_0 + B\int_0^{\frac{\hbar\omega_D}{kT}} \frac{\hbar\cdot(\frac{\hbar\omega}{kT})^3\cdot(\frac{kT}{\hbar})^3}{e^{\frac{\hbar\omega}{kT}}-1}\frac{kT}{\hbar}\mathrm{d}\frac{\hbar\omega}{kT}$$
$$= U_0 + B\hbar(\frac{kT}{\hbar})^4\int_0^{y_D}\frac{y^3}{e^y-1}\mathrm{d}y$$
$$= U_0 + \frac{9N}{\omega_D^3}\frac{(kT)^4}{\hbar^3}\int_0^{y_D}\frac{y^3}{e^y-1}\mathrm{d}y = U_0 + \frac{9N}{y_D^3}kT\int_0^{y_D}\frac{y^3}{e^y-1}\mathrm{d}y$$
$$\equiv U_0 + 3NkT\mathcal{D}(y_D)$$, where $\mathcal{D}(y_D) = \frac{3}{y_D^3}\int_0^{y_D}\frac{y^3}{e^y-1}\mathrm{d}y$.

$\boxed{U = U_0 + B\int_0^{\omega_D} \frac{\hbar\omega^3}{e^{\beta\hbar\omega}-1}\mathrm{d}\omega}$, $\boxed{\omega_D^3 = \frac{9N}{B}}$, $\boxed{y_D = \frac{\hbar\omega_D}{kT}}$

- $U = U_0 + B\int_0^{\frac{\hbar\omega_D}{kT}} \frac{\hbar\cdot(\frac{\hbar\omega}{kT})^3\cdot(\frac{kT}{\hbar})^3}{e^{\frac{\hbar\omega}{kT}}-1}\frac{kT}{\hbar}\mathrm{d}\frac{\hbar\omega}{kT}$
  $= U_0 + B\hbar(\frac{kT}{\hbar})^4\int_0^{y_D}\frac{y^3}{e^y-1}\mathrm{d}y$
  $= U_0 + \frac{9N}{\omega_D^3}\frac{(kT)^4}{\hbar^3}\int_0^{y_D}\frac{y^3}{e^y-1}\mathrm{d}y = U_0 + \frac{9N}{y_D^3}kT\int_0^{y_D}\frac{y^3}{e^y-1}\mathrm{d}y$
  $\equiv U_0 + 3NkT\mathcal{D}(y_D)$, where $\mathcal{D}(y_D) = \frac{3}{y_D^3}\int_0^{y_D}\frac{y^3}{e^y-1}\mathrm{d}y$.
- High temperature, $y_D \ll 1$,

$$\boxed{U = U_0 + B\int_0^{\omega_D}\frac{\hbar\omega^3}{e^{\beta\hbar\omega}-1}\mathrm{d}\omega}, \boxed{\omega_D^3 = \frac{9N}{B}}, \boxed{y_D = \frac{\hbar\omega_D}{kT}}$$

- $U = U_0 + B\int_0^{\frac{\hbar\omega_D}{kT}}\frac{\hbar\cdot(\frac{\hbar\omega}{kT})^3\cdot(\frac{kT}{\hbar})^3}{e^{\frac{\hbar\omega}{kT}}-1}\frac{kT}{\hbar}\mathrm{d}\frac{\hbar\omega}{kT}$
  $= U_0 + B\hbar(\frac{kT}{\hbar})^4\int_0^{y_D}\frac{y^3}{e^y-1}\mathrm{d}y$
  $= U_0 + \frac{9N}{\omega_D^3}\frac{(kT)^4}{\hbar^3}\int_0^{y_D}\frac{y^3}{e^y-1}\mathrm{d}y = U_0 + \frac{9N}{y_D^3}kT\int_0^{y_D}\frac{y^3}{e^y-1}\mathrm{d}y$
  $\equiv U_0 + 3NkT\mathcal{D}(y_D)$, where $\mathcal{D}(y_D) = \frac{3}{y_D^3}\int_0^{y_D}\frac{y^3}{e^y-1}\mathrm{d}y$.
- High temperature, $y_D \ll 1$, $\mathcal{D}(y_D) \simeq \frac{3}{y_D^3}\int_0^{y_D} y^2\mathrm{d}y$

$\boxed{U = U_0 + B\int_0^{\omega_D} \frac{\hbar\omega^3}{e^{\beta\hbar\omega}-1}\mathrm{d}\omega}$, $\boxed{\omega_D^3 = \frac{9N}{B}}$, $\boxed{y_D = \frac{\hbar\omega_D}{kT}}$

- $U = U_0 + B\int_0^{\frac{\hbar\omega_D}{kT}} \frac{\hbar\cdot(\frac{\hbar\omega}{kT})^3\cdot(\frac{kT}{\hbar})^3}{e^{\frac{\hbar\omega}{kT}}-1}\frac{kT}{\hbar}\mathrm{d}\frac{\hbar\omega}{kT}$
  $= U_0 + B\hbar(\frac{kT}{\hbar})^4\int_0^{y_D}\frac{y^3}{e^y-1}\mathrm{d}y$
  $= U_0 + \frac{9N}{\omega_D^3}\frac{(kT)^4}{\hbar^3}\int_0^{y_D}\frac{y^3}{e^y-1}\mathrm{d}y = U_0 + \frac{9N}{y_D^3}kT\int_0^{y_D}\frac{y^3}{e^y-1}\mathrm{d}y$
  $\equiv U_0 + 3NkT\mathcal{D}(y_D)$, where $\mathcal{D}(y_D) = \frac{3}{y_D^3}\int_0^{y_D}\frac{y^3}{e^y-1}\mathrm{d}y$.
- High temperature, $y_D \ll 1$, $\mathcal{D}(y_D) \simeq \frac{3}{y_D^3}\int_0^{y_D} y^2\mathrm{d}y$
  $= 1$.

$\boxed{U = U_0 + B\int_0^{\omega_D} \frac{\hbar\omega^3}{e^{\beta\hbar\omega}-1}\mathrm{d}\omega}$, $\boxed{\omega_D^3 = \frac{9N}{B}}$, $\boxed{y_D = \frac{\hbar\omega_D}{kT}}$

- $U = U_0 + B\int_0^{\frac{\hbar\omega_D}{kT}} \frac{\hbar\cdot(\frac{\hbar\omega}{kT})^3\cdot(\frac{kT}{\hbar})^3}{e^{\frac{\hbar\omega}{kT}}-1}\frac{kT}{\hbar}\mathrm{d}\frac{\hbar\omega}{kT}$
  $= U_0 + B\hbar(\frac{kT}{\hbar})^4\int_0^{y_D}\frac{y^3}{e^y-1}\mathrm{d}y$
  $= U_0 + \frac{9N}{\omega_D^3}\frac{(kT)^4}{\hbar^3}\int_0^{y_D}\frac{y^3}{e^y-1}\mathrm{d}y = U_0 + \frac{9N}{y_D^3}kT\int_0^{y_D}\frac{y^3}{e^y-1}\mathrm{d}y$
  $\equiv U_0 + 3NkT\mathcal{D}(y_D)$, where $\mathcal{D}(y_D) = \frac{3}{y_D^3}\int_0^{y_D}\frac{y^3}{e^y-1}\mathrm{d}y$.
- High temperature, $y_D \ll 1$, $\mathcal{D}(y_D) \simeq \frac{3}{y_D^3}\int_0^{y_D} y^2\mathrm{d}y$
  $= 1$. $U = U_0 + 3NkT$, $C_V = 3Nk$.

$\boxed{U = U_0 + B\int_0^{\omega_D} \frac{\hbar\omega^3}{e^{\beta\hbar\omega}-1}\mathrm{d}\omega}$, $\boxed{\omega_D^3 = \frac{9N}{B}}$, $\boxed{y_D = \frac{\hbar\omega_D}{kT}}$

- $U = U_0 + B\int_0^{\frac{\hbar\omega_D}{kT}} \frac{\hbar\cdot(\frac{\hbar\omega}{kT})^3\cdot(\frac{kT}{\hbar})^3}{e^{\frac{\hbar\omega}{kT}}-1}\frac{kT}{\hbar}\mathrm{d}\frac{\hbar\omega}{kT}$
  $= U_0 + B\hbar(\frac{kT}{\hbar})^4\int_0^{y_D} \frac{y^3}{e^y-1}\mathrm{d}y$
  $= U_0 + \frac{9N}{\omega_D^3}\frac{(kT)^4}{\hbar^3}\int_0^{y_D} \frac{y^3}{e^y-1}\mathrm{d}y = U_0 + \frac{9N}{y_D^3}kT\int_0^{y_D} \frac{y^3}{e^y-1}\mathrm{d}y$
  $\equiv U_0 + 3NkT\mathcal{D}(y_D)$, where $\mathcal{D}(y_D) = \frac{3}{y_D^3}\int_0^{y_D} \frac{y^3}{e^y-1}\mathrm{d}y$.
- High temperature, $y_D \ll 1$, $\mathcal{D}(y_D) \simeq \frac{3}{y_D^3}\int_0^{y_D} y^2\mathrm{d}y$
  $= 1$. $U = U_0 + 3NkT$, $C_V = 3Nk$.
- Low temperature, $y_D \gg 1$,

$$\boxed{U = U_0 + B\int_0^{\omega_D} \frac{\hbar\omega^3}{e^{\beta\hbar\omega}-1}\mathrm{d}\omega}, \quad \boxed{\omega_D^3 = \frac{9N}{B}}, \quad \boxed{y_D = \frac{\hbar\omega_D}{kT}}$$

- $U = U_0 + B\int_0^{\frac{\hbar\omega_D}{kT}} \frac{\hbar\cdot(\frac{\hbar\omega}{kT})^3\cdot(\frac{kT}{\hbar})^3}{e^{\frac{\hbar\omega}{kT}}-1}\frac{kT}{\hbar}\mathrm{d}\frac{\hbar\omega}{kT}$
  $= U_0 + B\hbar(\frac{kT}{\hbar})^4\int_0^{y_D}\frac{y^3}{e^y-1}\mathrm{d}y$
  $= U_0 + \frac{9N}{\omega_D^3}\frac{(kT)^4}{\hbar^3}\int_0^{y_D}\frac{y^3}{e^y-1}\mathrm{d}y = U_0 + \frac{9N}{y_D^3}kT\int_0^{y_D}\frac{y^3}{e^y-1}\mathrm{d}y$
  $\equiv U_0 + 3NkT\mathcal{D}(y_D)$, where $\mathcal{D}(y_D) = \frac{3}{y_D^3}\int_0^{y_D}\frac{y^3}{e^y-1}\mathrm{d}y$.
- High temperature, $y_D \ll 1$, $\mathcal{D}(y_D) \simeq \frac{3}{y_D^3}\int_0^{y_D} y^2\mathrm{d}y$
  $= 1$. $U = U_0 + 3NkT$, $C_V = 3Nk$.
- Low temperature, $y_D \gg 1$, $\mathcal{D}(y_D) \simeq \frac{3}{y_D^3}\int_0^{\infty}\frac{y^3}{e^y-1}\mathrm{d}y$

$\boxed{U = U_0 + B\int_0^{\omega_D} \frac{\hbar\omega^3}{e^{\beta\hbar\omega}-1}\mathrm{d}\omega}$, $\boxed{\omega_D^3 = \frac{9N}{B}}$, $\boxed{y_D = \frac{\hbar\omega_D}{kT}}$

- $U = U_0 + B\int_0^{\frac{\hbar\omega_D}{kT}} \frac{\hbar\cdot(\frac{\hbar\omega}{kT})^3\cdot(\frac{kT}{\hbar})^3}{e^{\frac{\hbar\omega}{kT}}-1}\frac{kT}{\hbar}\mathrm{d}\frac{\hbar\omega}{kT}$
  $= U_0 + B\hbar(\frac{kT}{\hbar})^4\int_0^{y_D}\frac{y^3}{e^y-1}\mathrm{d}y$
  $= U_0 + \frac{9N}{\omega_D^3}\frac{(kT)^4}{\hbar^3}\int_0^{y_D}\frac{y^3}{e^y-1}\mathrm{d}y = U_0 + \frac{9N}{y_D^3}kT\int_0^{y_D}\frac{y^3}{e^y-1}\mathrm{d}y$
  $\equiv U_0 + 3NkT\mathcal{D}(y_D)$, where $\mathcal{D}(y_D) = \frac{3}{y_D^3}\int_0^{y_D}\frac{y^3}{e^y-1}\mathrm{d}y$.
- High temperature, $y_D \ll 1$, $\mathcal{D}(y_D) \simeq \frac{3}{y_D^3}\int_0^{y_D} y^2\mathrm{d}y$
  $= 1$. $U = U_0 + 3NkT$, $C_V = 3Nk$.
- Low temperature, $y_D \gg 1$, $\mathcal{D}(y_D) \simeq \frac{3}{y_D^3}\int_0^{\infty}\frac{y^3}{e^y-1}\mathrm{d}y$
  $= \frac{3}{y_D^3}\frac{\pi^4}{15}$

$\boxed{U = U_0 + B\int_0^{\omega_D} \frac{\hbar\omega^3}{e^{\beta\hbar\omega}-1}\mathrm{d}\omega}$, $\boxed{\omega_D^3 = \frac{9N}{B}}$, $\boxed{y_D = \frac{\hbar\omega_D}{kT}}$

- $U = U_0 + B\int_0^{\frac{\hbar\omega_D}{kT}} \frac{\hbar\cdot(\frac{\hbar\omega}{kT})^3\cdot(\frac{kT}{\hbar})^3}{e^{\frac{\hbar\omega}{kT}}-1}\frac{kT}{\hbar}\mathrm{d}\frac{\hbar\omega}{kT}$
  $= U_0 + B\hbar(\frac{kT}{\hbar})^4\int_0^{y_D}\frac{y^3}{e^y-1}\mathrm{d}y$
  $= U_0 + \frac{9N}{\omega_D^3}\frac{(kT)^4}{\hbar^3}\int_0^{y_D}\frac{y^3}{e^y-1}\mathrm{d}y = U_0 + \frac{9N}{y_D^3}kT\int_0^{y_D}\frac{y^3}{e^y-1}\mathrm{d}y$
  $\equiv U_0 + 3NkT\mathcal{D}(y_D)$, where $\mathcal{D}(y_D) = \frac{3}{y_D^3}\int_0^{y_D}\frac{y^3}{e^y-1}\mathrm{d}y$.
- High temperature, $y_D \ll 1$, $\mathcal{D}(y_D) \simeq \frac{3}{y_D^3}\int_0^{y_D} y^2\mathrm{d}y$
  $= 1$. $U = U_0 + 3NkT$, $C_V = 3Nk$.
- Low temperature, $y_D \gg 1$, $\mathcal{D}(y_D) \simeq \frac{3}{y_D^3}\int_0^{\infty}\frac{y^3}{e^y-1}\mathrm{d}y$
  $= \frac{3}{y_D^3}\frac{\pi^4}{15} = \frac{\pi^4}{5y_D^3}$.

$\boxed{U = U_0 + B\int_0^{\omega_D} \frac{\hbar\omega^3}{e^{\beta\hbar\omega}-1}\mathrm{d}\omega}$, $\boxed{\omega_D^3 = \frac{9N}{B}}$, $\boxed{y_D = \frac{\hbar\omega_D}{kT}}$

- $U = U_0 + B\int_0^{\frac{\hbar\omega_D}{kT}} \frac{\hbar\cdot(\frac{\hbar\omega}{kT})^3\cdot(\frac{kT}{\hbar})^3}{e^{\frac{\hbar\omega}{kT}}-1}\frac{kT}{\hbar}\mathrm{d}\frac{\hbar\omega}{kT}$
$= U_0 + B\hbar(\frac{kT}{\hbar})^4\int_0^{y_D}\frac{y^3}{e^y-1}\mathrm{d}y$
$= U_0 + \frac{9N}{\omega_D^3}\frac{(kT)^4}{\hbar^3}\int_0^{y_D}\frac{y^3}{e^y-1}\mathrm{d}y = U_0 + \frac{9N}{y_D^3}kT\int_0^{y_D}\frac{y^3}{e^y-1}\mathrm{d}y$
$\equiv U_0 + 3NkT\mathcal{D}(y_D)$, where $\mathcal{D}(y_D) = \frac{3}{y_D^3}\int_0^{y_D}\frac{y^3}{e^y-1}\mathrm{d}y$.
- High temperature, $y_D \ll 1$, $\mathcal{D}(y_D) \simeq \frac{3}{y_D^3}\int_0^{y_D} y^2\mathrm{d}y$
$= 1$. $U = U_0 + 3NkT$, $C_V = 3Nk$.
- Low temperature, $y_D \gg 1$, $\mathcal{D}(y_D) \simeq \frac{3}{y_D^3}\int_0^{\infty}\frac{y^3}{e^y-1}\mathrm{d}y$
$= \frac{3}{y_D^3}\frac{\pi^4}{15} = \frac{\pi^4}{5y_D^3}$. $U = U_0 + 3Nk\cdot\frac{\pi^4}{5}\frac{T^4}{\theta_D^3}$,
$C_V = 3nk\frac{4\pi^4}{5}(\frac{T}{\theta_D})^3 \propto T^3$. Source of (8.5.20).

Table of contents

9.9 Ising model

9.9 Ising model

- Problem: phase transition.

9.9 Ising model

- Problem: phase transition.
- Question: can statistical mechanics deal with phase transition?

9.9 Ising model

- Problem: phase transition.
- Question: can statistical mechanics deal with phase transition?
- Object: N magnetons at N lattice points.

9.9 Ising model

- Problem: phase transition.
- Question: can statistical mechanics deal with phase transition?
- Object: N magnetons at N lattice points. Analyze the phase transition between paramagnet and ferromagnet. (simple)

9.9 Ising model

- Problem: phase transition.
- Question: can statistical mechanics deal with phase transition?
- Object: N magnetons at N lattice points. Analyze the phase transition between paramagnet and ferromagnet. (simple)
- Suppose the total angular momentum quantum number $\frac{1}{2}$ (simple),

9.9 Ising model

- Problem: phase transition.
- Question: can statistical mechanics deal with phase transition?
- Object: N magnetons at N lattice points. Analyze the phase transition between paramagnet and ferromagnet. (simple)
- Suppose the total angular momentum quantum number $\frac{1}{2}$ (simple), the magnetic momentum: $\mu = \frac{e\hbar}{2m}$.

9.9 Ising model

- Problem: phase transition.
- Question: can statistical mechanics deal with phase transition?
- Object: N magnetons at N lattice points. Analyze the phase transition between paramagnet and ferromagnet. (simple)
- Suppose the total angular momentum quantum number $\frac{1}{2}$ (simple), the magnetic momentum: $\mu = \frac{e\hbar}{2m}$.
- In single-axis ferromagnet, only 2 choices for each magnetic momentum ($\sigma = \pm 1$).

Ferromagnet

- Potential energy between two magnetic momenta: $J_1 \vec{\mu_1} \cdot \vec{\mu_2}$, where J_1 is a coefficient depending on position.

Ferromagnet

- Potential energy between two magnetic momenta: $J_1 \vec{\mu_1} \cdot \vec{\mu_2}$, where J_1 is a coefficient depending on position.
- $J_1 \vec{\mu_1} \cdot \vec{\mu_2} = J_2 \sigma_1 \sigma_2$.

Ferromagnet

- Potential energy between two magnetic momenta: $J_1\vec{\mu_1}\cdot\vec{\mu_2}$, where J_1 is a coefficient depending on position.
- $J_1\vec{\mu_1}\cdot\vec{\mu_2} = J_2\sigma_1\sigma_2$.
- Ising model: Similar form for the total interacting energy between two lattice points: $-J\sigma_1\sigma_2$, where J is a constant for neighbors, 0 for others.

Ferromagnet

- Potential energy between two magnetic momenta: $J_1 \vec{\mu_1} \cdot \vec{\mu_2}$, where J_1 is a coefficient depending on position.
- $J_1 \vec{\mu_1} \cdot \vec{\mu_2} = J_2 \sigma_1 \sigma_2$.
- Ising model: Similar form for the total interacting energy between two lattice points: $-J\sigma_1\sigma_2$, where J is a constant for neighbors, 0 for others.
- Total interacting energy: $-J \sum\limits_{i,j}{}' \sigma_i \sigma_j$, where $\sum\limits_{i,j}{}'$ means the summation only exerts on the neighbors.

Ferromagnet

- Potential energy between two magnetic momenta: $J_1\vec{\mu_1}\cdot\vec{\mu_2}$, where J_1 is a coefficient depending on position.
- $J_1\vec{\mu_1}\cdot\vec{\mu_2}=J_2\sigma_1\sigma_2$.
- Ising model: Similar form for the total interacting energy between two lattice points: $-J\sigma_1\sigma_2$, where J is a constant for neighbors, 0 for others.
- Total interacting energy: $-J\sum\limits_{i,j}{}'\sigma_i\sigma_j$, where $\sum\limits_{i,j}{}'$ means the summation only exerts on the neighbors. At absolute 0K, all directions being the same can get lowest total energy. Get macroscopic magnetic field, spontaneous magnetization.

Mean field approximation

- In external magnetic field, the total energy:
$E\{\sigma_i\} = -J \sum_{i,j}{}' \sigma_i \sigma_j - \mu B \sum_i \sigma_i.$

Mean field approximation

- In external magnetic field, the total energy:
  $E\{\sigma_i\} = -J\sum_{i,j}{}'\sigma_i\sigma_j - \mu B\sum_i \sigma_i.$
- The partition function: $Z = \sum_s e^{-\beta E_s}$

Mean field approximation

- In external magnetic field, the total energy: $E\{\sigma_i\} = -J\sum_{i,j}{}'\sigma_i\sigma_j - \mu B\sum_i \sigma_i$.
- The partition function: $Z = \sum_s e^{-\beta E_s} = \sum_{\{\sigma_i\}} e^{-\beta E\{\sigma_i\}}$

Mean field approximation

- In external magnetic field, the total energy: $E\{\sigma_i\} = -J\sum_{i,j}{}'\sigma_i\sigma_j - \mu B\sum_i \sigma_i$.
- The partition function: $Z = \sum_s e^{-\beta E_s} = \sum_{\{\sigma_i\}} e^{-\beta E\{\sigma_i\}}$

$$= \sum_{\sigma_1=\pm 1}\sum_{\sigma_2=\pm 1}\cdots\sum_{\sigma_N=\pm 1} e^{-\beta E\{\sigma_i\}}.$$

Mean field approximation

- In external magnetic field, the total energy:
  $E\{\sigma_i\} = -J\sum_{i,j}{}'\sigma_i\sigma_j - \mu B\sum_i \sigma_i.$
- The partition function: $Z = \sum_s e^{-\beta E_s} = \sum_{\{\sigma_i\}} e^{-\beta E\{\sigma_i\}}$
  $= \sum_{\sigma_1=\pm1}\sum_{\sigma_2=\pm1}\cdots\sum_{\sigma_N=\pm1} e^{-\beta E\{\sigma_i\}}.$
- Important task is to solve it.

Mean field approximation

- In external magnetic field, the total energy:
  $$E\{\sigma_i\} = -J\sum_{i,j}{}'\sigma_i\sigma_j - \mu B\sum_i \sigma_i.$$
- The partition function: $Z = \sum_s e^{-\beta E_s} = \sum_{\{\sigma_i\}} e^{-\beta E\{\sigma_i\}}$
  $$= \sum_{\sigma_1=\pm1}\sum_{\sigma_2=\pm1}\cdots\sum_{\sigma_N=\pm1} e^{-\beta E\{\sigma_i\}}.$$
- Important task is to solve it.
- An approximation solution: mean field approximation.

Mean field approximation

- In external magnetic field, the total energy:
  $E\{\sigma_i\} = -J\sum_{i,j}{}'\sigma_i\sigma_j - \mu B\sum_i \sigma_i.$
- The partition function: $Z = \sum_s e^{-\beta E_s} = \sum_{\{\sigma_i\}} e^{-\beta E\{\sigma_i\}}$
  $= \sum_{\sigma_1=\pm 1}\sum_{\sigma_2=\pm 1}\cdots\sum_{\sigma_N=\pm 1} e^{-\beta E\{\sigma_i\}}.$
- Important task is to solve it.
- An approximation solution: mean field approximation.
- Rewrite the total energy:
  $E\{\sigma_i\} = -\frac{1}{2}\sum_{i,j} J_{ij}\sigma_i\sigma_j - \mu B\sum_i \sigma_i$, where $J_{ij} = J$ for i and j being neighbors, 0 for other.

