Open Systems

Definition
The chemical potential $\mu$
Internal $\mu$
External $\mu$
Gravity
Magnetic
Gibbs factor and Gibbs sum
What determines $N$?

- Up to now (Ch. 1-3), we asked the following questions:
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    - What states $s$ do they take?
    - What are their average observables $<x>$?
What determines $N$?

- We also asked (Ch. 4):

  - The chemical potential $\mu$
  - Internal $\mu$
  - External $\mu$
  - Gravity
  - Magnetic
  - Gibbs factor and Gibbs sum
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    - aren’t conserved
  - Nevertheless, sort of like particles
    - Energy is quantized by occupancy $n$
    - Can ”collide,” exchange $\hbar \omega$ with other "particles"
What determines $N$?

- Many more cases where particles *can* move

**Figure:** Atmospheric circulation map (NOAA website)
What determines $N$?

- Many more cases where particles *can* move

*Figure*: Atmospheric circulation map (NOAA website)

- Why do they (gas molecules) go where they go?
The chemical potential $\mu$

**Figure**: Two regions
The chemical potential $\mu$

What determines energy flow? $T_1$, $T_2$
The chemical potential $\mu$

- What determines energy flow? $T_1, T_2$
- What determines particle flow?

**Figure:** Two regions
The chemical potential $\mu$

**Figure:** Two regions

- What determines energy flow? $T_1, T_2$
- What determines particle flow?
- How about concentrations?

$$n_1 = \frac{N_1}{V_1} \quad n_2 = \frac{N_2}{V_2} \quad (1)$$
The chemical potential $\mu$

- For const $\tau$, $V$, proved before: $F$ minimized, $\delta F \leq 0$
The chemical potential $\mu$

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In the case of the two regions 1, 2 in thermal and diffusive equilibrium

$$F = F_1 + F_2$$ (2)
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- $N$ is new variable. Expand $F = F(\tau, V, N)$:
The chemical potential $\mu$

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  $$dF = \left( \frac{\partial F}{\partial \tau} \right)_{V,N} d\tau + \left( \frac{\partial F}{\partial V} \right)_{\tau,N} dV + \left( \frac{\partial F}{\partial N} \right)_{\tau,V} dN$$ \hspace{1cm} (3)
The chemical potential $\mu$

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Constant $N = N_1 + N_2$, so $\delta N_1 = -\delta N_2$

  \[ dF = \left( \frac{\partial F_1}{\partial N_1} \right)_{\tau,V_1} \delta N_1 - \left( \frac{\partial F_2}{\partial N_2} \right)_{\tau,V_2} \delta N_1 \] (4)
The chemical potential $\mu$

- Define

$$\mu_{1,2} = \left( \frac{\partial F_{1,2}}{\partial N_{1,2}} \right)_{\tau, V_{1,2}}$$

(5)

Particle flow from 2 to 1 if $dF < 0$ for $\delta N_{1} > 0$

$$\left( \frac{\partial F_{1}}{\partial N_{1}} \right) \delta N_{1} - \left( \frac{\partial F_{2}}{\partial N_{2}} \right) \delta N_{1} < 0$$

(6)

Thus particle flow $2 \rightarrow 1$ if $\mu_{1} < \mu_{2}$

(7)

Particles flow towards regions of low chemical potential

Diffusive equilibrium: $\mu(z)$ is constant
The chemical potential $\mu$

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- Particles flow towards regions of low chemical potential

- Diffusive equilibrium: $\mu(z)$ is constant
Internal chemical potential $\mu$

- Example: ideal gas

$$Z = \frac{N!}{n^N}$$

$$F = -\tau \ln Z$$

$$F = \tau \left( \ln N - N \ln n + \frac{N!}{n^N} \right)$$

$$\mu = \left( \frac{\partial F}{\partial N} \right)_{\tau, V}$$
Internal chemical potential $\mu$

- Example: ideal gas

$$Z = \frac{1}{N!} (nQ V)^N$$  \hspace{1cm} (8)
Internal chemical potential $\mu$

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\[
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\[ \mu = \left( \frac{\partial F}{\partial N} \right)_{\tau, V} = \tau \left( \ln N + 1 - 1 - \ln nQ \, V \right) \]  \hfill (12)
Internal chemical potential $\mu$

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$$\mu = \left( \frac{\partial F}{\partial N} \right)_{\tau, V} = \tau \ln \left( \frac{n}{n_Q} \right)$$  \hspace{1cm} (13)
External chemical potential $\mu$

- Just found, for particle type $i$, ”internal” potential

$$\mu_{i}^{\text{int}} = \tau \ln \left( \frac{n_i}{n_{Q,i}} \right)$$  \hspace{1cm} (14)

(due to entropy of numbers)
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$$U = U' + U_0$$  \hspace{1cm} (15)
External chemical potential \( \mu \)

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- Not the whole story. Consider that we add to particle \( U \) an \textit{externally imposed} term \( U' \)

\[
U = U' + U_0 \tag{15}
\]

\[
\mu_{\text{ext}} \equiv U' \tag{16}
\]
External chemical potential $\mu$

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  $\mu_{\text{ext}} \equiv U'$ (16)

- Gravity, $U' = mgz$
- Magnetic field, $U' = \mu \cdot B$, $B = B(z)$
External chemical potential $\mu$

Now, at equilibrium:

$$\mu_i^{int} + \mu_i^{ext} = c$$  \hspace{1cm} (17)

where $c$ is a constant.
External chemical potential $\mu$

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Now we can calculate some interesting things!
External chemical potential $\mu$

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Now we can calculate some interesting things!