Mean field approximation $\boxed{E = -\frac{1}{2}\sum_{i,j} J_{ij}\sigma_i\sigma_j - \mu B \sum_i \sigma_i}$

- $-\sigma_i$ acts as the general displacement,

Mean field approximation $\boxed{E = -\frac{1}{2}\sum_{i,j} J_{ij}\sigma_i\sigma_j - \mu B \sum_i \sigma_i}$

- $-\sigma_i$ acts as the general displacement, the general force on lattice i: $-\frac{\partial E}{\partial \sigma_i} = \mu B + \sum_j J_{ij}\sigma_j$.

Mean field approximation $\boxed{E = -\frac{1}{2}\sum_{i,j} J_{ij}\sigma_i\sigma_j - \mu B \sum_i \sigma_i}$

- $-\sigma_i$ acts as the general displacement, the general force on lattice i: $-\frac{\partial E}{\partial \sigma_i} = \mu B + \sum_j J_{ij}\sigma_j$.
- Like an effective magnetic field exerted on lattice i: $B_i = B + \frac{1}{\mu}\sum_j J_{ij}\sigma_j$.

Mean field approximation $\boxed{E = -\frac{1}{2}\sum_{i,j} J_{ij}\sigma_i\sigma_j - \mu B \sum_i \sigma_i}$

- $-\sigma_i$ acts as the general displacement, the general force on lattice i: $-\frac{\partial E}{\partial \sigma_i} = \mu B + \sum_j J_{ij}\sigma_j$.
- Like an effective magnetic field exerted on lattice i: $B_i = B + \frac{1}{\mu}\sum_j J_{ij}\sigma_j$.
- As $\{\sigma_i\}$ changes for different states, the B_i is different for different states.

Mean field approximation $\boxed{E = -\frac{1}{2}\sum_{i,j} J_{ij}\sigma_i\sigma_j - \mu B \sum_i \sigma_i}$

- $-\sigma_i$ acts as the general displacement, the general force on lattice i: $-\frac{\partial E}{\partial \sigma_i} = \mu B + \sum_j J_{ij}\sigma_j$.
- Like an effective magnetic field exerted on lattice i: $B_i = B + \frac{1}{\mu}\sum_j J_{ij}\sigma_j$.
- As $\{\sigma_i\}$ changes for different states, the B_i is different for different states. However, choose an average value for the effective field: $\bar{B}_i = B + \frac{1}{\mu}\sum_j J_{ij}\bar{\sigma}_j$,

Mean field approximation $\boxed{E = -\frac{1}{2}\sum_{i,j} J_{ij}\sigma_i\sigma_j - \mu B \sum_i \sigma_i}$

- $-\sigma_i$ acts as the general displacement, the general force on lattice i: $-\frac{\partial E}{\partial \sigma_i} = \mu B + \sum_j J_{ij}\sigma_j$.
- Like an effective magnetic field exerted on lattice i: $B_i = B + \frac{1}{\mu}\sum_j J_{ij}\sigma_j$.
- As $\{\sigma_i\}$ changes for different states, the B_i is different for different states. However, choose an average value for the effective field: $\bar{B}_i = B + \frac{1}{\mu}\sum_j J_{ij}\bar{\sigma}_j$, called mean field approximation.

Mean field approximation $\boxed{\bar{B}_i = B + \frac{1}{\mu}\sum_j J_{ij}\bar{\sigma}_j}$

- As $\bar{\sigma}_j$ is an average value, which doesn't depend on j, $\bar{\sigma}_j = \bar{\sigma}_i$.

Mean field approximation $\boxed{\bar{B}_i = B + \frac{1}{\mu}\sum_j J_{ij}\bar{\sigma}_j}$

- As $\bar{\sigma}_j$ is an average value, which doesn't depend on j, $\bar{\sigma}_j = \bar{\sigma}_i$. $\rightarrow \sum\limits_j J_{ij}\bar{\sigma}_j = \bar{\sigma}_i \sum\limits_j J_{ij}$.

Mean field approximation $\boxed{\bar{B}_i = B + \frac{1}{\mu}\sum_j J_{ij}\bar{\sigma}_j}$

- As $\bar{\sigma}_j$ is an average value, which doesn't depend on j, $\bar{\sigma}_j = \bar{\sigma}_i$. $\rightarrow \sum\limits_j J_{ij}\bar{\sigma}_j = \bar{\sigma}_i \sum\limits_j J_{ij}$.
- $\sum\limits_j J_{ij} = Jz$, where z is the number of neighbors.

Mean field approximation $\boxed{\bar{B}_i = B + \frac{1}{\mu}\sum_j J_{ij}\bar{\sigma}_j}$

- As $\bar{\sigma}_j$ is an average value, which doesn't depend on j, $\bar{\sigma}_j = \bar{\sigma}_i$. $\rightarrow \sum\limits_j J_{ij}\bar{\sigma}_j = \bar{\sigma}_i \sum\limits_j J_{ij}$.
- $\sum\limits_j J_{ij} = Jz$, where z is the number of neighbors.
- $\Rightarrow \bar{B}_i = B + \frac{1}{\mu} Jz\bar{\sigma}_i$.

Mean field approximation $\boxed{\bar{B}_i = B + \frac{1}{\mu}\sum_j J_{ij}\bar{\sigma}_j}$

- As $\bar{\sigma}_j$ is an average value, which doesn't depend on j, $\bar{\sigma}_j = \bar{\sigma}_i$. $\rightarrow \sum\limits_j J_{ij}\bar{\sigma}_j = \bar{\sigma}_i \sum\limits_j J_{ij}$.
- $\sum\limits_j J_{ij} = Jz$, where z is the number of neighbors.
- $\Rightarrow \bar{B}_i = B + \frac{1}{\mu} Jz\bar{\sigma}_i$.
- As $\bar{\sigma}_i$ doesn't depend on i,

Mean field approximation $\boxed{\bar{B}_i = B + \frac{1}{\mu}\sum_j J_{ij}\bar{\sigma}_j}$

- As $\bar{\sigma}_j$ is an average value, which doesn't depend on j, $\bar{\sigma}_j = \bar{\sigma}_i$. $\rightarrow \sum\limits_j J_{ij}\bar{\sigma}_j = \bar{\sigma}_i \sum\limits_j J_{ij}$.
- $\sum\limits_j J_{ij} = Jz$, where z is the number of neighbors.
- $\Rightarrow \bar{B}_i = B + \frac{1}{\mu} Jz\bar{\sigma}_i$.
- As $\bar{\sigma}_i$ doesn't depend on i, $\bar{B} = B + \frac{1}{\mu} Jz\bar{\sigma}$.

Mean field approximation $\boxed{\bar{B}_i = B + \frac{1}{\mu}\sum_j J_{ij}\bar{\sigma}_j}$

- As $\bar{\sigma}_j$ is an average value, which doesn't depend on j, $\bar{\sigma}_j = \bar{\sigma}_i$. $\rightarrow \sum\limits_j J_{ij}\bar{\sigma}_j = \bar{\sigma}_i \sum\limits_j J_{ij}$.
- $\sum\limits_j J_{ij} = Jz$, where z is the number of neighbors.
- $\Rightarrow \bar{B}_i = B + \frac{1}{\mu} Jz\bar{\sigma}_i$.
- As $\bar{\sigma}_i$ doesn't depend on i, $\bar{B} = B + \frac{1}{\mu} Jz\bar{\sigma}$.
- The total energy is then: $E = -\mu\bar{B}\sum\limits_i \sigma_i$.

Mean field approximation $\boxed{\bar{B}_i = B + \frac{1}{\mu}\sum_j J_{ij}\bar{\sigma}_j}$

- As $\bar{\sigma}_j$ is an average value, which doesn't depend on j, $\bar{\sigma}_j = \bar{\sigma}_i$. $\rightarrow \sum_j J_{ij}\bar{\sigma}_j = \bar{\sigma}_i \sum_j J_{ij}$.
- $\sum_j J_{ij} = Jz$, where z is the number of neighbors.
- $\Rightarrow \bar{B}_i = B + \frac{1}{\mu} Jz\bar{\sigma}_i$.
- As $\bar{\sigma}_i$ doesn't depend on i, $\bar{B} = B + \frac{1}{\mu} Jz\bar{\sigma}$.
- The total energy is then: $E = -\mu\bar{B}\sum_i \sigma_i$.
- The partition function: $Z = \sum_{\sigma_1=\pm 1} \cdots \sum_{\sigma_N=\pm 1} e^{-\beta E\{\sigma_i\}}$

Mean field approximation $\boxed{\bar{B}_i = B + \frac{1}{\mu}\sum_j J_{ij}\bar{\sigma}_j}$

- As $\bar{\sigma}_j$ is an average value, which doesn't depend on j, $\bar{\sigma}_j = \bar{\sigma}_i$. $\to \sum\limits_j J_{ij}\bar{\sigma}_j = \bar{\sigma}_i \sum\limits_j J_{ij}$.
- $\sum\limits_j J_{ij} = Jz$, where z is the number of neighbors.
- $\Rightarrow \bar{B}_i = B + \frac{1}{\mu} Jz\bar{\sigma}_i$.
- As $\bar{\sigma}_i$ doesn't depend on i, $\bar{B} = B + \frac{1}{\mu} Jz\bar{\sigma}$.
- The total energy is then: $E = -\mu\bar{B}\sum\limits_i \sigma_i$.
- The partition function: $Z = \sum\limits_{\sigma_1=\pm1} \cdots \sum\limits_{\sigma_N=\pm1} e^{-\beta E\{\sigma_i\}}$

$$= \sum_{\sigma_1=\pm1} \cdots \sum_{\sigma_N=\pm1} e^{\beta\mu\bar{B}\sum\limits_i \sigma_i}$$

Mean field approximation $\boxed{\bar{B}_i = B + \frac{1}{\mu}\sum_j J_{ij}\bar{\sigma}_j}$

- As $\bar{\sigma}_j$ is an average value, which doesn't depend on j, $\bar{\sigma}_j = \bar{\sigma}_i$. $\to \sum_j J_{ij}\bar{\sigma}_j = \bar{\sigma}_i \sum_j J_{ij}$.
- $\sum_j J_{ij} = Jz$, where z is the number of neighbors.
- $\Rightarrow \bar{B}_i = B + \frac{1}{\mu} Jz\bar{\sigma}_i$.
- As $\bar{\sigma}_i$ doesn't depend on i, $\bar{B} = B + \frac{1}{\mu} Jz\bar{\sigma}$.
- The total energy is then: $E = -\mu\bar{B}\sum_i \sigma_i$.
- The partition function: $Z = \sum_{\sigma_1=\pm1} \cdots \sum_{\sigma_N=\pm1} e^{-\beta E\{\sigma_i\}}$

$$= \sum_{\sigma_1=\pm1} \cdots \sum_{\sigma_N=\pm1} e^{\beta\mu\bar{B}\sum_i \sigma_i} = \prod_i \sum_{\sigma_i} e^{\beta\mu\bar{B}\sigma_i}$$

Mean field approximation $\boxed{\bar{B} = B + \frac{1}{\mu} J z \bar{\sigma}}$

- $Z = \prod_i \sum_{\sigma_i} e^{\beta\mu\bar{B}\sigma_i}$

Mean field approximation $\boxed{\bar{B} = B + \frac{1}{\mu} J z \bar{\sigma}}$

- $Z = \prod_i \sum_{\sigma_i} e^{\beta\mu\bar{B}\sigma_i} = \prod_i (e^{\beta\mu\bar{B}} + e^{-\beta\mu\bar{B}})$

Mean field approximation $\boxed{\bar{B} = B + \frac{1}{\mu} J z \bar{\sigma}}$

- $Z = \prod_i \sum_{\sigma_i} e^{\beta\mu\bar{B}\sigma_i} = \prod_i (e^{\beta\mu\bar{B}} + e^{-\beta\mu\bar{B}}) = Z_1^N$, where $Z_1 = e^{\beta\mu\bar{B}} + e^{-\beta\mu\bar{B}}$. (Comparing with (7.8.1))

Mean field approximation $\boxed{\bar{B} = B + \frac{1}{\mu} J z \bar{\sigma}}$

- $Z = \prod_i \sum_{\sigma_i} e^{\beta\mu\bar{B}\sigma_i} = \prod_i (e^{\beta\mu\bar{B}} + e^{-\beta\mu\bar{B}}) = Z_1^N$, where $Z_1 = e^{\beta\mu\bar{B}} + e^{-\beta\mu\bar{B}}$. (Comparing with (7.8.1))
- Magnetic momentum $-m$ and magnetic field B are a pair of general force and general displacement (2.7.19),

Mean field approximation $\boxed{\bar{B} = B + \frac{1}{\mu} J z \bar{\sigma}}$

- $Z = \prod_i \sum_{\sigma_i} e^{\beta\mu\bar{B}\sigma_i} = \prod_i (e^{\beta\mu\bar{B}} + e^{-\beta\mu\bar{B}}) = Z_1^N$, where $Z_1 = e^{\beta\mu\bar{B}} + e^{-\beta\mu\bar{B}}$. (Comparing with (7.8.1))
- Magnetic momentum $-m$ and magnetic field B are a pair of general force and general displacement (2.7.19), $\bar{m} = \frac{1}{\beta}\frac{\partial \ln Z}{\partial \bar{B}}$

Mean field approximation $\boxed{\bar{B} = B + \frac{1}{\mu} J z \bar{\sigma}}$

- $Z = \prod_i \sum_{\sigma_i} e^{\beta\mu\bar{B}\sigma_i} = \prod_i (e^{\beta\mu\bar{B}} + e^{-\beta\mu\bar{B}}) = Z_1^N$, where $Z_1 = e^{\beta\mu\bar{B}} + e^{-\beta\mu\bar{B}}$. (Comparing with (7.8.1))
- Magnetic momentum $-m$ and magnetic field B are a pair of general force and general displacement (2.7.19), $\bar{m} = \frac{1}{\beta}\frac{\partial \ln Z}{\partial \bar{B}} = \frac{N}{\beta}\frac{\partial \ln Z_1}{\partial \bar{B}}$

Mean field approximation $\boxed{\bar{B} = B + \frac{1}{\mu} J z \bar{\sigma}}$

- $Z = \prod_i \sum_{\sigma_i} e^{\beta\mu\bar{B}\sigma_i} = \prod_i (e^{\beta\mu\bar{B}} + e^{-\beta\mu\bar{B}}) = Z_1^N$, where $Z_1 = e^{\beta\mu\bar{B}} + e^{-\beta\mu\bar{B}}$. (Comparing with (7.8.1))
- Magnetic momentum $-m$ and magnetic field B are a pair of general force and general displacement (2.7.19), $\bar{m} = \frac{1}{\beta}\frac{\partial \ln Z}{\partial \bar{B}} = \frac{N}{\beta}\frac{\partial \ln Z_1}{\partial \bar{B}} = N\mu \frac{e^{\beta\mu\bar{B}} - e^{-\beta\mu\bar{B}}}{e^{\beta\mu\bar{B}} + e^{-\beta\mu\bar{B}}}$.

Mean field approximation $\boxed{\bar{B} = B + \frac{1}{\mu} J z \bar{\sigma}}$

- $Z = \prod_i \sum_{\sigma_i} e^{\beta\mu\bar{B}\sigma_i} = \prod_i (e^{\beta\mu\bar{B}} + e^{-\beta\mu\bar{B}}) = Z_1^N$, where $Z_1 = e^{\beta\mu\bar{B}} + e^{-\beta\mu\bar{B}}$. (Comparing with (7.8.1))
- Magnetic momentum $-m$ and magnetic field B are a pair of general force and general displacement (2.7.19), $\bar{m} = \frac{1}{\beta}\frac{\partial \ln Z}{\partial \bar{B}} = \frac{N}{\beta}\frac{\partial \ln Z_1}{\partial \bar{B}} = N\mu \frac{e^{\beta\mu\bar{B}} - e^{-\beta\mu\bar{B}}}{e^{\beta\mu\bar{B}} + e^{-\beta\mu\bar{B}}}$.
- On the other hand, $\bar{m} = N\mu\bar{\sigma}$.

Mean field approximation $\boxed{\bar{B} = B + \frac{1}{\mu} J z \bar{\sigma}}$

- $Z = \prod_i \sum_{\sigma_i} e^{\beta\mu\bar{B}\sigma_i} = \prod_i (e^{\beta\mu\bar{B}} + e^{-\beta\mu\bar{B}}) = Z_1^N$, where $Z_1 = e^{\beta\mu\bar{B}} + e^{-\beta\mu\bar{B}}$. (Comparing with (7.8.1))
- Magnetic momentum $-m$ and magnetic field B are a pair of general force and general displacement (2.7.19), $\bar{m} = \frac{1}{\beta}\frac{\partial \ln Z}{\partial \bar{B}} = \frac{N}{\beta}\frac{\partial \ln Z_1}{\partial \bar{B}} = N\mu \frac{e^{\beta\mu\bar{B}} - e^{-\beta\mu\bar{B}}}{e^{\beta\mu\bar{B}} + e^{-\beta\mu\bar{B}}}$.
- On the other hand, $\bar{m} = N\mu\bar{\sigma}$.
- $\Rightarrow \bar{\sigma} = \frac{e^{\beta\mu\bar{B}} - e^{-\beta\mu\bar{B}}}{e^{\beta\mu\bar{B}} + e^{-\beta\mu\bar{B}}}$.

Mean field approximation $\boxed{\bar{B} = B + \frac{1}{\mu} J z \bar{\sigma}}$

- $Z = \prod_i \sum_{\sigma_i} e^{\beta\mu\bar{B}\sigma_i} = \prod_i (e^{\beta\mu\bar{B}} + e^{-\beta\mu\bar{B}}) = Z_1^N$, where $Z_1 = e^{\beta\mu\bar{B}} + e^{-\beta\mu\bar{B}}$. (Comparing with (7.8.1))
- Magnetic momentum $-m$ and magnetic field B are a pair of general force and general displacement (2.7.19), $\bar{m} = \frac{1}{\beta}\frac{\partial \ln Z}{\partial \bar{B}} = \frac{N}{\beta}\frac{\partial \ln Z_1}{\partial \bar{B}} = N\mu \frac{e^{\beta\mu\bar{B}} - e^{-\beta\mu\bar{B}}}{e^{\beta\mu\bar{B}} + e^{-\beta\mu\bar{B}}}$.
- On the other hand, $\bar{m} = N\mu\bar{\sigma}$.
- $\Rightarrow \bar{\sigma} = \frac{e^{\beta\mu\bar{B}} - e^{-\beta\mu\bar{B}}}{e^{\beta\mu\bar{B}} + e^{-\beta\mu\bar{B}}}$.
- Without external field, $\bar{B} = \frac{1}{\mu} J z \bar{\sigma}$.

Mean field approximation $\boxed{\bar{B} = B + \frac{1}{\mu} J z \bar{\sigma}}$

- $Z = \prod_i \sum_{\sigma_i} e^{\beta\mu\bar{B}\sigma_i} = \prod_i (e^{\beta\mu\bar{B}} + e^{-\beta\mu\bar{B}}) = Z_1^N$, where $Z_1 = e^{\beta\mu\bar{B}} + e^{-\beta\mu\bar{B}}$. (Comparing with (7.8.1))
- Magnetic momentum $-m$ and magnetic field B are a pair of general force and general displacement (2.7.19), $\bar{m} = \frac{1}{\beta}\frac{\partial \ln Z}{\partial \bar{B}} = \frac{N}{\beta}\frac{\partial \ln Z_1}{\partial \bar{B}} = N\mu \frac{e^{\beta\mu\bar{B}} - e^{-\beta\mu\bar{B}}}{e^{\beta\mu\bar{B}} + e^{-\beta\mu\bar{B}}}$.
- On the other hand, $\bar{m} = N\mu\bar{\sigma}$.
- $\Rightarrow \bar{\sigma} = \frac{e^{\beta\mu\bar{B}} - e^{-\beta\mu\bar{B}}}{e^{\beta\mu\bar{B}} + e^{-\beta\mu\bar{B}}}$.
- Without external field, $\bar{B} = \frac{1}{\mu} J z \bar{\sigma}$. $\rightarrow \beta\mu\bar{B} = \beta J z \bar{\sigma}$.

Mean field approximation $\boxed{\bar{B} = B + \frac{1}{\mu} J z \bar{\sigma}}$

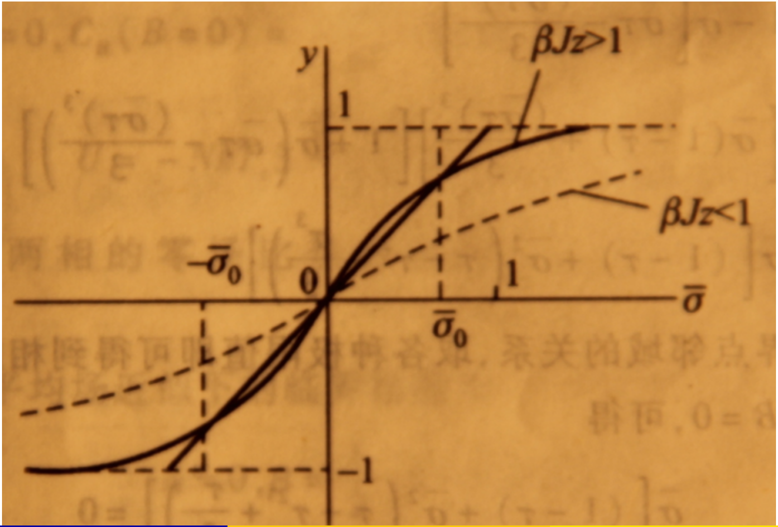
- $Z = \prod_i \sum_{\sigma_i} e^{\beta\mu\bar{B}\sigma_i} = \prod_i (e^{\beta\mu\bar{B}} + e^{-\beta\mu\bar{B}}) = Z_1^N$, where $Z_1 = e^{\beta\mu\bar{B}} + e^{-\beta\mu\bar{B}}$. (Comparing with (7.8.1))
- Magnetic momentum $-m$ and magnetic field B are a pair of general force and general displacement (2.7.19), $\bar{m} = \frac{1}{\beta}\frac{\partial \ln Z}{\partial \bar{B}} = \frac{N}{\beta}\frac{\partial \ln Z_1}{\partial \bar{B}} = N\mu \frac{e^{\beta\mu\bar{B}} - e^{-\beta\mu\bar{B}}}{e^{\beta\mu\bar{B}} + e^{-\beta\mu\bar{B}}}$.
- On the other hand, $\bar{m} = N\mu\bar{\sigma}$.
- $\Rightarrow \bar{\sigma} = \frac{e^{\beta\mu\bar{B}} - e^{-\beta\mu\bar{B}}}{e^{\beta\mu\bar{B}} + e^{-\beta\mu\bar{B}}}$.
- Without external field, $\bar{B} = \frac{1}{\mu} J z \bar{\sigma}$. $\rightarrow \beta\mu\bar{B} = \beta J z \bar{\sigma}$.
  $\therefore Z_1 = e^{\beta J z \bar{\sigma}} + e^{-\beta J z \bar{\sigma}}$;

Mean field approximation $\boxed{\bar{B} = B + \frac{1}{\mu} J z \bar{\sigma}}$

- $Z = \prod_i \sum_{\sigma_i} e^{\beta\mu\bar{B}\sigma_i} = \prod_i (e^{\beta\mu\bar{B}} + e^{-\beta\mu\bar{B}}) = Z_1^N$,
  where $Z_1 = e^{\beta\mu\bar{B}} + e^{-\beta\mu\bar{B}}$. (Comparing with (7.8.1))
- Magnetic momentum $-m$ and magnetic field B are a pair of general force and general displacement (2.7.19), $\bar{m} = \frac{1}{\beta}\frac{\partial \ln Z}{\partial \bar{B}} = \frac{N}{\beta}\frac{\partial \ln Z_1}{\partial \bar{B}} = N\mu \frac{e^{\beta\mu\bar{B}} - e^{-\beta\mu\bar{B}}}{e^{\beta\mu\bar{B}} + e^{-\beta\mu\bar{B}}}$.
- On the other hand, $\bar{m} = N\mu\bar{\sigma}$.
- $\Rightarrow \bar{\sigma} = \frac{e^{\beta\mu\bar{B}} - e^{-\beta\mu\bar{B}}}{e^{\beta\mu\bar{B}} + e^{-\beta\mu\bar{B}}}$.
- Without external field, $\bar{B} = \frac{1}{\mu} J z \bar{\sigma}$. $\to \beta\mu\bar{B} = \beta J z \bar{\sigma}$.
  $\therefore Z_1 = e^{\beta J z \bar{\sigma}} + e^{-\beta J z \bar{\sigma}}$;
  $\bar{\sigma} = \frac{e^{\beta J z \bar{\sigma}} - e^{-\beta J z \bar{\sigma}}}{e^{\beta J z \bar{\sigma}} + e^{-\beta J z \bar{\sigma}}}$.

Mean field approximation $\boxed{\bar{\sigma} = \frac{e^{\beta J z \bar{\sigma}} - e^{-\beta J z \bar{\sigma}}}{e^{\beta J z \bar{\sigma}} + e^{-\beta J z \bar{\sigma}}}}$ solution

The critical temperature ($\beta J z = 1$): $T_c = \frac{Jz}{k}$.



Thermal capacity $\boxed{Z_1 = e^{\beta J z\bar{\sigma}} + e^{-\beta J z\bar{\sigma}}}$, $\boxed{T_c = \frac{Jz}{k}}$, $\boxed{\bar{\sigma} = \frac{e^{\beta J z\bar{\sigma}} - e^{-\beta J z\bar{\sigma}}}{e^{\beta J z\bar{\sigma}} + e^{-\beta J z\bar{\sigma}}}}$, $\boxed{Z = Z_1^N}$

- Internal energy: $U = -\frac{\partial \ln Z}{\partial \beta}$

Thermal capacity $\boxed{Z_1 = e^{\beta J z\bar{\sigma}} + e^{-\beta J z\bar{\sigma}}}$, $\boxed{T_c = \frac{Jz}{k}}$, $\boxed{\bar{\sigma} = \frac{e^{\beta J z\bar{\sigma}} - e^{-\beta J z\bar{\sigma}}}{e^{\beta J z\bar{\sigma}} + e^{-\beta J z\bar{\sigma}}}}$, $\boxed{Z = Z_1^N}$

- Internal energy: $U = -\frac{\partial \ln Z}{\partial \beta} = -N\frac{\partial \ln Z_1}{\partial \beta}$

Thermal capacity $\boxed{Z_1 = e^{\beta J z \bar{\sigma}} + e^{-\beta J z \bar{\sigma}}}$, $\boxed{T_c = \frac{Jz}{k}}$, $\boxed{\bar{\sigma} = \frac{e^{\beta J z \bar{\sigma}} - e^{-\beta J z \bar{\sigma}}}{e^{\beta J z \bar{\sigma}} + e^{-\beta J z \bar{\sigma}}}}$, $\boxed{Z = Z_1^N}$

- Internal energy: $U = -\frac{\partial \ln Z}{\partial \beta} = -N \frac{\partial \ln Z_1}{\partial \beta}$
  $= -N J z \bar{\sigma} \frac{e^{\beta J z \bar{\sigma}} - e^{-\beta J z \bar{\sigma}}}{e^{\beta J z \bar{\sigma}} + e^{-\beta J z \bar{\sigma}}}$

Thermal capacity $\boxed{Z_1 = e^{\beta Jz\bar{\sigma}} + e^{-\beta Jz\bar{\sigma}}}$, $\boxed{T_c = \frac{Jz}{k}}$, $\boxed{\bar{\sigma} = \frac{e^{\beta Jz\bar{\sigma}} - e^{-\beta Jz\bar{\sigma}}}{e^{\beta Jz\bar{\sigma}} + e^{-\beta Jz\bar{\sigma}}}}$, $\boxed{Z = Z_1^N}$

- Internal energy: $U = -\frac{\partial \ln Z}{\partial \beta} = -N\frac{\partial \ln Z_1}{\partial \beta}$
  $= -NJz\bar{\sigma}\frac{e^{\beta Jz\bar{\sigma}} - e^{-\beta Jz\bar{\sigma}}}{e^{\beta Jz\bar{\sigma}} + e^{-\beta Jz\bar{\sigma}}} = -NJz\bar{\sigma}^2$

Thermal capacity $\boxed{Z_1 = e^{\beta J z \bar{\sigma}} + e^{-\beta J z \bar{\sigma}}}$, $\boxed{T_c = \frac{Jz}{k}}$, $\boxed{\bar{\sigma} = \frac{e^{\beta J z \bar{\sigma}} - e^{-\beta J z \bar{\sigma}}}{e^{\beta J z \bar{\sigma}} + e^{-\beta J z \bar{\sigma}}}}$, $\boxed{Z = Z_1^N}$

- Internal energy: $U = -\frac{\partial \ln Z}{\partial \beta} = -N \frac{\partial \ln Z_1}{\partial \beta}$
  $= -NJz\bar{\sigma} \frac{e^{\beta J z \bar{\sigma}} - e^{-\beta J z \bar{\sigma}}}{e^{\beta J z \bar{\sigma}} + e^{-\beta J z \bar{\sigma}}} = -NJz\bar{\sigma}^2 = -NkT_c\bar{\sigma}^2$.

Thermal capacity $\boxed{Z_1 = e^{\beta J z\bar{\sigma}} + e^{-\beta J z\bar{\sigma}}}$, $\boxed{T_c = \frac{Jz}{k}}$, $\boxed{\bar{\sigma} = \frac{e^{\beta J z\bar{\sigma}} - e^{-\beta J z\bar{\sigma}}}{e^{\beta J z\bar{\sigma}} + e^{-\beta J z\bar{\sigma}}}}$, $\boxed{Z = Z_1^N}$

- Internal energy: $U = -\frac{\partial \ln Z}{\partial \beta} = -N\frac{\partial \ln Z_1}{\partial \beta}$
  $= -NJz\bar{\sigma}\frac{e^{\beta J z\bar{\sigma}} - e^{-\beta J z\bar{\sigma}}}{e^{\beta J z\bar{\sigma}} + e^{-\beta J z\bar{\sigma}}} = -NJz\bar{\sigma}^2 = -NkT_c\bar{\sigma}^2$.
- $\bar{\sigma} = \frac{e^{\beta J z\bar{\sigma}} - e^{-\beta J z\bar{\sigma}}}{e^{\beta J z\bar{\sigma}} + e^{-\beta J z\bar{\sigma}}}$

Thermal capacity $\boxed{Z_1 = e^{\beta J z\bar{\sigma}} + e^{-\beta J z\bar{\sigma}}}$, $\boxed{T_c = \frac{Jz}{k}}$, $\boxed{\bar{\sigma} = \frac{e^{\beta J z\bar{\sigma}} - e^{-\beta J z\bar{\sigma}}}{e^{\beta J z\bar{\sigma}} + e^{-\beta J z\bar{\sigma}}}}$, $\boxed{Z = Z_1^N}$

- Internal energy: $U = -\frac{\partial \ln Z}{\partial \beta} = -N\frac{\partial \ln Z_1}{\partial \beta}$
  $= -NJz\bar{\sigma}\frac{e^{\beta J z\bar{\sigma}} - e^{-\beta J z\bar{\sigma}}}{e^{\beta J z\bar{\sigma}} + e^{-\beta J z\bar{\sigma}}} = -NJz\bar{\sigma}^2 = -NkT_c\bar{\sigma}^2.$
- $\bar{\sigma} = \frac{e^{\beta J z\bar{\sigma}} - e^{-\beta J z\bar{\sigma}}}{e^{\beta J z\bar{\sigma}} + e^{-\beta J z\bar{\sigma}}} = \frac{e^{\frac{T_c}{T}\bar{\sigma}} - e^{-\frac{T_c}{T}\bar{\sigma}}}{e^{\frac{T_c}{T}\bar{\sigma}} + e^{-\frac{T_c}{T}\bar{\sigma}}}.$

Thermal capacity $\boxed{Z_1 = e^{\beta J z\bar{\sigma}} + e^{-\beta J z\bar{\sigma}}}$, $\boxed{T_c = \frac{Jz}{k}}$, $\boxed{\bar{\sigma} = \frac{e^{\beta J z\bar{\sigma}} - e^{-\beta J z\bar{\sigma}}}{e^{\beta J z\bar{\sigma}} + e^{-\beta J z\bar{\sigma}}}}$, $\boxed{Z = Z_1^N}$

- Internal energy: $U = -\frac{\partial \ln Z}{\partial \beta} = -N\frac{\partial \ln Z_1}{\partial \beta}$
  $= -NJz\bar{\sigma}\frac{e^{\beta J z\bar{\sigma}} - e^{-\beta J z\bar{\sigma}}}{e^{\beta J z\bar{\sigma}} + e^{-\beta J z\bar{\sigma}}} = -NJz\bar{\sigma}^2 = -NkT_c\bar{\sigma}^2.$
- $\bar{\sigma} = \frac{e^{\beta J z\bar{\sigma}} - e^{-\beta J z\bar{\sigma}}}{e^{\beta J z\bar{\sigma}} + e^{-\beta J z\bar{\sigma}}} = \frac{e^{\frac{T_c}{T}\bar{\sigma}} - e^{-\frac{T_c}{T}\bar{\sigma}}}{e^{\frac{T_c}{T}\bar{\sigma}} + e^{-\frac{T_c}{T}\bar{\sigma}}}.$
  As $\bar{\sigma}(T \to T_c^-) \to 0$, $x \equiv \frac{T_c}{T}\bar{\sigma} \to 0$.

Thermal capacity $\boxed{Z_1 = e^{\beta J z\bar{\sigma}} + e^{-\beta J z\bar{\sigma}}}$, $\boxed{T_c = \frac{Jz}{k}}$, $\boxed{\bar{\sigma} = \frac{e^{\beta J z\bar{\sigma}} - e^{-\beta J z\bar{\sigma}}}{e^{\beta J z\bar{\sigma}} + e^{-\beta J z\bar{\sigma}}}}$, $\boxed{Z = Z_1^N}$

- Internal energy: $U = -\frac{\partial \ln Z}{\partial \beta} = -N\frac{\partial \ln Z_1}{\partial \beta}$
  $= -NJz\bar{\sigma}\frac{e^{\beta J z\bar{\sigma}} - e^{-\beta J z\bar{\sigma}}}{e^{\beta J z\bar{\sigma}} + e^{-\beta J z\bar{\sigma}}} = -NJz\bar{\sigma}^2 = -NkT_c\bar{\sigma}^2$.
- $\bar{\sigma} = \frac{e^{\beta J z\bar{\sigma}} - e^{-\beta J z\bar{\sigma}}}{e^{\beta J z\bar{\sigma}} + e^{-\beta J z\bar{\sigma}}} = \frac{e^{\frac{T_c}{T}\bar{\sigma}} - e^{-\frac{T_c}{T}\bar{\sigma}}}{e^{\frac{T_c}{T}\bar{\sigma}} + e^{-\frac{T_c}{T}\bar{\sigma}}}$.
  As $\bar{\sigma}(T \to T_c^-) \to 0$, $x \equiv \frac{T_c}{T}\bar{\sigma} \to 0$.
  $\bar{\sigma} = \frac{e^x - e^{-x}}{e^x + e^{-x}}$

Thermal capacity $\boxed{Z_1 = e^{\beta J z \bar\sigma} + e^{-\beta J z \bar\sigma}}$, $\boxed{T_c = \frac{Jz}{k}}$, $\boxed{\bar\sigma = \frac{e^{\beta J z \bar\sigma} - e^{-\beta J z \bar\sigma}}{e^{\beta J z \bar\sigma} + e^{-\beta J z \bar\sigma}}}$, $\boxed{Z = Z_1^N}$

- Internal energy: $U = -\frac{\partial \ln Z}{\partial \beta} = -N\frac{\partial \ln Z_1}{\partial \beta}$
  $= -NJz\bar\sigma\frac{e^{\beta J z \bar\sigma} - e^{-\beta J z \bar\sigma}}{e^{\beta J z \bar\sigma} + e^{-\beta J z \bar\sigma}} = -NJz\bar\sigma^2 = -NkT_c\bar\sigma^2.$
- $\bar\sigma = \frac{e^{\beta J z \bar\sigma} - e^{-\beta J z \bar\sigma}}{e^{\beta J z \bar\sigma} + e^{-\beta J z \bar\sigma}} = \frac{e^{\frac{T_c}{T}\bar\sigma} - e^{-\frac{T_c}{T}\bar\sigma}}{e^{\frac{T_c}{T}\bar\sigma} + e^{-\frac{T_c}{T}\bar\sigma}}.$
  As $\bar\sigma(T \to T_c^-) \to 0$, $x \equiv \frac{T_c}{T}\bar\sigma \to 0$.
  $\bar\sigma = \frac{e^x - e^{-x}}{e^x + e^{-x}} \simeq \frac{(1+x+\frac{1}{2}x^2+\frac{1}{6}x^3)-(1-x+\frac{1}{2}x^2-\frac{1}{6}x^3)}{(1+x+\frac{1}{2}x^2+\frac{1}{6}x^3)+(1-x+\frac{1}{2}x^2-\frac{1}{6}x^3)}$

Thermal capacity $\boxed{Z_1 = e^{\beta Jz\bar{\sigma}} + e^{-\beta Jz\bar{\sigma}}}$, $\boxed{T_c = \frac{Jz}{k}}$, $\boxed{\bar{\sigma} = \frac{e^{\beta Jz\bar{\sigma}} - e^{-\beta Jz\bar{\sigma}}}{e^{\beta Jz\bar{\sigma}} + e^{-\beta Jz\bar{\sigma}}}}$, $\boxed{Z = Z_1^N}$

- Internal energy: $U = -\frac{\partial \ln Z}{\partial \beta} = -N\frac{\partial \ln Z_1}{\partial \beta}$
  $= -NJz\bar{\sigma}\frac{e^{\beta Jz\bar{\sigma}} - e^{-\beta Jz\bar{\sigma}}}{e^{\beta Jz\bar{\sigma}} + e^{-\beta Jz\bar{\sigma}}} = -NJz\bar{\sigma}^2 = -NkT_c\bar{\sigma}^2.$
- $\bar{\sigma} = \frac{e^{\beta Jz\bar{\sigma}} - e^{-\beta Jz\bar{\sigma}}}{e^{\beta Jz\bar{\sigma}} + e^{-\beta Jz\bar{\sigma}}} = \frac{e^{\frac{T_c}{T}\bar{\sigma}} - e^{-\frac{T_c}{T}\bar{\sigma}}}{e^{\frac{T_c}{T}\bar{\sigma}} + e^{-\frac{T_c}{T}\bar{\sigma}}}.$
  As $\bar{\sigma}(T \to T_c^-) \to 0$, $x \equiv \frac{T_c}{T}\bar{\sigma} \to 0.$
  $\bar{\sigma} = \frac{e^x - e^{-x}}{e^x + e^{-x}} \simeq \frac{(1+x+\frac{1}{2}x^2+\frac{1}{6}x^3)-(1-x+\frac{1}{2}x^2-\frac{1}{6}x^3)}{(1+x+\frac{1}{2}x^2+\frac{1}{6}x^3)+(1-x+\frac{1}{2}x^2-\frac{1}{6}x^3)} = \frac{2x+\frac{1}{3}x^3}{2+x^2}$

Thermal capacity $\boxed{Z_1 = e^{\beta J z\bar{\sigma}} + e^{-\beta J z\bar{\sigma}}}$, $\boxed{T_c = \frac{Jz}{k}}$, $\boxed{\bar{\sigma} = \frac{e^{\beta J z\bar{\sigma}} - e^{-\beta J z\bar{\sigma}}}{e^{\beta J z\bar{\sigma}} + e^{-\beta J z\bar{\sigma}}}}$, $\boxed{Z = Z_1^N}$

- Internal energy: $U = -\frac{\partial \ln Z}{\partial \beta} = -N\frac{\partial \ln Z_1}{\partial \beta}$
  $= -NJz\bar{\sigma}\frac{e^{\beta J z\bar{\sigma}} - e^{-\beta J z\bar{\sigma}}}{e^{\beta J z\bar{\sigma}} + e^{-\beta J z\bar{\sigma}}} = -NJz\bar{\sigma}^2 = -NkT_c\bar{\sigma}^2$.
- $\bar{\sigma} = \frac{e^{\beta J z\bar{\sigma}} - e^{-\beta J z\bar{\sigma}}}{e^{\beta J z\bar{\sigma}} + e^{-\beta J z\bar{\sigma}}} = \frac{e^{\frac{T_c}{T}\bar{\sigma}} - e^{-\frac{T_c}{T}\bar{\sigma}}}{e^{\frac{T_c}{T}\bar{\sigma}} + e^{-\frac{T_c}{T}\bar{\sigma}}}$.
  As $\bar{\sigma}(T \to T_c^-) \to 0$, $x \equiv \frac{T_c}{T}\bar{\sigma} \to 0$.
  $\bar{\sigma} = \frac{e^x - e^{-x}}{e^x + e^{-x}} \simeq \frac{(1+x+\frac{1}{2}x^2+\frac{1}{6}x^3)-(1-x+\frac{1}{2}x^2-\frac{1}{6}x^3)}{(1+x+\frac{1}{2}x^2+\frac{1}{6}x^3)+(1-x+\frac{1}{2}x^2-\frac{1}{6}x^3)} = \frac{2x+\frac{1}{3}x^3}{2+x^2}$
  $= \frac{x+\frac{1}{6}x^3}{1+\frac{1}{2}x^2}$

Thermal capacity $\boxed{Z_1 = e^{\beta Jz\bar{\sigma}} + e^{-\beta Jz\bar{\sigma}}}$, $\boxed{T_c = \frac{Jz}{k}}$, $\boxed{\bar{\sigma} = \frac{e^{\beta Jz\bar{\sigma}} - e^{-\beta Jz\bar{\sigma}}}{e^{\beta Jz\bar{\sigma}} + e^{-\beta Jz\bar{\sigma}}}}$, $\boxed{Z = Z_1^N}$

- Internal energy: $U = -\frac{\partial \ln Z}{\partial \beta} = -N\frac{\partial \ln Z_1}{\partial \beta}$
  $= -NJz\bar{\sigma}\frac{e^{\beta Jz\bar{\sigma}} - e^{-\beta Jz\bar{\sigma}}}{e^{\beta Jz\bar{\sigma}} + e^{-\beta Jz\bar{\sigma}}} = -NJz\bar{\sigma}^2 = -NkT_c\bar{\sigma}^2$.
- $\bar{\sigma} = \frac{e^{\beta Jz\bar{\sigma}} - e^{-\beta Jz\bar{\sigma}}}{e^{\beta Jz\bar{\sigma}} + e^{-\beta Jz\bar{\sigma}}} = \frac{e^{\frac{T_c}{T}\bar{\sigma}} - e^{-\frac{T_c}{T}\bar{\sigma}}}{e^{\frac{T_c}{T}\bar{\sigma}} + e^{-\frac{T_c}{T}\bar{\sigma}}}$.
  As $\bar{\sigma}(T \to T_c^-) \to 0$, $x \equiv \frac{T_c}{T}\bar{\sigma} \to 0$.
  $\bar{\sigma} = \frac{e^x - e^{-x}}{e^x + e^{-x}} \simeq \frac{(1+x+\frac{1}{2}x^2+\frac{1}{6}x^3)-(1-x+\frac{1}{2}x^2-\frac{1}{6}x^3)}{(1+x+\frac{1}{2}x^2+\frac{1}{6}x^3)+(1-x+\frac{1}{2}x^2-\frac{1}{6}x^3)} = \frac{2x+\frac{1}{3}x^3}{2+x^2}$
  $= \frac{x+\frac{1}{6}x^3}{1+\frac{1}{2}x^2} \simeq x(1+\frac{1}{6}x^2)(1-\frac{1}{2}x^2)$

Thermal capacity $\boxed{Z_1 = e^{\beta J z\bar{\sigma}} + e^{-\beta J z\bar{\sigma}}}$, $\boxed{T_c = \frac{Jz}{k}}$,

$\boxed{\bar{\sigma} = \frac{e^{\beta J z\bar{\sigma}} - e^{-\beta J z\bar{\sigma}}}{e^{\beta J z\bar{\sigma}} + e^{-\beta J z\bar{\sigma}}}}$, $\boxed{Z = Z_1^N}$

- Internal energy: $U = -\frac{\partial \ln Z}{\partial \beta} = -N\frac{\partial \ln Z_1}{\partial \beta}$
  $= -NJz\bar{\sigma}\frac{e^{\beta J z\bar{\sigma}} - e^{-\beta J z\bar{\sigma}}}{e^{\beta J z\bar{\sigma}} + e^{-\beta J z\bar{\sigma}}} = -NJz\bar{\sigma}^2 = -NkT_c\bar{\sigma}^2.$
- $\bar{\sigma} = \frac{e^{\beta J z\bar{\sigma}} - e^{-\beta J z\bar{\sigma}}}{e^{\beta J z\bar{\sigma}} + e^{-\beta J z\bar{\sigma}}} = \frac{e^{\frac{T_c}{T}\bar{\sigma}} - e^{-\frac{T_c}{T}\bar{\sigma}}}{e^{\frac{T_c}{T}\bar{\sigma}} + e^{-\frac{T_c}{T}\bar{\sigma}}}.$
  As $\bar{\sigma}(T \to T_c^-) \to 0$, $x \equiv \frac{T_c}{T}\bar{\sigma} \to 0.$
  $\bar{\sigma} = \frac{e^x - e^{-x}}{e^x + e^{-x}} \simeq \frac{(1+x+\frac{1}{2}x^2+\frac{1}{6}x^3)-(1-x+\frac{1}{2}x^2-\frac{1}{6}x^3)}{(1+x+\frac{1}{2}x^2+\frac{1}{6}x^3)+(1-x+\frac{1}{2}x^2-\frac{1}{6}x^3)} = \frac{2x+\frac{1}{3}x^3}{2+x^2}$
  $= \frac{x+\frac{1}{6}x^3}{1+\frac{1}{2}x^2} \simeq x(1+\frac{1}{6}x^2)(1-\frac{1}{2}x^2) \simeq x(1-\frac{1}{3}x^2).$

Thermal capacity $\boxed{Z_1 = e^{\beta J z \bar{\sigma}} + e^{-\beta J z \bar{\sigma}}}$, $\boxed{T_c = \frac{Jz}{k}}$, $\boxed{\bar{\sigma} = \frac{e^{\beta J z \bar{\sigma}} - e^{-\beta J z \bar{\sigma}}}{e^{\beta J z \bar{\sigma}} + e^{-\beta J z \bar{\sigma}}}}$, $\boxed{Z = Z_1^N}$

- Internal energy: $U = -\frac{\partial \ln Z}{\partial \beta} = -N\frac{\partial \ln Z_1}{\partial \beta}$
  $= -NJz\bar{\sigma}\frac{e^{\beta J z \bar{\sigma}} - e^{-\beta J z \bar{\sigma}}}{e^{\beta J z \bar{\sigma}} + e^{-\beta J z \bar{\sigma}}} = -NJz\bar{\sigma}^2 = -NkT_c\bar{\sigma}^2.$
- $\bar{\sigma} = \frac{e^{\beta J z \bar{\sigma}} - e^{-\beta J z \bar{\sigma}}}{e^{\beta J z \bar{\sigma}} + e^{-\beta J z \bar{\sigma}}} = \frac{e^{\frac{T_c}{T}\bar{\sigma}} - e^{-\frac{T_c}{T}\bar{\sigma}}}{e^{\frac{T_c}{T}\bar{\sigma}} + e^{-\frac{T_c}{T}\bar{\sigma}}}.$
  As $\bar{\sigma}(T \to T_c^-) \to 0$, $x \equiv \frac{T_c}{T}\bar{\sigma} \to 0$.
  $\bar{\sigma} = \frac{e^x - e^{-x}}{e^x + e^{-x}} \simeq \frac{(1+x+\frac{1}{2}x^2+\frac{1}{6}x^3)-(1-x+\frac{1}{2}x^2-\frac{1}{6}x^3)}{(1+x+\frac{1}{2}x^2+\frac{1}{6}x^3)+(1-x+\frac{1}{2}x^2-\frac{1}{6}x^3)} = \frac{2x+\frac{1}{3}x^3}{2+x^2}$
  $= \frac{x+\frac{1}{6}x^3}{1+\frac{1}{2}x^2} \simeq x(1+\frac{1}{6}x^2)(1-\frac{1}{2}x^2) \simeq x(1-\frac{1}{3}x^2).$
  I.e., $\bar{\sigma} = \frac{T_c}{T}\bar{\sigma}[1 - \frac{1}{3}(\frac{T_c}{T}\bar{\sigma})^2]$.

Thermal capacity $\boxed{Z_1 = e^{\beta J z\bar\sigma} + e^{-\beta J z\bar\sigma}}$, $\boxed{T_c = \frac{Jz}{k}}$, $\boxed{\bar\sigma = \frac{e^{\beta J z\bar\sigma} - e^{-\beta J z\bar\sigma}}{e^{\beta J z\bar\sigma} + e^{-\beta J z\bar\sigma}}}$, $\boxed{Z = Z_1^N}$

- Internal energy: $U = -\frac{\partial \ln Z}{\partial \beta} = -N\frac{\partial \ln Z_1}{\partial \beta}$
  $= -NJz\bar\sigma \frac{e^{\beta J z\bar\sigma} - e^{-\beta J z\bar\sigma}}{e^{\beta J z\bar\sigma} + e^{-\beta J z\bar\sigma}} = -NJz\bar\sigma^2 = -NkT_c\bar\sigma^2.$
- $\bar\sigma = \frac{e^{\beta J z\bar\sigma} - e^{-\beta J z\bar\sigma}}{e^{\beta J z\bar\sigma} + e^{-\beta J z\bar\sigma}} = \frac{e^{\frac{T_c}{T}\bar\sigma} - e^{-\frac{T_c}{T}\bar\sigma}}{e^{\frac{T_c}{T}\bar\sigma} + e^{-\frac{T_c}{T}\bar\sigma}}.$
  As $\bar\sigma(T \to T_c^-) \to 0$, $x \equiv \frac{T_c}{T}\bar\sigma \to 0$.
  $\bar\sigma = \frac{e^x - e^{-x}}{e^x + e^{-x}} \simeq \frac{(1+x+\frac{1}{2}x^2+\frac{1}{6}x^3)-(1-x+\frac{1}{2}x^2-\frac{1}{6}x^3)}{(1+x+\frac{1}{2}x^2+\frac{1}{6}x^3)+(1-x+\frac{1}{2}x^2-\frac{1}{6}x^3)} = \frac{2x+\frac{1}{3}x^3}{2+x^2}$
  $= \frac{x+\frac{1}{6}x^3}{1+\frac{1}{2}x^2} \simeq x(1+\frac{1}{6}x^2)(1-\frac{1}{2}x^2) \simeq x(1-\frac{1}{3}x^2).$
  I.e., $\bar\sigma = \frac{T_c}{T}\bar\sigma[1 - \frac{1}{3}(\frac{T_c}{T}\bar\sigma)^2]$. $\Rightarrow \frac{T}{T_c} = 1 - \frac{1}{3}(\frac{T_c}{T}\bar\sigma)^2$

Thermal capacity $\boxed{Z_1 = e^{\beta J z \bar{\sigma}} + e^{-\beta J z \bar{\sigma}}}$, $\boxed{T_c = \frac{Jz}{k}}$, $\boxed{\bar{\sigma} = \frac{e^{\beta J z \bar{\sigma}} - e^{-\beta J z \bar{\sigma}}}{e^{\beta J z \bar{\sigma}} + e^{-\beta J z \bar{\sigma}}}}$, $\boxed{Z = Z_1^N}$

- Internal energy: $U = -\frac{\partial \ln Z}{\partial \beta} = -N\frac{\partial \ln Z_1}{\partial \beta}$
  $= -NJz\bar{\sigma}\frac{e^{\beta J z \bar{\sigma}} - e^{-\beta J z \bar{\sigma}}}{e^{\beta J z \bar{\sigma}} + e^{-\beta J z \bar{\sigma}}} = -NJz\bar{\sigma}^2 = -NkT_c\bar{\sigma}^2.$
- $\bar{\sigma} = \frac{e^{\beta J z \bar{\sigma}} - e^{-\beta J z \bar{\sigma}}}{e^{\beta J z \bar{\sigma}} + e^{-\beta J z \bar{\sigma}}} = \frac{e^{\frac{T_c}{T}\bar{\sigma}} - e^{-\frac{T_c}{T}\bar{\sigma}}}{e^{\frac{T_c}{T}\bar{\sigma}} + e^{-\frac{T_c}{T}\bar{\sigma}}}.$
  As $\bar{\sigma}(T \to T_c^-) \to 0$, $x \equiv \frac{T_c}{T}\bar{\sigma} \to 0.$
  $\bar{\sigma} = \frac{e^x - e^{-x}}{e^x + e^{-x}} \simeq \frac{(1+x+\frac{1}{2}x^2+\frac{1}{6}x^3)-(1-x+\frac{1}{2}x^2-\frac{1}{6}x^3)}{(1+x+\frac{1}{2}x^2+\frac{1}{6}x^3)+(1-x+\frac{1}{2}x^2-\frac{1}{6}x^3)} = \frac{2x+\frac{1}{3}x^3}{2+x^2}$
  $= \frac{x+\frac{1}{6}x^3}{1+\frac{1}{2}x^2} \simeq x(1+\frac{1}{6}x^2)(1-\frac{1}{2}x^2) \simeq x(1-\frac{1}{3}x^2).$
  I.e., $\bar{\sigma} = \frac{T_c}{T}\bar{\sigma}[1 - \frac{1}{3}(\frac{T_c}{T}\bar{\sigma})^2]. \Rightarrow \frac{T}{T_c} = 1 - \frac{1}{3}(\frac{T_c}{T}\bar{\sigma})^2$
  $\Rightarrow \bar{\sigma}^2 = \frac{1-\frac{T}{T_c}}{\frac{1}{3}(\frac{T_c}{T})^2} = 3(\frac{T}{T_c})^2\frac{T_c - T}{T_c}.$

Thermal capacity

$$\boxed{U = -NkT_c\bar{\sigma}^2,\ \bar{\sigma}^2(T \to T_c^-) = 3(\frac{T}{T_c})^2\frac{T_c - T}{T_c}}$$

- As $T > T_c$, $\bar{\sigma} = 0$ (from the figure),

Thermal capacity

$$\boxed{U = -NkT_c\bar{\sigma}^2,\ \bar{\sigma}^2(T \to T_c^-) = 3(\frac{T}{T_c})^2\frac{T_c - T}{T_c}}$$

- As $T > T_c$, $\bar{\sigma} = 0$ (from the figure), $U = 0$, $C_B(B = 0, T \to T_c^+) = 0$.

Thermal capacity

$$\boxed{U = -NkT_c\bar{\sigma}^2,\ \bar{\sigma}^2(T \to T_c^-) = 3(\frac{T}{T_c})^2\frac{T_c - T}{T_c}}$$

- As $T > T_c$, $\bar{\sigma} = 0$ (from the figure), $U = 0$, $C_B(B = 0, T \to T_c^+) = 0$.
- $T \to T_c^-$, $U(T \to T_c^-) = -NkT_c \cdot 3(\frac{T}{T_c})^2\frac{T_c - T}{T_c}$

Thermal capacity

$$\boxed{U = -NkT_c\bar{\sigma}^2,\ \bar{\sigma}^2(T \to T_c^-) = 3(\frac{T}{T_c})^2\frac{T_c-T}{T_c}}$$

- As $T > T_c$, $\bar{\sigma} = 0$ (from the figure), $U = 0$, $C_B(B = 0, T \to T_c^+) = 0$.
- $T \to T_c^-$, $U(T \to T_c^-) = -NkT_c \cdot 3(\frac{T}{T_c})^2\frac{T_c-T}{T_c}$ $= 3Nk\frac{T^2(T-T_c)}{T_c^2}$

Thermal capacity

$$\boxed{U = -NkT_c\bar{\sigma}^2,\ \bar{\sigma}^2(T \to T_c^-) = 3(\frac{T}{T_c})^2\frac{T_c-T}{T_c}}$$

- As $T > T_c$, $\bar{\sigma} = 0$ (from the figure), $U = 0$, $C_B(B = 0, T \to T_c^+) = 0$.
- $T \to T_c^-$, $U(T \to T_c^-) = -NkT_c \cdot 3(\frac{T}{T_c})^2\frac{T_c-T}{T_c}$ $= 3Nk\frac{T^2(T-T_c)}{T_c^2}$ (notice not suitable for non $T \to T_c^-$).

Thermal capacity

$$\boxed{U = -NkT_c\bar{\sigma}^2,\ \bar{\sigma}^2(T \to T_c^-) = 3(\frac{T}{T_c})^2\frac{T_c - T}{T_c}}$$

- As $T > T_c$, $\bar{\sigma} = 0$ (from the figure), $U = 0$,
  $C_B(B = 0, T \to T_c^+) = 0$.
- $T \to T_c^-$, $U(T \to T_c^-) = -NkT_c \cdot 3(\frac{T}{T_c})^2\frac{T_c - T}{T_c}$
  $= 3Nk\frac{T^2(T - T_c)}{T_c^2}$ (notice not suitable for non $T \to T_c^-$).
  $C_B(B = 0, T \to T_c^-) = 3Nk$.

Thermal capacity

$$\boxed{U=-NkT_c\bar{\sigma}^2,\ \bar{\sigma}^2(T\to T_c^-)=3(\frac{T}{T_c})^2\frac{T_c-T}{T_c}}$$

- As $T>T_c$, $\bar{\sigma}=0$ (from the figure), $U=0$,
  $C_B(B=0,T\to T_c^+)=0$.
- $T\to T_c^-$, $U(T\to T_c^-)=-NkT_c\cdot 3(\frac{T}{T_c})^2\frac{T_c-T}{T_c}$
  $=3Nk\frac{T^2(T-T_c)}{T_c^2}$ (notice not suitable for non $T\to T_c^-$).
  $C_B(B=0,T\to T_c^-)=3Nk$.
- Phase transition.

Table of contents

9.10 Grand canonical ensemble

9.10 Grand canonical ensemble

- N is also not fixed.

9.10 Grand canonical ensemble

- N is also not fixed.
- System and the reservoir have particles and energy exchange.

9.10 Grand canonical ensemble

- N is also not fixed.
- System and the reservoir have particles and energy exchange.
- The combined system: $E + E_r = E^{(0)}$, $N + N_r = N^{(0)}$.

9.10 Grand canonical ensemble

- N is also not fixed.
- System and the reservoir have particles and energy exchange.
- The combined system: $E + E_r = E^{(0)}$, $N + N_r = N^{(0)}$.
- For a given micro-state of the system Ns, number of micro-states of the reservoir: $\Omega_r(N^{(0)} - N, E^{(0)} - E_s)$.

9.10 Grand canonical ensemble

- N is also not fixed.
- System and the reservoir have particles and energy exchange.
- The combined system: $E + E_r = E^{(0)}$, $N + N_r = N^{(0)}$.
- For a given micro-state of the system Ns, number of micro-states of the reservoir: $\Omega_r(N^{(0)} - N, E^{(0)} - E_s)$.
- Using the equal probability principle, $\rho_{Ns} \propto \Omega_r$.

9.10 Grand canonical ensemble

- N is also not fixed.
- System and the reservoir have particles and energy exchange.
- The combined system: $E + E_r = E^{(0)}$, $N + N_r = N^{(0)}$.
- For a given micro-state of the system Ns, number of micro-states of the reservoir: $\Omega_r(N^{(0)} - N, E^{(0)} - E_s)$.
- Using the equal probability principle, $\rho_{Ns} \propto \Omega_r$.
- Considering $N \ll N^{(0)}$, $E \ll E^{(0)}$,

9.10 Grand canonical ensemble

- N is also not fixed.
- System and the reservoir have particles and energy exchange.
- The combined system: $E + E_r = E^{(0)}$, $N + N_r = N^{(0)}$.
- For a given micro-state of the system Ns, number of micro-states of the reservoir: $\Omega_r(N^{(0)} - N, E^{(0)} - E_s)$.
- Using the equal probability principle, $\rho_{Ns} \propto \Omega_r$.
- Considering $N \ll N^{(0)}$, $E \ll E^{(0)}$,
  $\ln \Omega_r(N^{(0)} - N, E^{(0)} - E_s)$
  $\simeq \ln \Omega_r(N^{(0)}, E^{(0)}) - \frac{\partial \ln \Omega_r}{\partial N_r}\big|_{N_r = N^{(0)}} N - \frac{\partial \ln \Omega_r}{\partial E_r}\big|_{E_r = E^{(0)}} E_s$

9.10 Grand canonical ensemble

- N is also not fixed.
- System and the reservoir have particles and energy exchange.
- The combined system: $E + E_r = E^{(0)}$, $N + N_r = N^{(0)}$.
- For a given micro-state of the system Ns, number of micro-states of the reservoir: $\Omega_r(N^{(0)} - N, E^{(0)} - E_s)$.
- Using the equal probability principle, $\rho_{Ns} \propto \Omega_r$.
- Considering $N \ll N^{(0)}$, $E \ll E^{(0)}$,
  $\ln \Omega_r(N^{(0)} - N, E^{(0)} - E_s)$
  $\simeq \ln \Omega_r(N^{(0)}, E^{(0)}) - \frac{\partial \ln \Omega_r}{\partial N_r}|_{N_r = N^{(0)}} N - \frac{\partial \ln \Omega_r}{\partial E_r}|_{E_r = E^{(0)}} E_s$
  $= \ln \Omega_r(N^{(0)}, E^{(0)}) - \alpha N - \beta E_s$.

Grand canonical ensemble

- $\alpha = \frac{\partial \ln \Omega_r}{\partial N_r}\Big|_{N_r=N^{(0)}} = -\frac{\mu}{kT}$,

Grand canonical ensemble

- $\alpha = \frac{\partial \ln \Omega_r}{\partial N_r}\Big|_{N_r = N^{(0)}} = -\frac{\mu}{kT}$, $\beta = \frac{\partial \ln \Omega_r}{\partial E_r}\Big|_{E_r = E^{(0)}} = \frac{1}{kT}$.

Grand canonical ensemble

- $\alpha = \frac{\partial \ln \Omega_r}{\partial N_r}\big|_{N_r = N^{(0)}} = -\frac{\mu}{kT}$, $\beta = \frac{\partial \ln \Omega_r}{\partial E_r}\big|_{E_r = E^{(0)}} = \frac{1}{kT}$.
- $\rho_{Ns} \propto e^{\ln \Omega_r(N^{(0)}, E^{(0)}) - \alpha N - \beta E_s}$

Grand canonical ensemble

- $\alpha = \frac{\partial \ln \Omega_r}{\partial N_r}\big|_{N_r = N^{(0)}} = -\frac{\mu}{kT}$, $\beta = \frac{\partial \ln \Omega_r}{\partial E_r}\big|_{E_r = E^{(0)}} = \frac{1}{kT}$.
- $\rho_{Ns} \propto e^{\ln \Omega_r (N^{(0)}, E^{(0)}) - \alpha N - \beta E_s} \propto e^{-\alpha N - \beta E_s}$

Grand canonical ensemble

- $\alpha = \frac{\partial \ln \Omega_r}{\partial N_r}\Big|_{N_r = N^{(0)}} = -\frac{\mu}{kT}$, $\beta = \frac{\partial \ln \Omega_r}{\partial E_r}\Big|_{E_r = E^{(0)}} = \frac{1}{kT}$.
- $\rho_{Ns} \propto e^{\ln \Omega_r (N^{(0)}, E^{(0)}) - \alpha N - \beta E_s} \propto e^{-\alpha N - \beta E_s}$
  $= \frac{1}{\mathcal{Z}} e^{-\alpha N - \beta E_s}$.

Grand canonical ensemble

- $\alpha = \frac{\partial \ln \Omega_r}{\partial N_r}\Big|_{N_r=N^{(0)}} = -\frac{\mu}{kT}$, $\beta = \frac{\partial \ln \Omega_r}{\partial E_r}\Big|_{E_r=E^{(0)}} = \frac{1}{kT}$.
- $\rho_{Ns} \propto e^{\ln \Omega_r(N^{(0)},E^{(0)})-\alpha N-\beta E_s} \propto e^{-\alpha N-\beta E_s}$ $= \frac{1}{\mathcal{Z}} e^{-\alpha N-\beta E_s}$.

  The grand partition function: $\mathcal{Z} = \sum_{N=0}^{\infty} \sum_s e^{-\alpha N-\beta E_s}$.

Grand canonical ensemble

- $\alpha = \frac{\partial \ln \Omega_r}{\partial N_r}\Big|_{N_r=N^{(0)}} = -\frac{\mu}{kT}$, $\beta = \frac{\partial \ln \Omega_r}{\partial E_r}\Big|_{E_r=E^{(0)}} = \frac{1}{kT}$.
- $\rho_{Ns} \propto e^{\ln \Omega_r(N^{(0)},E^{(0)})-\alpha N-\beta E_s} \propto e^{-\alpha N-\beta E_s}$
  $= \frac{1}{\mathcal{Z}} e^{-\alpha N-\beta E_s}$.

  The grand partition function: $\mathcal{Z} = \sum_{N=0}^{\infty}\sum_s e^{-\alpha N-\beta E_s}$.
- Continuous case: $\rho_N(q,p)\mathrm{d}\Omega = \frac{1}{N!h^{Nr}}\frac{e^{-\alpha N-\beta E(q,p)}}{\mathcal{Z}}\mathrm{d}\Omega$.

Grand canonical ensemble

- $\alpha = \frac{\partial \ln \Omega_r}{\partial N_r}\big|_{N_r = N^{(0)}} = -\frac{\mu}{kT}$, $\beta = \frac{\partial \ln \Omega_r}{\partial E_r}\big|_{E_r = E^{(0)}} = \frac{1}{kT}$.
- $\rho_{Ns} \propto e^{\ln \Omega_r(N^{(0)}, E^{(0)}) - \alpha N - \beta E_s} \propto e^{-\alpha N - \beta E_s}$
  $= \frac{1}{\mathcal{Z}} e^{-\alpha N - \beta E_s}$.

  The grand partition function: $\mathcal{Z} = \sum_{N=0}^{\infty} \sum_s e^{-\alpha N - \beta E_s}$.
- Continuous case: $\rho_N(q,p)\mathrm{d}\Omega = \frac{1}{N! h^{Nr}} \frac{e^{-\alpha N - \beta E(q,p)}}{\mathcal{Z}} \mathrm{d}\Omega$.
  Normalization: $\sum_N \int \rho_N \mathrm{d}\Omega = 1$,

Grand canonical ensemble

- $\alpha = \frac{\partial \ln \Omega_r}{\partial N_r}\Big|_{N_r=N^{(0)}} = -\frac{\mu}{kT}$, $\beta = \frac{\partial \ln \Omega_r}{\partial E_r}\Big|_{E_r=E^{(0)}} = \frac{1}{kT}$.
- $\rho_{Ns} \propto e^{\ln \Omega_r(N^{(0)},E^{(0)})-\alpha N-\beta E_s} \propto e^{-\alpha N-\beta E_s}$
  $= \frac{1}{\mathcal{Z}} e^{-\alpha N-\beta E_s}$.

  The grand partition function: $\mathcal{Z} = \sum_{N=0}^{\infty} \sum_{s} e^{-\alpha N-\beta E_s}$.
- Continuous case: $\rho_N(q,p)\mathrm{d}\Omega = \frac{1}{N!h^{Nr}} \frac{e^{-\alpha N-\beta E(q,p)}}{\mathcal{Z}} \mathrm{d}\Omega$.
  Normalization: $\sum_N \int \rho_N \mathrm{d}\Omega = 1$, i.e.,

  $\sum_N \frac{1}{N!h^{Nr}} \int \frac{e^{-\alpha N-\beta E(q,p)}}{\mathcal{Z}} \mathrm{d}\Omega = 1$,

Grand canonical ensemble

- $\alpha = \frac{\partial \ln \Omega_r}{\partial N_r}\Big|_{N_r=N^{(0)}} = -\frac{\mu}{kT}$, $\beta = \frac{\partial \ln \Omega_r}{\partial E_r}\Big|_{E_r=E^{(0)}} = \frac{1}{kT}$.
- $\rho_{Ns} \propto e^{\ln \Omega_r(N^{(0)},E^{(0)})-\alpha N-\beta E_s} \propto e^{-\alpha N-\beta E_s}$
  $= \frac{1}{\mathcal{Z}} e^{-\alpha N-\beta E_s}$.

  The grand partition function: $\mathcal{Z} = \sum_{N=0}^{\infty} \sum_s e^{-\alpha N-\beta E_s}$.
- Continuous case: $\rho_N(q,p)\mathrm{d}\Omega = \frac{1}{N! h^{Nr}} \frac{e^{-\alpha N-\beta E(q,p)}}{\mathcal{Z}} \mathrm{d}\Omega$.
  Normalization: $\sum_N \int \rho_N \mathrm{d}\Omega = 1$, i.e.,

  $$\sum_N \frac{1}{N! h^{Nr}} \int \frac{e^{-\alpha N-\beta E(q,p)}}{\mathcal{Z}} \mathrm{d}\Omega = 1,$$

  $$\Rightarrow \mathcal{Z} = \sum_N \frac{e^{-\alpha N}}{N! h^{Nr}} \int e^{-\beta E(q,p)} \mathrm{d}\Omega.$$

Table of contents

9.11 Thermodynamics in grand canonical ensemble

9.11 Thermodynamics in grand canonical ensemble

- Average number of particles: $\overline{N} = \sum_N \sum_s N \rho_{Ns}$

9.11 Thermodynamics in grand canonical ensemble

- Average number of particles: $\overline{N} = \sum_N \sum_s N \rho_{Ns}$

$$= \frac{1}{\mathcal{Z}} \sum_N \sum_s N e^{-\alpha N - \beta E_s}$$

9.11 Thermodynamics in grand canonical ensemble

- Average number of particles: $\overline{N} = \sum_N \sum_s N \rho_{Ns}$
$= \frac{1}{\mathcal{Z}} \sum_N \sum_s N e^{-\alpha N - \beta E_s} = \frac{1}{\mathcal{Z}} (-\frac{\partial}{\partial \alpha}) \sum_N \sum_s e^{-\alpha N - \beta E_s}$

9.11 Thermodynamics in grand canonical ensemble

- Average number of particles: $\overline{N} = \sum_N \sum_s N \rho_{Ns}$
  $= \frac{1}{\mathcal{Z}} \sum_N \sum_s N e^{-\alpha N - \beta E_s} = \frac{1}{\mathcal{Z}} (-\frac{\partial}{\partial \alpha}) \sum_N \sum_s e^{-\alpha N - \beta E_s}$
  $= \frac{1}{\mathcal{Z}} (-\frac{\partial}{\partial \alpha}) \mathcal{Z}$

9.11 Thermodynamics in grand canonical ensemble

- Average number of particles: $\overline{N} = \sum_N \sum_s N\rho_{Ns}$

$$= \frac{1}{\mathcal{Z}} \sum_N \sum_s N e^{-\alpha N - \beta E_s} = \frac{1}{\mathcal{Z}}\left(-\frac{\partial}{\partial \alpha}\right) \sum_N \sum_s e^{-\alpha N - \beta E_s}$$

$$= \frac{1}{\mathcal{Z}}\left(-\frac{\partial}{\partial \alpha}\right)\mathcal{Z} = -\frac{\partial \ln \mathcal{Z}}{\partial \alpha}.$$

9.11 Thermodynamics in grand canonical ensemble

- Average number of particles: $\overline{N} = \sum\limits_N \sum\limits_s N\rho_{Ns}$
  $= \frac{1}{\mathcal{Z}} \sum\limits_N \sum\limits_s N e^{-\alpha N - \beta E_s} = \frac{1}{\mathcal{Z}} (-\frac{\partial}{\partial \alpha}) \sum\limits_N \sum\limits_s e^{-\alpha N - \beta E_s}$
  $= \frac{1}{\mathcal{Z}} (-\frac{\partial}{\partial \alpha}) \mathcal{Z} = -\frac{\partial \ln \mathcal{Z}}{\partial \alpha}$.
- Internal energy: $U = \overline{E}$

9.11 Thermodynamics in grand canonical ensemble

- Average number of particles: $\overline{N} = \sum_N \sum_s N\rho_{Ns}$
  $= \frac{1}{\mathcal{Z}} \sum_N \sum_s N e^{-\alpha N - \beta E_s} = \frac{1}{\mathcal{Z}} (-\frac{\partial}{\partial \alpha}) \sum_N \sum_s e^{-\alpha N - \beta E_s}$
  $= \frac{1}{\mathcal{Z}} (-\frac{\partial}{\partial \alpha}) \mathcal{Z} = -\frac{\partial \ln \mathcal{Z}}{\partial \alpha}$.
- Internal energy: $U = \overline{E} = \frac{1}{\mathcal{Z}} \sum_N \sum_s E_s e^{-\alpha N - \beta E_s}$

9.11 Thermodynamics in grand canonical ensemble

- Average number of particles: $\overline{N} = \sum_N \sum_s N\rho_{Ns}$
  $= \frac{1}{\mathcal{Z}} \sum_N \sum_s N e^{-\alpha N - \beta E_s} = \frac{1}{\mathcal{Z}}(-\frac{\partial}{\partial \alpha}) \sum_N \sum_s e^{-\alpha N - \beta E_s}$
  $= \frac{1}{\mathcal{Z}}(-\frac{\partial}{\partial \alpha})\mathcal{Z} = -\frac{\partial \ln \mathcal{Z}}{\partial \alpha}$.
- Internal energy: $U = \overline{E} = \frac{1}{\mathcal{Z}} \sum_N \sum_s E_s e^{-\alpha N - \beta E_s}$
  $= \frac{1}{\mathcal{Z}}(-\frac{\partial}{\partial \beta}) \sum_N \sum_s e^{-\alpha N - \beta E_s}$

9.11 Thermodynamics in grand canonical ensemble

- Average number of particles: $\overline{N} = \sum_N \sum_s N \rho_{Ns}$

$$= \frac{1}{\mathcal{Z}} \sum_N \sum_s N e^{-\alpha N - \beta E_s} = \frac{1}{\mathcal{Z}} (-\frac{\partial}{\partial \alpha}) \sum_N \sum_s e^{-\alpha N - \beta E_s}$$

$$= \frac{1}{\mathcal{Z}} (-\frac{\partial}{\partial \alpha}) \mathcal{Z} = -\frac{\partial \ln \mathcal{Z}}{\partial \alpha}.$$

- Internal energy: $U = \overline{E} = \frac{1}{\mathcal{Z}} \sum_N \sum_s E_s e^{-\alpha N - \beta E_s}$

$$= \frac{1}{\mathcal{Z}} (-\frac{\partial}{\partial \beta}) \sum_N \sum_s e^{-\alpha N - \beta E_s} = \frac{1}{\mathcal{Z}} (-\frac{\partial}{\partial \beta}) \mathcal{Z}$$

9.11 Thermodynamics in grand canonical ensemble

- Average number of particles: $\overline{N} = \sum_N \sum_s N\rho_{Ns}$
$$= \frac{1}{\mathcal{Z}} \sum_N \sum_s N e^{-\alpha N - \beta E_s} = \frac{1}{\mathcal{Z}} (-\frac{\partial}{\partial \alpha}) \sum_N \sum_s e^{-\alpha N - \beta E_s}$$
$$= \frac{1}{\mathcal{Z}} (-\frac{\partial}{\partial \alpha}) \mathcal{Z} = -\frac{\partial \ln \mathcal{Z}}{\partial \alpha}.$$
- Internal energy: $U = \overline{E} = \frac{1}{\mathcal{Z}} \sum_N \sum_s E_s e^{-\alpha N - \beta E_s}$
$$= \frac{1}{\mathcal{Z}} (-\frac{\partial}{\partial \beta}) \sum_N \sum_s e^{-\alpha N - \beta E_s} = \frac{1}{\mathcal{Z}} (-\frac{\partial}{\partial \beta}) \mathcal{Z} = -\frac{\partial \ln \mathcal{Z}}{\partial \beta}.$$

9.11 Thermodynamics in grand canonical ensemble

- Average number of particles: $\overline{N} = \sum_N \sum_s N \rho_{Ns}$
  $= \frac{1}{\mathcal{Z}} \sum_N \sum_s N e^{-\alpha N - \beta E_s} = \frac{1}{\mathcal{Z}} (-\frac{\partial}{\partial \alpha}) \sum_N \sum_s e^{-\alpha N - \beta E_s}$
  $= \frac{1}{\mathcal{Z}} (-\frac{\partial}{\partial \alpha}) \mathcal{Z} = -\frac{\partial \ln \mathcal{Z}}{\partial \alpha}.$
- Internal energy: $U = \overline{E} = \frac{1}{\mathcal{Z}} \sum_N \sum_s E_s e^{-\alpha N - \beta E_s}$
  $= \frac{1}{\mathcal{Z}} (-\frac{\partial}{\partial \beta}) \sum_N \sum_s e^{-\alpha N - \beta E_s} = \frac{1}{\mathcal{Z}} (-\frac{\partial}{\partial \beta}) \mathcal{Z} = -\frac{\partial \ln \mathcal{Z}}{\partial \beta}.$
- Generalized force: $Y = \frac{1}{\mathcal{Z}} \sum_N \sum_s \frac{\partial E_s}{\partial y} e^{-\alpha N - \beta E_s}$

9.11 Thermodynamics in grand canonical ensemble

- Average number of particles: $\overline{N} = \sum_N \sum_s N\rho_{Ns}$

$$= \frac{1}{\mathcal{Z}} \sum_N \sum_s N e^{-\alpha N - \beta E_s} = \frac{1}{\mathcal{Z}}(-\frac{\partial}{\partial \alpha}) \sum_N \sum_s e^{-\alpha N - \beta E_s}$$

$$= \frac{1}{\mathcal{Z}}(-\frac{\partial}{\partial \alpha})\mathcal{Z} = -\frac{\partial \ln \mathcal{Z}}{\partial \alpha}.$$

- Internal energy: $U = \overline{E} = \frac{1}{\mathcal{Z}} \sum_N \sum_s E_s e^{-\alpha N - \beta E_s}$

$$= \frac{1}{\mathcal{Z}}(-\frac{\partial}{\partial \beta}) \sum_N \sum_s e^{-\alpha N - \beta E_s} = \frac{1}{\mathcal{Z}}(-\frac{\partial}{\partial \beta})\mathcal{Z} = -\frac{\partial \ln \mathcal{Z}}{\partial \beta}.$$

- Generalized force: $Y = \frac{1}{\mathcal{Z}} \sum_N \sum_s \frac{\partial E_s}{\partial y} e^{-\alpha N - \beta E_s}$

$$= \frac{1}{\mathcal{Z}}(-\frac{1}{\beta}\frac{\partial}{\partial y}) \sum_N \sum_s e^{-\alpha N - \beta E_s}$$

9.11 Thermodynamics in grand canonical ensemble

- Average number of particles: $\overline{N} = \sum_N \sum_s N\rho_{Ns}$
  $= \frac{1}{\mathcal{Z}} \sum_N \sum_s N e^{-\alpha N - \beta E_s} = \frac{1}{\mathcal{Z}}(-\frac{\partial}{\partial \alpha}) \sum_N \sum_s e^{-\alpha N - \beta E_s}$
  $= \frac{1}{\mathcal{Z}}(-\frac{\partial}{\partial \alpha})\mathcal{Z} = -\frac{\partial \ln \mathcal{Z}}{\partial \alpha}$.
- Internal energy: $U = \overline{E} = \frac{1}{\mathcal{Z}} \sum_N \sum_s E_s e^{-\alpha N - \beta E_s}$
  $= \frac{1}{\mathcal{Z}}(-\frac{\partial}{\partial \beta}) \sum_N \sum_s e^{-\alpha N - \beta E_s} = \frac{1}{\mathcal{Z}}(-\frac{\partial}{\partial \beta})\mathcal{Z} = -\frac{\partial \ln \mathcal{Z}}{\partial \beta}$.
- Generalized force: $Y = \frac{1}{\mathcal{Z}} \sum_N \sum_s \frac{\partial E_s}{\partial y} e^{-\alpha N - \beta E_s}$
  $= \frac{1}{\mathcal{Z}}(-\frac{1}{\beta}\frac{\partial}{\partial y}) \sum_N \sum_s e^{-\alpha N - \beta E_s} = \frac{1}{\mathcal{Z}}(-\frac{1}{\beta}\frac{\partial}{\partial y})\mathcal{Z}$

9.11 Thermodynamics in grand canonical ensemble

- Average number of particles: $\overline{N} = \sum_N \sum_s N\rho_{Ns}$
$$= \frac{1}{\mathcal{Z}} \sum_N \sum_s N e^{-\alpha N - \beta E_s} = \frac{1}{\mathcal{Z}}(-\frac{\partial}{\partial \alpha}) \sum_N \sum_s e^{-\alpha N - \beta E_s}$$
$$= \frac{1}{\mathcal{Z}}(-\frac{\partial}{\partial \alpha})\mathcal{Z} = -\frac{\partial \ln \mathcal{Z}}{\partial \alpha}.$$
- Internal energy: $U = \overline{E} = \frac{1}{\mathcal{Z}} \sum_N \sum_s E_s e^{-\alpha N - \beta E_s}$
$$= \frac{1}{\mathcal{Z}}(-\frac{\partial}{\partial \beta}) \sum_N \sum_s e^{-\alpha N - \beta E_s} = \frac{1}{\mathcal{Z}}(-\frac{\partial}{\partial \beta})\mathcal{Z} = -\frac{\partial \ln \mathcal{Z}}{\partial \beta}.$$
- Generalized force: $Y = \frac{1}{\mathcal{Z}} \sum_N \sum_s \frac{\partial E_s}{\partial y} e^{-\alpha N - \beta E_s}$
$$= \frac{1}{\mathcal{Z}}(-\frac{1}{\beta}\frac{\partial}{\partial y}) \sum_N \sum_s e^{-\alpha N - \beta E_s} = \frac{1}{\mathcal{Z}}(-\frac{1}{\beta}\frac{\partial}{\partial y})\mathcal{Z} = -\frac{1}{\beta}\frac{\partial \ln \mathcal{Z}}{\partial y}.$$

9.11 Thermodynamics in grand canonical ensemble

- Average number of particles: $\overline{N} = \sum_N \sum_s N\rho_{Ns}$
  $$= \frac{1}{\mathcal{Z}} \sum_N \sum_s N e^{-\alpha N - \beta E_s} = \frac{1}{\mathcal{Z}}(-\frac{\partial}{\partial\alpha}) \sum_N \sum_s e^{-\alpha N - \beta E_s}$$
  $$= \frac{1}{\mathcal{Z}}(-\frac{\partial}{\partial\alpha})\mathcal{Z} = -\frac{\partial \ln \mathcal{Z}}{\partial\alpha}.$$
- Internal energy: $U = \overline{E} = \frac{1}{\mathcal{Z}} \sum_N \sum_s E_s e^{-\alpha N - \beta E_s}$
  $$= \frac{1}{\mathcal{Z}}(-\frac{\partial}{\partial\beta}) \sum_N \sum_s e^{-\alpha N - \beta E_s} = \frac{1}{\mathcal{Z}}(-\frac{\partial}{\partial\beta})\mathcal{Z} = -\frac{\partial \ln \mathcal{Z}}{\partial\beta}.$$
- Generalized force: $Y = \frac{1}{\mathcal{Z}} \sum_N \sum_s \frac{\partial E_s}{\partial y} e^{-\alpha N - \beta E_s}$
  $$= \frac{1}{\mathcal{Z}}(-\frac{1}{\beta}\frac{\partial}{\partial y}) \sum_N \sum_s e^{-\alpha N - \beta E_s} = \frac{1}{\mathcal{Z}}(-\frac{1}{\beta}\frac{\partial}{\partial y})\mathcal{Z} = -\frac{1}{\beta}\frac{\partial \ln \mathcal{Z}}{\partial y}.$$
- Entropy (same procedure as canonical ensemble):
  $$S = k(\ln \mathcal{Z} - \alpha\frac{\partial \ln \mathcal{Z}}{\partial\alpha} - \beta\frac{\partial \ln \mathcal{Z}}{\partial\beta}).$$

Thermodynamics in grand canonical ensemble

- Grand potential (characteristic function) (3.2.10):
  $J = F - \mu N$

Thermodynamics in grand canonical ensemble

- Grand potential (characteristic function) (3.2.10):
  $J = F - \mu N = U - TS - \mu N$
  $= -\frac{\partial \ln \mathcal{Z}}{\partial \beta} - kT(\ln \mathcal{Z} - \alpha \frac{\partial \ln \mathcal{Z}}{\partial \alpha} - \beta \frac{\partial \ln \mathcal{Z}}{\partial \beta}) - \mu N$

Thermodynamics in grand canonical ensemble

- Grand potential (characteristic function) (3.2.10):
$$J = F - \mu N = U - TS - \mu N$$
$$= -\frac{\partial \ln \mathcal{Z}}{\partial \beta} - kT(\ln \mathcal{Z} - \alpha \frac{\partial \ln \mathcal{Z}}{\partial \alpha} - \beta \frac{\partial \ln \mathcal{Z}}{\partial \beta}) - \mu N$$
$$= -kT(\ln \mathcal{Z} - \frac{\mu}{kT}\overline{N}) - \mu N$$

Thermodynamics in grand canonical ensemble

- Grand potential (characteristic function) (3.2.10):
$$J = F - \mu N = U - TS - \mu N$$
$$= -\frac{\partial \ln \mathcal{Z}}{\partial \beta} - kT(\ln \mathcal{Z} - \alpha \frac{\partial \ln \mathcal{Z}}{\partial \alpha} - \beta \frac{\partial \ln \mathcal{Z}}{\partial \beta}) - \mu N$$
$$= -kT(\ln \mathcal{Z} - \frac{\mu}{kT}\overline{N}) - \mu N = -kT \ln \mathcal{Z}.$$

Thermodynamics in grand canonical ensemble

- Grand potential (characteristic function) (3.2.10):
  $$J = F - \mu N = U - TS - \mu N$$
  $$= -\frac{\partial \ln \mathcal{Z}}{\partial \beta} - kT(\ln \mathcal{Z} - \alpha \frac{\partial \ln \mathcal{Z}}{\partial \alpha} - \beta \frac{\partial \ln \mathcal{Z}}{\partial \beta}) - \mu N$$
  $$= -kT(\ln \mathcal{Z} - \frac{\mu}{kT}\overline{N}) - \mu N = -kT \ln \mathcal{Z}.$$
- Fluctuation of particle number:
  $$\overline{(N - \overline{N})^2}$$

Thermodynamics in grand canonical ensemble

- Grand potential (characteristic function) (3.2.10):
  $J = F - \mu N = U - TS - \mu N$
  $= -\frac{\partial \ln \mathcal{Z}}{\partial \beta} - kT(\ln \mathcal{Z} - \alpha \frac{\partial \ln \mathcal{Z}}{\partial \alpha} - \beta \frac{\partial \ln \mathcal{Z}}{\partial \beta}) - \mu N$
  $= -kT(\ln \mathcal{Z} - \frac{\mu}{kT}\overline{N}) - \mu N = -kT \ln \mathcal{Z}$.
- Fluctuation of particle number:
  $\overline{(N - \overline{N})^2} = \overline{N^2 - 2N\overline{N} + \overline{N}^2}$

Thermodynamics in grand canonical ensemble

- Grand potential (characteristic function) (3.2.10):
$$J = F - \mu N = U - TS - \mu N$$
$$= -\frac{\partial \ln \mathcal{Z}}{\partial \beta} - kT(\ln \mathcal{Z} - \alpha \frac{\partial \ln \mathcal{Z}}{\partial \alpha} - \beta \frac{\partial \ln \mathcal{Z}}{\partial \beta}) - \mu N$$
$$= -kT(\ln \mathcal{Z} - \frac{\mu}{kT}\overline{N}) - \mu N = -kT \ln \mathcal{Z}.$$
- Fluctuation of particle number:
$$\overline{(N - \overline{N})^2} = \overline{N^2 - 2N\overline{N} + \overline{N}^2} = \overline{N^2} - \overline{N}^2;$$

Thermodynamics in grand canonical ensemble

- Grand potential (characteristic function) (3.2.10):
$$J = F - \mu N = U - TS - \mu N$$
$$= -\frac{\partial \ln \mathcal{Z}}{\partial \beta} - kT(\ln \mathcal{Z} - \alpha \frac{\partial \ln \mathcal{Z}}{\partial \alpha} - \beta \frac{\partial \ln \mathcal{Z}}{\partial \beta}) - \mu N$$
$$= -kT(\ln \mathcal{Z} - \frac{\mu}{kT}\overline{N}) - \mu N = -kT \ln \mathcal{Z}.$$
- Fluctuation of particle number:
$$\overline{(N - \overline{N})^2} = \overline{N^2 - 2N\overline{N} + \overline{N}^2} = \overline{N^2} - \overline{N}^2;$$
- $\frac{\partial \overline{N}}{\partial \alpha}$

Thermodynamics in grand canonical ensemble

- Grand potential (characteristic function) (3.2.10):
$$J = F - \mu N = U - TS - \mu N$$
$$= -\frac{\partial \ln \mathcal{Z}}{\partial \beta} - kT(\ln \mathcal{Z} - \alpha\frac{\partial \ln \mathcal{Z}}{\partial \alpha} - \beta\frac{\partial \ln \mathcal{Z}}{\partial \beta}) - \mu N$$
$$= -kT(\ln \mathcal{Z} - \frac{\mu}{kT}\overline{N}) - \mu N = -kT \ln \mathcal{Z}.$$
- Fluctuation of particle number:
$$\overline{(N - \overline{N})^2} = \overline{N^2 - 2N\overline{N} + \overline{N}^2} = \overline{N^2} - \overline{N}^2;$$
- $\frac{\partial \overline{N}}{\partial \alpha} = \frac{\partial}{\partial \alpha}(\frac{1}{\mathcal{Z}}\sum_N \sum_s N e^{-\alpha N - \beta E_s})$

Thermodynamics in grand canonical ensemble

- Grand potential (characteristic function) (3.2.10):
$$J = F - \mu N = U - TS - \mu N$$
$$= -\frac{\partial \ln \mathcal{Z}}{\partial \beta} - kT(\ln \mathcal{Z} - \alpha \frac{\partial \ln \mathcal{Z}}{\partial \alpha} - \beta \frac{\partial \ln \mathcal{Z}}{\partial \beta}) - \mu N$$
$$= -kT(\ln \mathcal{Z} - \frac{\mu}{kT}\overline{N}) - \mu N = -kT \ln \mathcal{Z}.$$
- Fluctuation of particle number:
$$\overline{(N - \overline{N})^2} = \overline{N^2 - 2N\overline{N} + \overline{N}^2} = \overline{N^2} - \overline{N}^2;$$
- $$\frac{\partial \overline{N}}{\partial \alpha} = \frac{\partial}{\partial \alpha}(\frac{1}{\mathcal{Z}}\sum_N \sum_s N e^{-\alpha N - \beta E_s}) = \frac{\partial}{\partial \alpha}\frac{\sum\limits_N \sum\limits_s N e^{-\alpha N - \beta E_s}}{\sum\limits_N \sum\limits_s e^{-\alpha N - \beta E_s}}$$

Thermodynamics in grand canonical ensemble

- Grand potential (characteristic function) (3.2.10):
$$J = F - \mu N = U - TS - \mu N$$
$$= -\frac{\partial \ln \Xi}{\partial \beta} - kT(\ln \Xi - \alpha\frac{\partial \ln \Xi}{\partial \alpha} - \beta\frac{\partial \ln \Xi}{\partial \beta}) - \mu N$$
$$= -kT(\ln \Xi - \frac{\mu}{kT}\overline{N}) - \mu N = -kT\ln \Xi.$$
- Fluctuation of particle number:
$$\overline{(N-\overline{N})^2} = \overline{N^2 - 2N\overline{N} + \overline{N}^2} = \overline{N^2} - \overline{N}^2;$$
- $$\frac{\partial \overline{N}}{\partial \alpha} = \frac{\partial}{\partial \alpha}(\frac{1}{\Xi}\sum_N\sum_s N e^{-\alpha N - \beta E_s}) = \frac{\partial}{\partial \alpha}\frac{\sum\limits_N\sum\limits_s N e^{-\alpha N-\beta E_s}}{\sum\limits_N\sum\limits_s e^{-\alpha N-\beta E_s}}$$
$$= -\frac{\sum\limits_N\sum\limits_s N^2 e^{-\alpha N-\beta E_s}}{\sum\limits_N\sum\limits_s e^{-\alpha N-\beta E_s}} + \frac{(\sum\limits_N\sum\limits_s N e^{-\alpha N-\beta E_s})^2}{(\sum\limits_N\sum\limits_s e^{-\alpha N-\beta E_s})^2}$$

Thermodynamics in grand canonical ensemble

- Grand potential (characteristic function) (3.2.10):
$$J = F - \mu N = U - TS - \mu N$$
$$= -\frac{\partial \ln \mathcal{Z}}{\partial \beta} - kT(\ln \mathcal{Z} - \alpha\frac{\partial \ln \mathcal{Z}}{\partial \alpha} - \beta\frac{\partial \ln \mathcal{Z}}{\partial \beta}) - \mu N$$
$$= -kT(\ln \mathcal{Z} - \frac{\mu}{kT}\overline{N}) - \mu N = -kT \ln \mathcal{Z}.$$
- Fluctuation of particle number:
$$\overline{(N-\overline{N})^2} = \overline{N^2 - 2N\overline{N} + \overline{N}^2} = \overline{N^2} - \overline{N}^2;$$
- $$\frac{\partial \overline{N}}{\partial \alpha} = \frac{\partial}{\partial \alpha}\left(\frac{1}{\mathcal{Z}}\sum_N\sum_s N e^{-\alpha N - \beta E_s}\right) = \frac{\partial}{\partial \alpha}\frac{\sum\limits_N\sum\limits_s N e^{-\alpha N-\beta E_s}}{\sum\limits_N\sum\limits_s e^{-\alpha N-\beta E_s}}$$
$$= -\frac{\sum\limits_N\sum\limits_s N^2 e^{-\alpha N-\beta E_s}}{\sum\limits_N\sum\limits_s e^{-\alpha N-\beta E_s}} + \frac{(\sum\limits_N\sum\limits_s N e^{-\alpha N-\beta E_s})^2}{(\sum\limits_N\sum\limits_s e^{-\alpha N-\beta E_s})^2} = -\overline{N^2} + \overline{N}^2.$$

Thermodynamics in grand canonical ensemble

- Grand potential (characteristic function) (3.2.10):

$$J = F - \mu N = U - TS - \mu N$$
$$= -\frac{\partial \ln \mathcal{Z}}{\partial \beta} - kT(\ln \mathcal{Z} - \alpha \frac{\partial \ln \mathcal{Z}}{\partial \alpha} - \beta \frac{\partial \ln \mathcal{Z}}{\partial \beta}) - \mu N$$
$$= -kT(\ln \mathcal{Z} - \frac{\mu}{kT}\overline{N}) - \mu N = -kT \ln \mathcal{Z}.$$

- Fluctuation of particle number:

$$\overline{(N-\overline{N})^2} = \overline{N^2 - 2N\overline{N} + \overline{N}^2} = \overline{N^2} - \overline{N}^2;$$

- $$\frac{\partial \overline{N}}{\partial \alpha} = \frac{\partial}{\partial \alpha}\left(\frac{1}{\mathcal{Z}} \sum_N \sum_s N e^{-\alpha N - \beta E_s}\right) = \frac{\partial}{\partial \alpha} \frac{\sum\limits_N \sum\limits_s N e^{-\alpha N - \beta E_s}}{\sum\limits_N \sum\limits_s e^{-\alpha N - \beta E_s}}$$
$$= -\frac{\sum\limits_N \sum\limits_s N^2 e^{-\alpha N - \beta E_s}}{\sum\limits_N \sum\limits_s e^{-\alpha N - \beta E_s}} + \frac{(\sum\limits_N \sum\limits_s N e^{-\alpha N - \beta E_s})^2}{(\sum\limits_N \sum\limits_s e^{-\alpha N - \beta E_s})^2} = -\overline{N^2} + \overline{N}^2.$$

- $$\Rightarrow \overline{(N-\overline{N})^2} = -\left(\frac{\partial \overline{N}}{\partial \alpha}\right)_{\beta, y}$$

Thermodynamics in grand canonical ensemble

- Grand potential (characteristic function) (3.2.10):

$$J = F - \mu N = U - TS - \mu N$$
$$= -\frac{\partial \ln \mathcal{Z}}{\partial \beta} - kT(\ln \mathcal{Z} - \alpha \frac{\partial \ln \mathcal{Z}}{\partial \alpha} - \beta \frac{\partial \ln \mathcal{Z}}{\partial \beta}) - \mu N$$
$$= -kT(\ln \mathcal{Z} - \frac{\mu}{kT}\overline{N}) - \mu N = -kT \ln \mathcal{Z}.$$

- Fluctuation of particle number:

$$\overline{(N - \overline{N})^2} = \overline{N^2 - 2N\overline{N} + \overline{N}^2} = \overline{N^2} - \overline{N}^2;$$

- $$\frac{\partial \overline{N}}{\partial \alpha} = \frac{\partial}{\partial \alpha}(\frac{1}{\mathcal{Z}} \sum_N \sum_s N e^{-\alpha N - \beta E_s}) = \frac{\partial}{\partial \alpha} \frac{\sum\limits_N \sum\limits_s N e^{-\alpha N - \beta E_s}}{\sum\limits_N \sum\limits_s e^{-\alpha N - \beta E_s}}$$
$$= -\frac{\sum\limits_N \sum\limits_s N^2 e^{-\alpha N - \beta E_s}}{\sum\limits_N \sum\limits_s e^{-\alpha N - \beta E_s}} + \frac{(\sum\limits_N \sum\limits_s N e^{-\alpha N - \beta E_s})^2}{(\sum\limits_N \sum\limits_s e^{-\alpha N - \beta E_s})^2} = -\overline{N^2} + \overline{N}^2.$$

- $$\Rightarrow \overline{(N - \overline{N})^2} = -(\frac{\partial \overline{N}}{\partial \alpha})_{\beta,y} = kT(\frac{\partial \overline{N}}{\partial \mu})_{T,V}.$$

Fluctuation of particle number $\boxed{\overline{(N-\overline{N})^2} = kT(\frac{\partial \overline{N}}{\partial \mu})_{T,V}}$

- (3.2.2) $\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p + \mu\mathrm{d}\overline{N}$,

Fluctuation of particle number $\boxed{\overline{(N-\overline{N})^2} = kT(\frac{\partial \overline{N}}{\partial \mu})_{T,V}}$

- (3.2.2) $\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p + \mu\mathrm{d}\overline{N}$,
  i.e., $\mathrm{d}(\overline{N}\mu) = -(\overline{N}s)\mathrm{d}T + (\overline{N}v)\mathrm{d}p + \mu\mathrm{d}\overline{N}$

Fluctuation of particle number $\boxed{\overline{(N-\overline{N})^2} = kT(\frac{\partial \overline{N}}{\partial \mu})_{T,V}}$

- (3.2.2) $\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p + \mu\mathrm{d}\overline{N}$,
  i.e., $\mathrm{d}(\overline{N}\mu) = -(\overline{N}s)\mathrm{d}T + (\overline{N}v)\mathrm{d}p + \mu\mathrm{d}\overline{N}$
  $\Rightarrow \overline{N}\mathrm{d}\mu = -\overline{N}s\mathrm{d}T + \overline{N}v\mathrm{d}p$

Fluctuation of particle number $\boxed{\overline{(N-\overline{N})^2} = kT(\frac{\partial \overline{N}}{\partial \mu})_{T,V}}$

- (3.2.2) $\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p + \mu \mathrm{d}\overline{N}$,
  i.e., $\mathrm{d}(\overline{N}\mu) = -(\overline{N}s)\mathrm{d}T + (\overline{N}v)\mathrm{d}p + \mu \mathrm{d}\overline{N}$
  $\Rightarrow \overline{N}\mathrm{d}\mu = -\overline{N}s\mathrm{d}T + \overline{N}v\mathrm{d}p$
  $\Rightarrow \mathrm{d}\mu = v\mathrm{d}p - s\mathrm{d}T$

Fluctuation of particle number $\boxed{\overline{(N-\overline{N})^2} = kT(\frac{\partial \overline{N}}{\partial \mu})_{T,V}}$

- (3.2.2) $\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p + \mu \mathrm{d}\overline{N}$,
  i.e., $\mathrm{d}(\overline{N}\mu) = -(\overline{N}s)\mathrm{d}T + (\overline{N}v)\mathrm{d}p + \mu\mathrm{d}\overline{N}$
  $\Rightarrow \overline{N}\mathrm{d}\mu = -\overline{N}s\mathrm{d}T + \overline{N}v\mathrm{d}p$
  $\Rightarrow \mathrm{d}\mu = v\mathrm{d}p - s\mathrm{d}T$
  $\Rightarrow (\frac{\partial \mu}{\partial v})_T = v(\frac{\partial p}{\partial v})_T$,

Fluctuation of particle number $\boxed{\overline{(N-\overline{N})^2} = kT(\frac{\partial \overline{N}}{\partial \mu})_{T,V}}$

- (3.2.2) $\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p + \mu\mathrm{d}\overline{N}$,
  i.e., $\mathrm{d}(\overline{N}\mu) = -(\overline{N}s)\mathrm{d}T + (\overline{N}v)\mathrm{d}p + \mu\mathrm{d}\overline{N}$
  $\Rightarrow \overline{N}\mathrm{d}\mu = -\overline{N}s\mathrm{d}T + \overline{N}v\mathrm{d}p$
  $\Rightarrow \mathrm{d}\mu = v\mathrm{d}p - s\mathrm{d}T$
  $\Rightarrow (\frac{\partial \mu}{\partial v})_T = v(\frac{\partial p}{\partial v})_T$, and
  $(\frac{\partial \mu}{\partial v})_T = (\frac{\partial \mu}{\partial \frac{V}{\overline{N}}})_T = -\frac{\overline{N}^2}{V}(\frac{\partial \mu}{\partial \overline{N}})_{T,V}$

Fluctuation of particle number $\boxed{\overline{(N-\overline{N})^2} = kT(\frac{\partial \overline{N}}{\partial \mu})_{T,V}}$

- (3.2.2) $\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p + \mu\mathrm{d}\overline{N}$,
  i.e., $\mathrm{d}(\overline{N}\mu) = -(\overline{N}s)\mathrm{d}T + (\overline{N}v)\mathrm{d}p + \mu\mathrm{d}\overline{N}$
  $\Rightarrow \overline{N}\mathrm{d}\mu = -\overline{N}s\mathrm{d}T + \overline{N}v\mathrm{d}p$
  $\Rightarrow \mathrm{d}\mu = v\mathrm{d}p - s\mathrm{d}T$
  $\Rightarrow (\frac{\partial \mu}{\partial v})_T = v(\frac{\partial p}{\partial v})_T$, and
  $(\frac{\partial \mu}{\partial v})_T = (\frac{\partial \mu}{\partial \frac{V}{\overline{N}}})_T = -\frac{\overline{N}^2}{V}(\frac{\partial \mu}{\partial \overline{N}})_{T,V}$
  $\Rightarrow (\frac{\partial \overline{N}}{\partial \mu})_{T,V} = -\frac{\overline{N}^2}{V}\frac{1}{v}(\frac{\partial v}{\partial p})_T$.

Fluctuation of particle number $\boxed{\overline{(N-\overline{N})^2} = kT(\frac{\partial \overline{N}}{\partial \mu})_{T,V}}$

- (3.2.2) $\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p + \mu\mathrm{d}\overline{N}$,
  i.e., $\mathrm{d}(\overline{N}\mu) = -(\overline{N}s)\mathrm{d}T + (\overline{N}v)\mathrm{d}p + \mu\mathrm{d}\overline{N}$
  $\Rightarrow \overline{N}\mathrm{d}\mu = -\overline{N}s\mathrm{d}T + \overline{N}v\mathrm{d}p$
  $\Rightarrow \mathrm{d}\mu = v\mathrm{d}p - s\mathrm{d}T$
  $\Rightarrow (\frac{\partial \mu}{\partial v})_T = v(\frac{\partial p}{\partial v})_T$, and
  $(\frac{\partial \mu}{\partial v})_T = (\frac{\partial \mu}{\partial \frac{V}{\overline{N}}})_T = -\frac{\overline{N}^2}{V}(\frac{\partial \mu}{\partial \overline{N}})_{T,V}$
  $\Rightarrow (\frac{\partial \overline{N}}{\partial \mu})_{T,V} = -\frac{\overline{N}^2}{V}\frac{1}{v}(\frac{\partial v}{\partial p})_T$.
- $\frac{\overline{(N-\overline{N})^2}}{(\overline{N})^2}$

Fluctuation of particle number $\boxed{\overline{(N-\overline{N})^2} = kT(\frac{\partial \overline{N}}{\partial \mu})_{T,V}}$

- (3.2.2) $\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p + \mu\mathrm{d}\overline{N}$,
  i.e., $\mathrm{d}(\overline{N}\mu) = -(\overline{N}s)\mathrm{d}T + (\overline{N}v)\mathrm{d}p + \mu\mathrm{d}\overline{N}$
  $\Rightarrow \overline{N}\mathrm{d}\mu = -\overline{N}s\mathrm{d}T + \overline{N}v\mathrm{d}p$
  $\Rightarrow \mathrm{d}\mu = v\mathrm{d}p - s\mathrm{d}T$
  $\Rightarrow (\frac{\partial \mu}{\partial v})_T = v(\frac{\partial p}{\partial v})_T$, and
  $(\frac{\partial \mu}{\partial v})_T = (\frac{\partial \mu}{\partial \frac{V}{\overline{N}}})_T = -\frac{\overline{N}^2}{V}(\frac{\partial \mu}{\partial \overline{N}})_{T,V}$
  $\Rightarrow (\frac{\partial \overline{N}}{\partial \mu})_{T,V} = -\frac{\overline{N}^2}{V}\frac{1}{v}(\frac{\partial v}{\partial p})_T$.
- $\frac{\overline{(N-\overline{N})^2}}{(\overline{N})^2} = \frac{kT}{(\overline{N})^2} \cdot (-\frac{\overline{N}^2}{V}) \cdot \frac{1}{v}(\frac{\partial v}{\partial p})_T$

Fluctuation of particle number $\boxed{\overline{(N-\overline{N})^2} = kT(\frac{\partial \overline{N}}{\partial \mu})_{T,V}}$

- (3.2.2) $\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p + \mu\mathrm{d}\overline{N}$,
  i.e., $\mathrm{d}(\overline{N}\mu) = -(\overline{N}s)\mathrm{d}T + (\overline{N}v)\mathrm{d}p + \mu\mathrm{d}\overline{N}$
  $\Rightarrow \overline{N}\mathrm{d}\mu = -\overline{N}s\mathrm{d}T + \overline{N}v\mathrm{d}p$
  $\Rightarrow \mathrm{d}\mu = v\mathrm{d}p - s\mathrm{d}T$
  $\Rightarrow (\frac{\partial \mu}{\partial v})_T = v(\frac{\partial p}{\partial v})_T$, and
  $(\frac{\partial \mu}{\partial v})_T = (\frac{\partial \mu}{\partial \frac{V}{\overline{N}}})_T = -\frac{\overline{N}^2}{V}(\frac{\partial \mu}{\partial \overline{N}})_{T,V}$
  $\Rightarrow (\frac{\partial \overline{N}}{\partial \mu})_{T,V} = -\frac{\overline{N}^2}{V}\frac{1}{v}(\frac{\partial v}{\partial p})_T$.
- $\frac{\overline{(N-\overline{N})^2}}{(\overline{N})^2} = \frac{kT}{(\overline{N})^2} \cdot (-\frac{\overline{N}^2}{V}) \cdot \frac{1}{v}(\frac{\partial v}{\partial p})_T = \frac{kT}{V}\kappa_T$

Fluctuation of particle number $\boxed{\overline{(N-\overline{N})^2} = kT(\frac{\partial \overline{N}}{\partial \mu})_{T,V}}$

- (3.2.2) $\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p + \mu \mathrm{d}\overline{N}$,
  i.e., $\mathrm{d}(\overline{N}\mu) = -(\overline{N}s)\mathrm{d}T + (\overline{N}v)\mathrm{d}p + \mu\mathrm{d}\overline{N}$
  $\Rightarrow \overline{N}\mathrm{d}\mu = -\overline{N}s\mathrm{d}T + \overline{N}v\mathrm{d}p$
  $\Rightarrow \mathrm{d}\mu = v\mathrm{d}p - s\mathrm{d}T$
  $\Rightarrow (\frac{\partial \mu}{\partial v})_T = v(\frac{\partial p}{\partial v})_T$, and
  $(\frac{\partial \mu}{\partial v})_T = (\frac{\partial \mu}{\partial \frac{V}{\overline{N}}})_T = -\frac{\overline{N}^2}{V}(\frac{\partial \mu}{\partial \overline{N}})_{T,V}$
  $\Rightarrow (\frac{\partial \overline{N}}{\partial \mu})_{T,V} = -\frac{\overline{N}^2}{V}\frac{1}{v}(\frac{\partial v}{\partial p})_T$.
- $\frac{\overline{(N-\overline{N})^2}}{(\overline{N})^2} = \frac{kT}{(\overline{N})^2} \cdot (-\frac{\overline{N}^2}{V}) \cdot \frac{1}{v}(\frac{\partial v}{\partial p})_T = \frac{kT}{V}\kappa_T$
  $\propto \frac{1}{\overline{N}}$, in general;

Fluctuation of particle number $\boxed{\overline{(N-\overline{N})^2} = kT(\frac{\partial \overline{N}}{\partial \mu})_{T,V}}$

- (3.2.2) $\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p + \mu \mathrm{d}\overline{N}$,
  i.e., $\mathrm{d}(\overline{N}\mu) = -(\overline{N}s)\mathrm{d}T + (\overline{N}v)\mathrm{d}p + \mu \mathrm{d}\overline{N}$
  $\Rightarrow \overline{N}\mathrm{d}\mu = -\overline{N}s\mathrm{d}T + \overline{N}v\mathrm{d}p$
  $\Rightarrow \mathrm{d}\mu = v\mathrm{d}p - s\mathrm{d}T$
  $\Rightarrow (\frac{\partial \mu}{\partial v})_T = v(\frac{\partial p}{\partial v})_T$, and
  $(\frac{\partial \mu}{\partial v})_T = (\frac{\partial \mu}{\partial \frac{V}{\overline{N}}})_T = -\frac{\overline{N}^2}{V}(\frac{\partial \mu}{\partial \overline{N}})_{T,V}$
  $\Rightarrow (\frac{\partial \overline{N}}{\partial \mu})_{T,V} = -\frac{\overline{N}^2}{V}\frac{1}{v}(\frac{\partial v}{\partial p})_T$.
- $\frac{\overline{(N-\overline{N})^2}}{(\overline{N})^2} = \frac{kT}{(\overline{N})^2} \cdot (-\frac{\overline{N}^2}{V}) \cdot \frac{1}{v}(\frac{\partial v}{\partial p})_T = \frac{kT}{V}\kappa_T$
  $\propto \frac{1}{\overline{N}}$, in general;
  $\rightarrow 1$, when κ_T is very large (phase transition).

Table of contents

9.12 Applications of the grand canonical ensemble

9.12 Applications of the grand canonical ensemble

- App 1. Absorption.

9.12 Applications of the grand canonical ensemble

- App 1. Absorption.
- N_0 absorbing points, each one with energy $-\varepsilon_0$, require $\frac{N}{N_0}$ at temperature T.

9.12 Applications of the grand canonical ensemble

- App 1. Absorption.
- N_0 absorbing points, each one with energy $-\varepsilon_0$, require $\frac{N}{N_0}$ at temperature T.
- The system of absorbing points obeys grand canonical distribution.

9.12 Applications of the grand canonical ensemble

- App 1. Absorption.
- N_0 absorbing points, each one with energy $-\varepsilon_0$, require $\frac{N}{N_0}$ at temperature T.
- The system of absorbing points obeys grand canonical distribution.
- $\mathcal{Z} = \sum_{N=0}^{N_0} \sum_s e^{-\alpha N - \beta E_s}$

9.12 Applications of the grand canonical ensemble

- App 1. Absorption.
- N_0 absorbing points, each one with energy $-\varepsilon_0$, require $\frac{N}{N_0}$ at temperature T.
- The system of absorbing points obeys grand canonical distribution.
- $\mathcal{Z} = \sum_{N=0}^{N_0} \sum_s e^{-\alpha N - \beta E_s} = \sum_{N=0}^{N_0} \frac{N_0!}{N!(N_0-N)!} e^{-\alpha N + \beta \varepsilon_0 N}$,

9.12 Applications of the grand canonical ensemble

- App 1. Absorption.
- N_0 absorbing points, each one with energy $-\varepsilon_0$, require $\frac{N}{N_0}$ at temperature T.
- The system of absorbing points obeys grand canonical distribution.
- $\mathcal{Z} = \sum_{N=0}^{N_0} \sum_s e^{-\alpha N - \beta E_s} = \sum_{N=0}^{N_0} \frac{N_0!}{N!(N_0-N)!} e^{-\alpha N + \beta \varepsilon_0 N}$,
- As $-\alpha N + \beta \varepsilon_0 N = \beta(\mu + \varepsilon_0) N$,

9.12 Applications of the grand canonical ensemble

- App 1. Absorption.
- N_0 absorbing points, each one with energy $-\varepsilon_0$, require $\frac{N}{N_0}$ at temperature T.
- The system of absorbing points obeys grand canonical distribution.
- $\mathcal{Z} = \sum_{N=0}^{N_0} \sum_s e^{-\alpha N - \beta E_s} = \sum_{N=0}^{N_0} \frac{N_0!}{N!(N_0-N)!} e^{-\alpha N + \beta \varepsilon_0 N}$,
- As $-\alpha N + \beta \varepsilon_0 N = \beta(\mu + \varepsilon_0) N$, and $\sum_{N=0}^{N_0} \frac{N_0!}{N!(N_0-N)!} x^N = (1+x)^{N_0}$ (9.12.15),

9.12 Applications of the grand canonical ensemble

- App 1. Absorption.
- N_0 absorbing points, each one with energy $-\varepsilon_0$, require $\frac{N}{N_0}$ at temperature T.
- The system of absorbing points obeys grand canonical distribution.
- $\mathcal{Z} = \sum_{N=0}^{N_0} \sum_s e^{-\alpha N - \beta E_s} = \sum_{N=0}^{N_0} \frac{N_0!}{N!(N_0-N)!} e^{-\alpha N + \beta \varepsilon_0 N}$,
- As $-\alpha N + \beta \varepsilon_0 N = \beta(\mu + \varepsilon_0)N$, and $\sum_{N=0}^{N_0} \frac{N_0!}{N!(N_0-N)!} x^N = (1+x)^{N_0}$ (9.12.15), $\mathcal{Z} = [1 + e^{\beta(\mu+\varepsilon_0)}]^{N_0}$.

Absorption $\boxed{\mathcal{Z} = \left[1 + e^{\beta(\mu+\varepsilon_0)}\right]^{N_0}}$

- $\overline{N} = -\frac{\partial \ln \mathcal{Z}}{\partial \alpha}$

Absorption $\boxed{\mathcal{Z} = [1 + e^{\beta(\mu+\varepsilon_0)}]^{N_0}}$

- $\overline{N} = -\frac{\partial \ln \mathcal{Z}}{\partial \alpha} = kT\frac{\partial \ln \mathcal{Z}}{\partial \mu}$

Absorption $\boxed{\mathcal{Z} = [1 + e^{\beta(\mu+\varepsilon_0)}]^{N_0}}$

- $\overline{N} = -\frac{\partial \ln \mathcal{Z}}{\partial \alpha} = kT\frac{\partial \ln \mathcal{Z}}{\partial \mu} = kT\frac{\partial \{N_0 \ln[1+e^{\beta(\mu+\varepsilon_0)}]\}}{\partial \mu}$

Absorption $\boxed{\mathcal{Z} = [1 + e^{\beta(\mu+\varepsilon_0)}]^{N_0}}$

- $\overline{N} = -\frac{\partial \ln \mathcal{Z}}{\partial \alpha} = kT\frac{\partial \ln \mathcal{Z}}{\partial \mu} = kT\frac{\partial \{N_0 \ln[1+e^{\beta(\mu+\varepsilon_0)}]\}}{\partial \mu}$
  $= \frac{N_0 e^{\beta(\mu+\varepsilon_0)}}{1+e^{\beta(\mu+\varepsilon_0)}}$.

Absorption $\boxed{\mathcal{Z} = [1 + e^{\beta(\mu+\varepsilon_0)}]^{N_0}}$

- $\overline{N} = -\frac{\partial \ln \mathcal{Z}}{\partial \alpha} = kT\frac{\partial \ln \mathcal{Z}}{\partial \mu} = kT\frac{\partial\{N_0 \ln[1+e^{\beta(\mu+\varepsilon_0)}]\}}{\partial \mu}$
  $= \frac{N_0 e^{\beta(\mu+\varepsilon_0)}}{1+e^{\beta(\mu+\varepsilon_0)}}$.
- If ideal gas, $e^{\frac{\mu}{kT}} = \frac{p}{kT}(\frac{h^2}{2\pi mkT})^{\frac{3}{2}}$ (7.6.8),

Absorption $\boxed{\mathcal{Z} = [1 + e^{\beta(\mu+\varepsilon_0)}]^{N_0}}$

- $\overline{N} = -\frac{\partial \ln \mathcal{Z}}{\partial \alpha} = kT \frac{\partial \ln \mathcal{Z}}{\partial \mu} = kT \frac{\partial \{N_0 \ln[1+e^{\beta(\mu+\varepsilon_0)}]\}}{\partial \mu}$
  $= \frac{N_0 e^{\beta(\mu+\varepsilon_0)}}{1+e^{\beta(\mu+\varepsilon_0)}}$.
- If ideal gas, $e^{\frac{\mu}{kT}} = \frac{p}{kT}(\frac{h^2}{2\pi mkT})^{\frac{3}{2}}$ (7.6.8),
  $\frac{\overline{N}}{N_0} = [1 + \frac{kT}{p}(\frac{2\pi mkT}{h^2})^{\frac{3}{2}} e^{-\frac{\varepsilon_0}{kT}}]^{-1}$.

Absorption $\boxed{\mathcal{Z} = [1 + e^{\beta(\mu+\varepsilon_0)}]^{N_0}}$

- $\overline{N} = -\frac{\partial \ln \mathcal{Z}}{\partial \alpha} = kT\frac{\partial \ln \mathcal{Z}}{\partial \mu} = kT\frac{\partial\{N_0 \ln[1+e^{\beta(\mu+\varepsilon_0)}]\}}{\partial \mu}$
  $= \frac{N_0 e^{\beta(\mu+\varepsilon_0)}}{1+e^{\beta(\mu+\varepsilon_0)}}$.
- If ideal gas, $e^{\frac{\mu}{kT}} = \frac{p}{kT}(\frac{h^2}{2\pi mkT})^{\frac{3}{2}}$ (7.6.8),
  $\frac{\overline{N}}{N_0} = [1 + \frac{kT}{p}(\frac{2\pi mkT}{h^2})^{\frac{3}{2}} e^{-\frac{\varepsilon_0}{kT}}]^{-1}$.
- App 2. $\overline{a}_l$ of nearly independent particles.

Absorption $\boxed{\mathcal{Z} = [1 + e^{\beta(\mu+\varepsilon_0)}]^{N_0}}$

- $\overline{N} = -\frac{\partial \ln \mathcal{Z}}{\partial \alpha} = kT\frac{\partial \ln \mathcal{Z}}{\partial \mu} = kT\frac{\partial\{N_0 \ln[1+e^{\beta(\mu+\varepsilon_0)}]\}}{\partial \mu}$
  $= \frac{N_0 e^{\beta(\mu+\varepsilon_0)}}{1+e^{\beta(\mu+\varepsilon_0)}}$.
- If ideal gas, $e^{\frac{\mu}{kT}} = \frac{p}{kT}(\frac{h^2}{2\pi mkT})^{\frac{3}{2}}$ (7.6.8),
  $\frac{\overline{N}}{N_0} = [1 + \frac{kT}{p}(\frac{2\pi mkT}{h^2})^{\frac{3}{2}} e^{-\frac{\varepsilon_0}{kT}}]^{-1}$.
- App 2. $\overline{a}_l$ of nearly independent particles.
- Grand canonical distribution: $\rho_{NS} = \frac{1}{\mathcal{Z}} e^{-\alpha N - \beta E_S}$, where S is the micro-state of the **system**.

Absorption $\boxed{\mathcal{Z} = [1 + e^{\beta(\mu+\varepsilon_0)}]^{N_0}}$

- $\overline{N} = -\frac{\partial \ln \mathcal{Z}}{\partial \alpha} = kT\frac{\partial \ln \mathcal{Z}}{\partial \mu} = kT\frac{\partial\{N_0 \ln[1+e^{\beta(\mu+\varepsilon_0)}]\}}{\partial \mu}$
  $= \frac{N_0 e^{\beta(\mu+\varepsilon_0)}}{1+e^{\beta(\mu+\varepsilon_0)}}$.
- If ideal gas, $e^{\frac{\mu}{kT}} = \frac{p}{kT}(\frac{h^2}{2\pi mkT})^{\frac{3}{2}}$ (7.6.8),
  $\frac{\overline{N}}{N_0} = [1 + \frac{kT}{p}(\frac{2\pi mkT}{h^2})^{\frac{3}{2}} e^{-\frac{\varepsilon_0}{kT}}]^{-1}$.
- App 2. $\overline{a}_l$ of nearly independent particles.
- Grand canonical distribution: $\rho_{NS} = \frac{1}{\mathcal{Z}} e^{-\alpha N - \beta E_S}$, where S is the micro-state of the **system**.
- a_s represents the number of particles at the particle's state s, then

Absorption $\boxed{\mathcal{Z} = [1 + e^{\beta(\mu+\varepsilon_0)}]^{N_0}}$

- $\overline{N} = -\frac{\partial \ln \mathcal{Z}}{\partial \alpha} = kT \frac{\partial \ln \mathcal{Z}}{\partial \mu} = kT \frac{\partial \{N_0 \ln[1+e^{\beta(\mu+\varepsilon_0)}]\}}{\partial \mu}$
  $= \frac{N_0 e^{\beta(\mu+\varepsilon_0)}}{1+e^{\beta(\mu+\varepsilon_0)}}$.
- If ideal gas, $e^{\frac{\mu}{kT}} = \frac{p}{kT}(\frac{h^2}{2\pi mkT})^{\frac{3}{2}}$ (7.6.8),
  $\frac{\overline{N}}{N_0} = [1 + \frac{kT}{p}(\frac{2\pi mkT}{h^2})^{\frac{3}{2}} e^{-\frac{\varepsilon_0}{kT}}]^{-1}$.
- App 2. $\overline{a}_l$ of nearly independent particles.
- Grand canonical distribution: $\rho_{NS} = \frac{1}{\mathcal{Z}} e^{-\alpha N - \beta E_S}$,
  where S is the micro-state of the **system**.
- a_s represents the number of particles at the particle's state s, then
  $N = \sum_s a_s$, $E_S = \sum_s \varepsilon_s a_s$.

$\overline{a}_l$ of nearly independent particles

- Grand partition function: $\mathcal{Z} = \sum_N \sum_S e^{-\alpha N - \beta E_S}$

$\overline{a}_l$ of nearly independent particles

- Grand partition function: $\mathcal{Z} = \sum_N \sum_S e^{-\alpha N - \beta E_S}$

$$= \sum_{\{a_s\}} e^{-\sum_s (\alpha + \beta \varepsilon_s) a_s}$$

$\overline{a}_l$ of nearly independent particles

- Grand partition function: $\mathscr{Z} = \sum_N \sum_S e^{-\alpha N - \beta E_S}$

$$= \sum_{\{a_s\}} e^{-\sum_s (\alpha+\beta\varepsilon_s)a_s} = \sum_{\{a_s\}} \prod_s e^{-(\alpha+\beta\varepsilon_s)a_s}$$

$\overline{a}_l$ of nearly independent particles

- Grand partition function: $\mathcal{Z} = \sum\limits_N \sum\limits_S e^{-\alpha N - \beta E_S}$

$$= \sum_{\{a_s\}} e^{-\sum\limits_s (\alpha+\beta\varepsilon_s)a_s} = \sum_{\{a_s\}} \prod_s e^{-(\alpha+\beta\varepsilon_s)a_s}$$

$$= \prod_s \sum_{a_s} e^{-(\alpha+\beta\varepsilon_s)a_s}.$$

$\overline{a}_l$ of nearly independent particles

- Grand partition function: $\mathcal{Z} = \sum_N \sum_S e^{-\alpha N - \beta E_S}$

$$= \sum_{\{a_s\}} e^{-\sum_s (\alpha+\beta\varepsilon_s) a_s} = \sum_{\{a_s\}} \prod_s e^{-(\alpha+\beta\varepsilon_s) a_s}$$

$$= \prod_s \sum_{a_s} e^{-(\alpha+\beta\varepsilon_s) a_s}.$$

- Set $\mathcal{Z}_s = \sum_{a_s} e^{-(\alpha+\beta\varepsilon_s) a_s}$, then $\mathcal{Z} = \prod_s \mathcal{Z}_s$.

$\bar{a}_l$ of nearly independent particles

- Grand partition function: $\mathcal{Z} = \sum_N \sum_S e^{-\alpha N - \beta E_S}$

$$= \sum_{\{a_s\}} e^{-\sum_s (\alpha+\beta\varepsilon_s)a_s} = \sum_{\{a_s\}} \prod_s e^{-(\alpha+\beta\varepsilon_s)a_s}$$

$$= \prod_s \sum_{a_s} e^{-(\alpha+\beta\varepsilon_s)a_s}.$$

- Set $\mathcal{Z}_s = \sum_{a_s} e^{-(\alpha+\beta\varepsilon_s)a_s}$, then $\mathcal{Z} = \prod_s \mathcal{Z}_s$.
- For Bosons, $\mathcal{Z}_s = \sum_{a_s=0}^{\infty} e^{-(\alpha+\beta\varepsilon_s)a_s}$

$\bar{a}_l$ of nearly independent particles

- Grand partition function: $\mathcal{Z} = \sum_N \sum_S e^{-\alpha N - \beta E_S}$

$$= \sum_{\{a_s\}} e^{-\sum_s (\alpha+\beta\varepsilon_s) a_s} = \sum_{\{a_s\}} \prod_s e^{-(\alpha+\beta\varepsilon_s) a_s}$$

$$= \prod_s \sum_{a_s} e^{-(\alpha+\beta\varepsilon_s) a_s}.$$

- Set $\mathcal{Z}_s = \sum_{a_s} e^{-(\alpha+\beta\varepsilon_s) a_s}$, then $\mathcal{Z} = \prod_s \mathcal{Z}_s$.
- For Bosons, $\mathcal{Z}_s = \sum_{a_s=0}^{\infty} e^{-(\alpha+\beta\varepsilon_s) a_s} = \frac{1}{1-e^{-\alpha-\beta\varepsilon_s}}$;

$\bar{a}_l$ of nearly independent particles

- Grand partition function: $\mathcal{Z} = \sum_N \sum_S e^{-\alpha N - \beta E_S}$

$$= \sum_{\{a_s\}} e^{-\sum_s (\alpha+\beta\varepsilon_s) a_s} = \sum_{\{a_s\}} \prod_s e^{-(\alpha+\beta\varepsilon_s) a_s}$$

$$= \prod_s \sum_{a_s} e^{-(\alpha+\beta\varepsilon_s) a_s}.$$

- Set $\mathcal{Z}_s = \sum_{a_s} e^{-(\alpha+\beta\varepsilon_s) a_s}$, then $\mathcal{Z} = \prod_s \mathcal{Z}_s$.
- For Bosons, $\mathcal{Z}_s = \sum_{a_s=0}^{\infty} e^{-(\alpha+\beta\varepsilon_s) a_s} = \frac{1}{1-e^{-\alpha-\beta\varepsilon_s}}$;
- For Fermions, $\mathcal{Z}_s = \sum_{a_s=0}^{1} e^{-(\alpha+\beta\varepsilon_s) a_s}$

$\bar{a}_l$ of nearly independent particles

- Grand partition function: $\mathcal{Z} = \sum_N \sum_S e^{-\alpha N - \beta E_S}$

$$= \sum_{\{a_s\}} e^{-\sum_s (\alpha+\beta\varepsilon_s) a_s} = \sum_{\{a_s\}} \prod_s e^{-(\alpha+\beta\varepsilon_s) a_s}$$

$$= \prod_s \sum_{a_s} e^{-(\alpha+\beta\varepsilon_s) a_s}.$$

- Set $\mathcal{Z}_s = \sum_{a_s} e^{-(\alpha+\beta\varepsilon_s) a_s}$, then $\mathcal{Z} = \prod_s \mathcal{Z}_s$.
- For Bosons, $\mathcal{Z}_s = \sum_{a_s=0}^{\infty} e^{-(\alpha+\beta\varepsilon_s) a_s} = \frac{1}{1-e^{-\alpha-\beta\varepsilon_s}}$;
- For Fermions, $\mathcal{Z}_s = \sum_{a_s=0}^{1} e^{-(\alpha+\beta\varepsilon_s) a_s} = 1 + e^{-\alpha-\beta\varepsilon_s}$.

$\overline{a}_l$ $\boxed{\mathcal{Z}_{s,\mathrm{Bose}} = \frac{1}{1-e^{-\alpha-\beta\varepsilon_s}}}$, $\boxed{\mathcal{Z}_{s,\mathrm{Fermi}} = 1 + e^{-\alpha-\beta\varepsilon_s}}$

- Average number of particles (6.7.10):

$\overline{a}_l$ $\boxed{\mathcal{Z}_{s,\text{Bose}} = \frac{1}{1-e^{-\alpha-\beta\varepsilon_s}}}$, $\boxed{\mathcal{Z}_{s,\text{Fermi}} = 1 + e^{-\alpha-\beta\varepsilon_s}}$

- Average number of particles (6.7.10):
  $f_s = \overline{a}_s$

$\overline{a}_l$ $\boxed{\mathcal{Z}_{s,\mathrm{Bose}} = \frac{1}{1-e^{-\alpha-\beta\varepsilon_s}}}$, $\boxed{\mathcal{Z}_{s,\mathrm{Fermi}} = 1 + e^{-\alpha-\beta\varepsilon_s}}$

- Average number of particles (6.7.10):
  $f_s = \overline{a}_s = \frac{1}{\mathcal{Z}} \sum_N \sum_{S'} a_s e^{-\alpha N - \beta E_{S'}}$

$\bar{a}_l$ $\boxed{\mathcal{Z}_{s,\text{Bose}} = \frac{1}{1-e^{-\alpha-\beta\varepsilon_s}}}$, $\boxed{\mathcal{Z}_{s,\text{Fermi}} = 1 + e^{-\alpha-\beta\varepsilon_s}}$

- Average number of particles (6.7.10):

$$f_s = \bar{a}_s = \frac{1}{\mathcal{Z}} \sum_N \sum_{S'} a_s e^{-\alpha N - \beta E_{S'}}$$
$$= \frac{1}{\mathcal{Z}} \sum_N \sum_{S'} a_s e^{-\sum (\alpha + \beta\varepsilon_{s'}) a_{s'}}$$

$\overline{a}_l$ $\boxed{\mathcal{Z}_{s,\text{Bose}} = \frac{1}{1-e^{-\alpha-\beta\varepsilon_s}}}$, $\boxed{\mathcal{Z}_{s,\text{Fermi}} = 1 + e^{-\alpha-\beta\varepsilon_s}}$

- Average number of particles (6.7.10):

$$f_s = \overline{a}_s = \frac{1}{\mathcal{Z}} \sum_N \sum_{S'} a_s e^{-\alpha N - \beta E_{S'}}$$
$$= \frac{1}{\mathcal{Z}} \sum_N \sum_{S'} a_s e^{-\sum(\alpha+\beta\varepsilon_{s'})a_{s'}} = \frac{1}{\mathcal{Z}} \sum_{\{a_{s'}\}} a_s e^{-\sum(\alpha+\beta\varepsilon_{s'})a_{s'}}$$

$\overline{a}_l$ $\boxed{\mathcal{Z}_{s,\text{Bose}} = \frac{1}{1-e^{-\alpha-\beta\varepsilon_s}}}$, $\boxed{\mathcal{Z}_{s,\text{Fermi}} = 1 + e^{-\alpha-\beta\varepsilon_s}}$

- Average number of particles (6.7.10):

$$f_s = \overline{a}_s = \frac{1}{\mathcal{Z}} \sum_N \sum_{S'} a_s e^{-\alpha N - \beta E_{S'}}$$

$$= \frac{1}{\mathcal{Z}} \sum_N \sum_{S'} a_s e^{-\sum(\alpha+\beta\varepsilon_{s'})a_{s'}} = \frac{1}{\mathcal{Z}} \sum_{\{a_{s'}\}} a_s e^{-\sum(\alpha+\beta\varepsilon_{s'})a_{s'}}$$

$$= \frac{1}{\mathcal{Z}} \sum_{\{a_{s'}\}} a_s \prod_{s'} e^{-(\alpha+\beta\varepsilon_{s'})a_{s'}}$$

$\overline{a}_l$ $\boxed{\mathcal{Z}_{s,\text{Bose}} = \frac{1}{1-e^{-\alpha-\beta\varepsilon_s}}}$, $\boxed{\mathcal{Z}_{s,\text{Fermi}} = 1 + e^{-\alpha-\beta\varepsilon_s}}$

- Average number of particles (6.7.10):

$$f_s = \overline{a}_s = \frac{1}{\mathcal{Z}} \sum_N \sum_{S'} a_s e^{-\alpha N - \beta E_{S'}}$$

$$= \frac{1}{\mathcal{Z}} \sum_N \sum_{S'} a_s e^{-\sum(\alpha+\beta\varepsilon_{s'})a_{s'}} = \frac{1}{\mathcal{Z}} \sum_{\{a_{s'}\}} a_s e^{-\sum(\alpha+\beta\varepsilon_{s'})a_{s'}}$$

$$= \frac{1}{\mathcal{Z}} \sum_{\{a_{s'}\}} a_s \prod_{s'} e^{-(\alpha+\beta\varepsilon_{s'})a_{s'}} = \frac{1}{\mathcal{Z}} \prod_{s'} \sum_{a_{s'}} a_s^{\frac{1}{?}} e^{-(\alpha+\beta\varepsilon_{s'})a_{s'}}$$

$\overline{a}_l$ $\boxed{\mathcal{Z}_{s,\text{Bose}} = \frac{1}{1-e^{-\alpha-\beta\varepsilon_s}}}$, $\boxed{\mathcal{Z}_{s,\text{Fermi}} = 1 + e^{-\alpha-\beta\varepsilon_s}}$

- Average number of particles (6.7.10):

$$
\begin{aligned}
f_s = \overline{a}_s &= \frac{1}{\mathcal{Z}} \sum_N \sum_{S'} a_s e^{-\alpha N - \beta E_{S'}} \\
&= \frac{1}{\mathcal{Z}} \sum_N \sum_{S'} a_s e^{-\sum(\alpha+\beta\varepsilon_{s'})a_{s'}} = \frac{1}{\mathcal{Z}} \sum_{\{a_{s'}\}} a_s e^{-\sum(\alpha+\beta\varepsilon_{s'})a_{s'}} \\
&= \frac{1}{\mathcal{Z}} \sum_{\{a_{s'}\}} a_s \prod_{s'} e^{-(\alpha+\beta\varepsilon_{s'})a_{s'}} = \frac{1}{\mathcal{Z}} \prod_{s'} \sum_{a_{s'}} a_s^{\overset{1}{?}} e^{-(\alpha+\beta\varepsilon_{s'})a_{s'}} \\
&= \frac{1}{\mathcal{Z}} \sum_{a_s} a_s e^{-(\alpha+\beta\varepsilon_s)a_s} \cdot \prod_{s'\neq s} \sum_{a_{s'}} e^{-(\alpha+\beta\varepsilon_{s'})a_{s'}}
\end{aligned}
$$

$\overline{a}_l$ $\boxed{\mathcal{Z}_{s,\text{Bose}} = \frac{1}{1-e^{-\alpha-\beta\varepsilon_s}}}$, $\boxed{\mathcal{Z}_{s,\text{Fermi}} = 1 + e^{-\alpha-\beta\varepsilon_s}}$

- Average number of particles (6.7.10):

$$f_s = \overline{a}_s = \frac{1}{\mathcal{Z}} \sum_N \sum_{S'} a_s e^{-\alpha N - \beta E_{S'}}$$

$$= \frac{1}{\mathcal{Z}} \sum_N \sum_{S'} a_s e^{-\sum(\alpha+\beta\varepsilon_{s'})a_{s'}} = \frac{1}{\mathcal{Z}} \sum_{\{a_{s'}\}} a_s e^{-\sum(\alpha+\beta\varepsilon_{s'})a_{s'}}$$

$$= \frac{1}{\mathcal{Z}} \sum_{\{a_{s'}\}} a_s \prod_{s'} e^{-(\alpha+\beta\varepsilon_{s'})a_{s'}} = \frac{1}{\mathcal{Z}} \prod_{s'} \sum_{a_{s'}} a_s^{\frac{1}{?}} e^{-(\alpha+\beta\varepsilon_{s'})a_{s'}}$$

$$= \frac{1}{\mathcal{Z}} \sum_{a_s} a_s e^{-(\alpha+\beta\varepsilon_s)a_s} \cdot \prod_{s'\neq s} \sum_{a_{s'}} e^{-(\alpha+\beta\varepsilon_{s'})a_{s'}}$$

$$= \frac{1}{\mathcal{Z}_s} \sum_{a_s} a_s e^{-(\alpha+\beta\varepsilon_s)a_s}$$

$\overline{a}_l$ $\boxed{\mathcal{Z}_{s,\mathrm{Bose}} = \frac{1}{1-e^{-\alpha-\beta\varepsilon_s}}}$, $\boxed{\mathcal{Z}_{s,\mathrm{Fermi}} = 1 + e^{-\alpha-\beta\varepsilon_s}}$

- Average number of particles (6.7.10):

$$f_s = \overline{a}_s = \frac{1}{\mathcal{Z}} \sum_N \sum_{S'} a_s e^{-\alpha N - \beta E_{S'}}$$

$$= \frac{1}{\mathcal{Z}} \sum_N \sum_{S'} a_s e^{-\sum(\alpha+\beta\varepsilon_{s'})a_{s'}} = \frac{1}{\mathcal{Z}} \sum_{\{a_{s'}\}} a_s e^{-\sum(\alpha+\beta\varepsilon_{s'})a_{s'}}$$

$$= \frac{1}{\mathcal{Z}} \sum_{\{a_{s'}\}} a_s \prod_{s'} e^{-(\alpha+\beta\varepsilon_{s'})a_{s'}} = \frac{1}{\mathcal{Z}} \prod_{s'} \sum_{a_{s'}} a_s^{\overset{1}{?}} e^{-(\alpha+\beta\varepsilon_{s'})a_{s'}}$$

$$= \frac{1}{\mathcal{Z}} \sum_{a_s} a_s e^{-(\alpha+\beta\varepsilon_s)a_s} \cdot \prod_{s'\neq s} \sum_{a_{s'}} e^{-(\alpha+\beta\varepsilon_{s'})a_{s'}}$$

$$= \frac{1}{\mathcal{Z}_s} \sum_{a_s} a_s e^{-(\alpha+\beta\varepsilon_s)a_s} = \frac{1}{\mathcal{Z}_s}\left(-\frac{\partial}{\partial\alpha}\right)\mathcal{Z}_s$$

- Average number of particles (6.7.10):

$$
\begin{aligned}
f_s = \bar{a}_s &= \frac{1}{\mathcal{Z}} \sum_N \sum_{S'} a_s e^{-\alpha N - \beta E_{S'}} \\
&= \frac{1}{\mathcal{Z}} \sum_N \sum_{S'} a_s e^{-\sum(\alpha+\beta\varepsilon_{s'})a_{s'}} = \frac{1}{\mathcal{Z}} \sum_{\{a_{s'}\}} a_s e^{-\sum(\alpha+\beta\varepsilon_{s'})a_{s'}} \\
&= \frac{1}{\mathcal{Z}} \sum_{\{a_{s'}\}} a_s \prod_{s'} e^{-(\alpha+\beta\varepsilon_{s'})a_{s'}} = \frac{1}{\mathcal{Z}} \prod_{s'} \sum_{a_{s'}} a_s^{\overset{1}{\overset{?}{}}} e^{-(\alpha+\beta\varepsilon_{s'})a_{s'}} \\
&= \frac{1}{\mathcal{Z}} \sum_{a_s} a_s e^{-(\alpha+\beta\varepsilon_s)a_s} \cdot \prod_{s'\neq s} \sum_{a_{s'}} e^{-(\alpha+\beta\varepsilon_{s'})a_{s'}} \\
&= \frac{1}{\mathcal{Z}_s} \sum_{a_s} a_s e^{-(\alpha+\beta\varepsilon_s)a_s} = \frac{1}{\mathcal{Z}_s}\left(-\frac{\partial}{\partial\alpha}\right)\mathcal{Z}_s = -\frac{\partial \ln \mathcal{Z}_s}{\partial\alpha}.
\end{aligned}
$$

$\overline{a}_l$ $\boxed{\mathcal{Z}_{s,\text{Bose}} = \frac{1}{1-e^{-\alpha-\beta\varepsilon_s}}}$, $\boxed{\mathcal{Z}_{s,\text{Fermi}} = 1 + e^{-\alpha-\beta\varepsilon_s}}$

- Average number of particles (6.7.10):

$$f_s = \overline{a}_s = \frac{1}{\mathcal{Z}}\sum_N \sum_{S'} a_s e^{-\alpha N - \beta E_{S'}}$$

$$= \frac{1}{\mathcal{Z}}\sum_N \sum_{S'} a_s e^{-\sum(\alpha+\beta\varepsilon_{s'})a_{s'}} = \frac{1}{\mathcal{Z}}\sum_{\{a_{s'}\}} a_s e^{-\sum(\alpha+\beta\varepsilon_{s'})a_{s'}}$$

$$= \frac{1}{\mathcal{Z}}\sum_{\{a_{s'}\}} a_s \prod_{s'} e^{-(\alpha+\beta\varepsilon_{s'})a_{s'}} = \frac{1}{\mathcal{Z}}\prod_{s'}\sum_{a_{s'}} a_s^{\overset{1}{?}} e^{-(\alpha+\beta\varepsilon_{s'})a_{s'}}$$

$$= \frac{1}{\mathcal{Z}}\sum_{a_s} a_s e^{-(\alpha+\beta\varepsilon_s)a_s} \cdot \prod_{s'\neq s}\sum_{a_{s'}} e^{-(\alpha+\beta\varepsilon_{s'})a_{s'}}$$

$$= \frac{1}{\mathcal{Z}_s}\sum_{a_s} a_s e^{-(\alpha+\beta\varepsilon_s)a_s} = \frac{1}{\mathcal{Z}_s}\left(-\frac{\partial}{\partial\alpha}\right)\mathcal{Z}_s = -\frac{\partial \ln \mathcal{Z}_s}{\partial\alpha}.$$

- For Bosons: $\overline{a}_s = \frac{1}{e^{\alpha+\beta\varepsilon_s}-1}$,

$\overline{a}_l$ $\boxed{\mathcal{Z}_{s,\text{Bose}} = \frac{1}{1-e^{-\alpha-\beta\varepsilon_s}}}$, $\boxed{\mathcal{Z}_{s,\text{Fermi}} = 1 + e^{-\alpha-\beta\varepsilon_s}}$

- Average number of particles (6.7.10):

$$f_s = \overline{a}_s = \frac{1}{\mathcal{Z}}\sum_N \sum_{S'} a_s e^{-\alpha N - \beta E_{S'}}$$
$$= \frac{1}{\mathcal{Z}}\sum_N \sum_{S'} a_s e^{-\sum(\alpha+\beta\varepsilon_{s'})a_{s'}} = \frac{1}{\mathcal{Z}}\sum_{\{a_{s'}\}} a_s e^{-\sum(\alpha+\beta\varepsilon_{s'})a_{s'}}$$
$$= \frac{1}{\mathcal{Z}}\sum_{\{a_{s'}\}} a_s \prod_{s'} e^{-(\alpha+\beta\varepsilon_{s'})a_{s'}} = \frac{1}{\mathcal{Z}}\prod_{s'}\sum_{a_{s'}} a_s^{\overset{1}{?}} e^{-(\alpha+\beta\varepsilon_{s'})a_{s'}}$$
$$= \frac{1}{\mathcal{Z}}\sum_{a_s} a_s e^{-(\alpha+\beta\varepsilon_s)a_s} \cdot \prod_{s'\neq s}\sum_{a_{s'}} e^{-(\alpha+\beta\varepsilon_{s'})a_{s'}}$$
$$= \frac{1}{\mathcal{Z}_s}\sum_{a_s} a_s e^{-(\alpha+\beta\varepsilon_s)a_s} = \frac{1}{\mathcal{Z}_s}\left(-\frac{\partial}{\partial\alpha}\right)\mathcal{Z}_s = -\frac{\partial \ln \mathcal{Z}_s}{\partial \alpha}.$$

- For Bosons: $\overline{a}_s = \frac{1}{e^{\alpha+\beta\varepsilon_s}-1}$, for Fermions, $\overline{a}_s = \frac{1}{e^{\alpha+\beta\varepsilon_s}+1}$.

$\overline{a}_l$ $\boxed{\mathcal{Z}_{s,\text{Bose}} = \frac{1}{1-e^{-\alpha-\beta\varepsilon_s}}}$, $\boxed{\mathcal{Z}_{s,\text{Fermi}} = 1 + e^{-\alpha-\beta\varepsilon_s}}$

- Average number of particles (6.7.10):

$$f_s = \overline{a}_s = \frac{1}{\mathcal{Z}} \sum_N \sum_{S'} a_s e^{-\alpha N - \beta E_{S'}}$$
$$= \frac{1}{\mathcal{Z}} \sum_N \sum_{S'} a_s e^{-\sum(\alpha+\beta\varepsilon_{s'})a_{s'}} = \frac{1}{\mathcal{Z}} \sum_{\{a_{s'}\}} a_s e^{-\sum(\alpha+\beta\varepsilon_{s'})a_{s'}}$$
$$= \frac{1}{\mathcal{Z}} \sum_{\{a_{s'}\}} a_s \prod_{s'} e^{-(\alpha+\beta\varepsilon_{s'})a_{s'}} = \frac{1}{\mathcal{Z}} \prod_{s'} \sum_{a_{s'}} a_s^{\frac{1}{?}} e^{-(\alpha+\beta\varepsilon_{s'})a_{s'}}$$
$$= \frac{1}{\mathcal{Z}} \sum_{a_s} a_s e^{-(\alpha+\beta\varepsilon_s)a_s} \cdot \prod_{s'\neq s} \sum_{a_{s'}} e^{-(\alpha+\beta\varepsilon_{s'})a_{s'}}$$
$$= \frac{1}{\mathcal{Z}_s} \sum_{a_s} a_s e^{-(\alpha+\beta\varepsilon_s)a_s} = \frac{1}{\mathcal{Z}_s}\left(-\frac{\partial}{\partial\alpha}\right)\mathcal{Z}_s = -\frac{\partial \ln \mathcal{Z}_s}{\partial\alpha}.$$

- For Bosons: $\overline{a}_s = \frac{1}{e^{\alpha+\beta\varepsilon_s}-1}$, for Fermions, $\overline{a}_s = \frac{1}{e^{\alpha+\beta\varepsilon_s}+1}$.
- For degenerated states: $\overline{a}_l = \sum^{\omega_l} \overline{a}_s$

$\overline{a}_l$ $\boxed{\mathcal{Z}_{s,\mathrm{Bose}} = \frac{1}{1-e^{-\alpha-\beta\varepsilon_s}}}$, $\boxed{\mathcal{Z}_{s,\mathrm{Fermi}} = 1 + e^{-\alpha-\beta\varepsilon_s}}$

- Average number of particles (6.7.10):

$$f_s = \overline{a}_s = \frac{1}{\mathcal{Z}} \sum_N \sum_{S'} a_s e^{-\alpha N - \beta E_{S'}}$$
$$= \frac{1}{\mathcal{Z}} \sum_N \sum_{S'} a_s e^{-\sum(\alpha+\beta\varepsilon_{s'})a_{s'}} = \frac{1}{\mathcal{Z}} \sum_{\{a_{s'}\}} a_s e^{-\sum(\alpha+\beta\varepsilon_{s'})a_{s'}}$$
$$= \frac{1}{\mathcal{Z}} \sum_{\{a_{s'}\}} a_s \prod_{s'} e^{-(\alpha+\beta\varepsilon_{s'})a_{s'}} = \frac{1}{\mathcal{Z}} \prod_{s'} \sum_{a_{s'}} a_s^{\overset{1}{?}} e^{-(\alpha+\beta\varepsilon_{s'})a_{s'}}$$
$$= \frac{1}{\mathcal{Z}} \sum_{a_s} a_s e^{-(\alpha+\beta\varepsilon_s)a_s} \cdot \prod_{s'\neq s} \sum_{a_{s'}} e^{-(\alpha+\beta\varepsilon_{s'})a_{s'}}$$
$$= \frac{1}{\mathcal{Z}_s} \sum_{a_s} a_s e^{-(\alpha+\beta\varepsilon_s)a_s} = \frac{1}{\mathcal{Z}_s}\left(-\frac{\partial}{\partial\alpha}\right)\mathcal{Z}_s = -\frac{\partial \ln \mathcal{Z}_s}{\partial\alpha}.$$

- For Bosons: $\overline{a}_s = \frac{1}{e^{\alpha+\beta\varepsilon_s}-1}$, for Fermions, $\overline{a}_s = \frac{1}{e^{\alpha+\beta\varepsilon_s}+1}$.
- For degenerated states: $\overline{a}_l = \sum^{\omega_l} \overline{a}_s = \frac{\omega_l}{e^{\alpha+\beta\varepsilon_l}\pm 1}$.

Fluctuation of Bose/Fermi distribution $\boxed{\overline{a}_l = \frac{\omega_l}{e^{\alpha+\beta\varepsilon_l}\pm 1}}$

- App 3. Fluctuation of Bose/Fermi distribution.

Fluctuation of Bose/Fermi distribution $\boxed{\overline{a}_l = \frac{\omega_l}{e^{\alpha+\beta\varepsilon_l}\pm 1}}$

- App 3. Fluctuation of Bose/Fermi distribution.
- Take the particles at energy level ε_l as an open system.

Fluctuation of Bose/Fermi distribution $\boxed{\overline{a}_l = \frac{\omega_l}{e^{\alpha+\beta\varepsilon_l} \pm 1}}$

- App 3. Fluctuation of Bose/Fermi distribution.
- Take the particles at energy level ε_l as an open system. a_l acts like N in (9.11.8).

Fluctuation of Bose/Fermi distribution $\boxed{\overline{a}_l = \frac{\omega_l}{e^{\alpha+\beta\varepsilon_l}\pm 1}}$

- App 3. Fluctuation of Bose/Fermi distribution.
- Take the particles at energy level ε_l as an open system. a_l acts like N in (9.11.8).
- $\overline{(a_l - \overline{a}_l)^2} = -\frac{\partial \overline{a}_l}{\partial \alpha}$

Fluctuation of Bose/Fermi distribution $\boxed{\overline{a}_l = \frac{\omega_l}{e^{\alpha+\beta\varepsilon_l}\pm 1}}$

- App 3. Fluctuation of Bose/Fermi distribution.
- Take the particles at energy level ε_l as an open system. a_l acts like N in (9.11.8).
- $\overline{(a_l - \overline{a}_l)^2} = -\frac{\partial \overline{a}_l}{\partial \alpha} = -\frac{\partial \frac{\omega_l}{e^{\alpha+\beta\varepsilon_l}\pm 1}}{\partial \alpha}$

Fluctuation of Bose/Fermi distribution $\boxed{\overline{a}_l = \frac{\omega_l}{e^{\alpha+\beta\varepsilon_l}\pm 1}}$

- App 3. Fluctuation of Bose/Fermi distribution.
- Take the particles at energy level ε_l as an open system. a_l acts like N in (9.11.8).
- $\overline{(a_l - \overline{a}_l)^2} = -\frac{\partial \overline{a}_l}{\partial \alpha} = -\frac{\partial \frac{\omega_l}{e^{\alpha+\beta\varepsilon_l}\pm 1}}{\partial \alpha} = \frac{\omega_l e^{\alpha+\beta\varepsilon_l}}{(e^{\alpha+\beta\varepsilon_l}\pm 1)^2}$

Fluctuation of Bose/Fermi distribution $\boxed{\overline{a}_l = \frac{\omega_l}{e^{\alpha+\beta\varepsilon_l}\pm 1}}$

- App 3. Fluctuation of Bose/Fermi distribution.
- Take the particles at energy level ε_l as an open system. a_l acts like N in (9.11.8).
- $\overline{(a_l - \overline{a}_l)^2} = -\frac{\partial \overline{a}_l}{\partial \alpha} = -\frac{\partial \frac{\omega_l}{e^{\alpha+\beta\varepsilon_l}\pm 1}}{\partial \alpha} = \frac{\omega_l e^{\alpha+\beta\varepsilon_l}}{(e^{\alpha+\beta\varepsilon_l}\pm 1)^2}$
  $= \overline{a}_l \frac{e^{\alpha+\beta\varepsilon_l}}{e^{\alpha+\beta\varepsilon_l}\pm 1}$

Fluctuation of Bose/Fermi distribution $\boxed{\overline{a}_l = \frac{\omega_l}{e^{\alpha+\beta\varepsilon_l}\pm 1}}$

- App 3. Fluctuation of Bose/Fermi distribution.
- Take the particles at energy level ε_l as an open system. a_l acts like N in (9.11.8).
- $\overline{(a_l - \overline{a}_l)^2} = -\frac{\partial \overline{a}_l}{\partial \alpha} = -\frac{\partial \frac{\omega_l}{e^{\alpha+\beta\varepsilon_l}\pm 1}}{\partial \alpha} = \frac{\omega_l e^{\alpha+\beta\varepsilon_l}}{(e^{\alpha+\beta\varepsilon_l}\pm 1)^2}$
  $= \overline{a}_l \frac{e^{\alpha+\beta\varepsilon_l}}{e^{\alpha+\beta\varepsilon_l}\pm 1} = \overline{a}_l (1 \mp \frac{1}{e^{\alpha+\beta\varepsilon_l}\pm 1})$

Fluctuation of Bose/Fermi distribution $\boxed{\overline{a}_l = \frac{\omega_l}{e^{\alpha+\beta\varepsilon_l}\pm 1}}$

- App 3. Fluctuation of Bose/Fermi distribution.
- Take the particles at energy level ε_l as an open system. a_l acts like N in (9.11.8).
- $\overline{(a_l - \overline{a}_l)^2} = -\frac{\partial \overline{a}_l}{\partial \alpha} = -\frac{\partial \frac{\omega_l}{e^{\alpha+\beta\varepsilon_l}\pm 1}}{\partial \alpha} = \frac{\omega_l e^{\alpha+\beta\varepsilon_l}}{(e^{\alpha+\beta\varepsilon_l}\pm 1)^2}$
  $= \overline{a}_l \frac{e^{\alpha+\beta\varepsilon_l}}{e^{\alpha+\beta\varepsilon_l}\pm 1} = \overline{a}_l (1 \mp \frac{1}{e^{\alpha+\beta\varepsilon_l}\pm 1}) = \overline{a}_l (1 \mp \frac{\overline{a}_l}{\omega_l})$.

Fluctuation of Bose/Fermi distribution $\boxed{\overline{a}_l = \frac{\omega_l}{e^{\alpha+\beta\varepsilon_l} \pm 1}}$

- App 3. Fluctuation of Bose/Fermi distribution.
- Take the particles at energy level ε_l as an open system. a_l acts like N in (9.11.8).
- $\overline{(a_l - \overline{a}_l)^2} = -\frac{\partial \overline{a}_l}{\partial \alpha} = -\frac{\partial \frac{\omega_l}{e^{\alpha+\beta\varepsilon_l} \pm 1}}{\partial \alpha} = \frac{\omega_l e^{\alpha+\beta\varepsilon_l}}{(e^{\alpha+\beta\varepsilon_l} \pm 1)^2}$
  $= \overline{a}_l \frac{e^{\alpha+\beta\varepsilon_l}}{e^{\alpha+\beta\varepsilon_l} \pm 1} = \overline{a}_l (1 \mp \frac{1}{e^{\alpha+\beta\varepsilon_l} \pm 1}) = \overline{a}_l (1 \mp \frac{\overline{a}_l}{\omega_l})$.
- For Fermions, $\varepsilon < \mu$, $\frac{\overline{a}_l}{\omega_l} \simeq 1$; $\varepsilon > \mu$, $\overline{a}_l \simeq 0$, so the fluctuation is small.

Fluctuation of Bose/Fermi distribution $\boxed{\overline{a}_l = \frac{\omega_l}{e^{\alpha+\beta\varepsilon_l} \pm 1}}$

- App 3. Fluctuation of Bose/Fermi distribution.
- Take the particles at energy level ε_l as an open system. a_l acts like N in (9.11.8).
- $\overline{(a_l - \overline{a}_l)^2} = -\frac{\partial \overline{a}_l}{\partial \alpha} = -\frac{\partial \frac{\omega_l}{e^{\alpha+\beta\varepsilon_l} \pm 1}}{\partial \alpha} = \frac{\omega_l e^{\alpha+\beta\varepsilon_l}}{(e^{\alpha+\beta\varepsilon_l} \pm 1)^2}$ $= \overline{a}_l \frac{e^{\alpha+\beta\varepsilon_l}}{e^{\alpha+\beta\varepsilon_l} \pm 1} = \overline{a}_l (1 \mp \frac{1}{e^{\alpha+\beta\varepsilon_l} \pm 1}) = \overline{a}_l (1 \mp \frac{\overline{a}_l}{\omega_l})$.
- For Fermions, $\varepsilon < \mu$, $\frac{\overline{a}_l}{\omega_l} \simeq 1$; $\varepsilon > \mu$, $\overline{a}_l \simeq 0$, so the fluctuation is small. For Bosons, no such restrict.

Fluctuation of Bose/Fermi distribution $\boxed{\overline{a}_l = \frac{\omega_l}{e^{\alpha+\beta\varepsilon_l}\pm 1}}$

- App 3. Fluctuation of Bose/Fermi distribution.
- Take the particles at energy level ε_l as an open system. a_l acts like N in (9.11.8).
- $\overline{(a_l - \overline{a}_l)^2} = -\frac{\partial \overline{a}_l}{\partial \alpha} = -\frac{\partial \frac{\omega_l}{e^{\alpha+\beta\varepsilon_l}\pm 1}}{\partial \alpha} = \frac{\omega_l e^{\alpha+\beta\varepsilon_l}}{(e^{\alpha+\beta\varepsilon_l}\pm 1)^2}$
  $= \overline{a}_l \frac{e^{\alpha+\beta\varepsilon_l}}{e^{\alpha+\beta\varepsilon_l}\pm 1} = \overline{a}_l(1 \mp \frac{1}{e^{\alpha+\beta\varepsilon_l}\pm 1}) = \overline{a}_l(1 \mp \frac{\overline{a}_l}{\omega_l})$.
- For Fermions, $\varepsilon < \mu$, $\frac{\overline{a}_l}{\omega_l} \simeq 1$; $\varepsilon > \mu$, $\overline{a}_l \simeq 0$, so the fluctuation is small. For Bosons, no such restrict.
- The correlation: $\overline{a_l a_m}$

Fluctuation of Bose/Fermi distribution $\boxed{\overline{a}_l = \frac{\omega_l}{e^{\alpha+\beta\varepsilon_l}\pm 1}}$

- App 3. Fluctuation of Bose/Fermi distribution.
- Take the particles at energy level ε_l as an open system. a_l acts like N in (9.11.8).
- $\overline{(a_l - \overline{a}_l)^2} = -\frac{\partial \overline{a}_l}{\partial \alpha} = -\frac{\partial \frac{\omega_l}{e^{\alpha+\beta\varepsilon_l}\pm 1}}{\partial \alpha} = \frac{\omega_l e^{\alpha+\beta\varepsilon_l}}{(e^{\alpha+\beta\varepsilon_l}\pm 1)^2}$
  $= \overline{a}_l \frac{e^{\alpha+\beta\varepsilon_l}}{e^{\alpha+\beta\varepsilon_l}\pm 1} = \overline{a}_l (1 \mp \frac{1}{e^{\alpha+\beta\varepsilon_l}\pm 1}) = \overline{a}_l (1 \mp \frac{\overline{a}_l}{\omega_l})$.
- For Fermions, $\varepsilon < \mu$, $\frac{\overline{a}_l}{\omega_l} \simeq 1$; $\varepsilon > \mu$, $\overline{a}_l \simeq 0$, so the fluctuation is small. For Bosons, no such restrict.
- The correlation: $\overline{a_l a_m} = \frac{1}{\Xi} \sum_N \sum_S a_l a_m e^{-(\alpha N + \beta E_S)}$

Fluctuation of Bose/Fermi distribution $\boxed{\overline{a}_l = \frac{\omega_l}{e^{\alpha+\beta\varepsilon_l}\pm 1}}$

- App 3. Fluctuation of Bose/Fermi distribution.
- Take the particles at energy level ε_l as an open system. a_l acts like N in (9.11.8).
- $\overline{(a_l-\overline{a}_l)^2} = -\frac{\partial \overline{a}_l}{\partial\alpha} = -\frac{\partial \frac{\omega_l}{e^{\alpha+\beta\varepsilon_l}\pm 1}}{\partial\alpha} = \frac{\omega_l e^{\alpha+\beta\varepsilon_l}}{(e^{\alpha+\beta\varepsilon_l}\pm 1)^2}$
  $= \overline{a}_l \frac{e^{\alpha+\beta\varepsilon_l}}{e^{\alpha+\beta\varepsilon_l}\pm 1} = \overline{a}_l(1 \mp \frac{1}{e^{\alpha+\beta\varepsilon_l}\pm 1}) = \overline{a}_l(1 \mp \frac{\overline{a}_l}{\omega_l})$.
- For Fermions, $\varepsilon < \mu$, $\frac{\overline{a}_l}{\omega_l} \simeq 1$; $\varepsilon > \mu$, $\overline{a}_l \simeq 0$, so the fluctuation is small. For Bosons, no such restrict.
- The correlation: $\overline{a_l a_m} = \frac{1}{\mathcal{Z}} \sum_N \sum_S a_l a_m e^{-(\alpha N + \beta E_S)}$
  $= \frac{1}{\mathcal{Z}_l}[\sum_{a_l} a_l e^{-(\alpha+\beta\varepsilon_l)a_l}] \cdot \frac{1}{\mathcal{Z}_m}[\sum_{a_m} a_m e^{-(\alpha+\beta\varepsilon_m)a_m}]$

Fluctuation of Bose/Fermi distribution $\boxed{\overline{a}_l = \frac{\omega_l}{e^{\alpha+\beta\varepsilon_l}\pm 1}}$

- App 3. Fluctuation of Bose/Fermi distribution.
- Take the particles at energy level ε_l as an open system. a_l acts like N in (9.11.8).
- $\overline{(a_l-\overline{a}_l)^2} = -\frac{\partial \overline{a}_l}{\partial\alpha} = -\frac{\partial\frac{\omega_l}{e^{\alpha+\beta\varepsilon_l}\pm 1}}{\partial\alpha} = \frac{\omega_l e^{\alpha+\beta\varepsilon_l}}{(e^{\alpha+\beta\varepsilon_l}\pm 1)^2}$
  $= \overline{a}_l\frac{e^{\alpha+\beta\varepsilon_l}}{e^{\alpha+\beta\varepsilon_l}\pm 1} = \overline{a}_l(1\mp\frac{1}{e^{\alpha+\beta\varepsilon_l}\pm 1}) = \overline{a}_l(1\mp\frac{\overline{a}_l}{\omega_l})$.
- For Fermions, $\varepsilon<\mu$, $\frac{\overline{a}_l}{\omega_l}\simeq 1$; $\varepsilon>\mu$, $\overline{a}_l\simeq 0$, so the fluctuation is small. For Bosons, no such restrict.
- The correlation: $\overline{a_l a_m} = \frac{1}{\mathcal{Z}}\sum_N\sum_S a_l a_m e^{-(\alpha N+\beta E_S)}$
  $= \frac{1}{\mathcal{Z}_l}[\sum_{a_l} a_l e^{-(\alpha+\beta\varepsilon_l)a_l}]\cdot\frac{1}{\mathcal{Z}_m}[\sum_{a_m} a_m e^{-(\alpha+\beta\varepsilon_m)a_m}] = \overline{a}_l\overline{a}_m$.

Fluctuation of Bose/Fermi distribution $\boxed{\overline{a}_l = \frac{\omega_l}{e^{\alpha+\beta\varepsilon_l}\pm 1}}$

- App 3. Fluctuation of Bose/Fermi distribution.
- Take the particles at energy level ε_l as an open system. a_l acts like N in (9.11.8).
- $\overline{(a_l-\overline{a}_l)^2} = -\frac{\partial \overline{a}_l}{\partial \alpha} = -\frac{\partial \frac{\omega_l}{e^{\alpha+\beta\varepsilon_l}\pm 1}}{\partial \alpha} = \frac{\omega_l e^{\alpha+\beta\varepsilon_l}}{(e^{\alpha+\beta\varepsilon_l}\pm 1)^2}$
  $= \overline{a}_l \frac{e^{\alpha+\beta\varepsilon_l}}{e^{\alpha+\beta\varepsilon_l}\pm 1} = \overline{a}_l(1 \mp \frac{1}{e^{\alpha+\beta\varepsilon_l}\pm 1}) = \overline{a}_l(1\mp\frac{\overline{a}_l}{\omega_l})$.
- For Fermions, $\varepsilon<\mu$, $\frac{\overline{a}_l}{\omega_l}\simeq 1$; $\varepsilon>\mu$, $\overline{a}_l\simeq 0$, so the fluctuation is small. For Bosons, no such restrict.
- The correlation: $\overline{a_l a_m} = \frac{1}{\mathcal{Z}}\sum_N\sum_S a_l a_m e^{-(\alpha N+\beta E_S)}$
  $= \frac{1}{\mathcal{Z}_l}[\sum_{a_l} a_l e^{-(\alpha+\beta\varepsilon_l)a_l}] \cdot \frac{1}{\mathcal{Z}_m}[\sum_{a_m} a_m e^{-(\alpha+\beta\varepsilon_m)a_m}] = \overline{a}_l\overline{a}_m$.
- $\overline{(a_l-\overline{a}_l)(a_m-\overline{a}_m)} = \overline{a_l a_m} - \overline{a}_l\overline{a}_m = 0$, no correlation.

Table of contents