- Consider gravity acting on gas (const $T$!)

$$\tau \ln \left( \frac{n}{n_{Q}} \right) + m g z = c$$  \hspace{1cm} (18)
External chemical potential $\mu$

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\[ \mu_i^{\text{int}} + \mu_i^{\text{ext}} = c \]  

where $c$ is a constant.

Now we can calculate some interesting things!

- Consider gravity acting on gas (const $T$!)

\[ \tau \ln \left( \frac{n}{nQ} \right) + mgz = c \]  

\[ PV = n\tau \]
External chemical potential $\mu$

- Now, at equilibrium:

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$$P V = n \tau$$ \hfill (19)

$$\tau \ln \left( \frac{P V}{\tau n_Q} \right) + m g z = c$$ \hfill (20)
Gravitational potential: atmosphere

\[ \tau \ln \left( \frac{P V}{\tau nQ} \right) + m g z = c \] (21)

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\[ \tau \ln \left( \frac{P V}{\tau nQ} \right) + mgz = c \]  \hspace{1cm} (21)

\[ \frac{P V}{\tau nQ} = \exp \left( \frac{c}{\tau} - \frac{mgz}{\tau} \right) \]  \hspace{1cm} (22)
Gravitational potential: atmosphere

\[ \tau \ln \left( \frac{P \, V}{\tau \, n_Q} \right) + m \, g \, z = c \]  \hspace{1cm} (21)

\[ \frac{P \, V}{\tau \, n_Q} = \exp \left( \frac{c}{T} - \frac{m \, g \, z}{\tau} \right) \]  \hspace{1cm} (22)

\[ P = \frac{\tau \, n_Q}{V} \exp \left( \frac{c}{T} - \frac{m \, g \, z}{\tau} \right) \]  \hspace{1cm} (23)
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\[ P = \frac{\tau n Q}{V} \exp \left( \frac{c}{\tau} - \frac{m g z}{\tau} \right) \]  \hspace{1cm} (23)

\[ P = P_0 \exp -\frac{z}{\lambda} \quad \lambda \equiv \frac{\tau}{m g} \]  \hspace{1cm} (24)
Gravitational potential: atmosphere

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\tau \ln \left( \frac{P V}{\tau nQ} \right) + mgz = c \quad (21)
\]

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\frac{P V}{\tau nQ} = \exp \left( \frac{c}{\tau} - \frac{mgz}{\tau} \right) \quad (22)
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\[
P = P_0 \exp \left( -\frac{Z}{\lambda} \right) \quad \lambda \equiv \frac{\tau}{mg} \quad (24)
\]

- \( \lambda \) tells how rapidly the pressure drops with elevation.
Gravitational potential: atmosphere

- Most relevant for us: consider $O_2$ molecule
Gravitational potential: atmosphere

- *Most relevant for us:* consider O$_2$ molecule
  32 g/mol, N$_A$ at/mol
Gravitational potential: atmosphere

- *Most relevant for us:* consider O₂ molecule
  32 g/mol, Nₐ at/mol
  \[ m_{O_2} \cdot g = \frac{32}{6.022} \times 10^{-26} \text{kg/at} \cdot 9.8 \text{ m s}^{-2} = N \]
Gravitational potential: atmosphere

- **Most relevant for us:** consider O\(_2\) molecule
  - 32 g/mol, N\(_A\) at/mol
  - \(m_{O_2} \cdot g = \frac{32}{6.022} \times 10^{-26} \text{kg/atom} \times 9.8 \text{ m s}^{-2} = 25.86 \text{ meV} \approx 25.86 \text{ meV (1.6} \times 10^{-22} \text{ J/meV)}\)
Gravitational potential: atmosphere

- **Most relevant for us:** consider O$_2$ molecule

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  \[ m_{O_2} \cdot g = \frac{32}{6.022} \times 10^{-26} \text{kg/at} \cdot 9.8 \text{ m s}^{-2} = \text{N} \]

  \[ \tau = 25.86 \text{ meV} = 25.86 \text{ meV} \left(1.6 \times 10^{-22} \text{ J/meV}\right) \]

  \[ \lambda = 40 \times 10^{-22} \text{ N m} / 50 \times 10^{-26} \text{ N} \sim 8 \text{ km} \]
Gravitational potential: atmosphere

- **Most relevant for us:** consider $O_2$ molecule
  32 g/mol, $N_A$ at/mol

  \[
  m_{O_2} \cdot g = \frac{32}{6.022 \times 10^{-26}} \text{kg/at} \times 9.8 \text{ m/s}^2 = 25.86 \text{ meV (1.6 \times 10^{-22} J/meV)}
  \]

- **In Nederland, CO, your brain would be deprived of $O_2$ by factor $\sim 0.73$ (27% less)**
Gravitational potential: atmosphere

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- On top of Everest (8 km), by factor $1/e$ (0.37!)
Magnetic potential

- Remember: no magnetic monopoles $\nabla \cdot \mathbf{B} = 0$
Magnetic potential

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- On a dipole, only a torque (no force) in $\mathbf{B}$ const
Magnetic potential

- Remember: no magnetic monopoles $\nabla \cdot \mathbf{B} = 0$
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- Need a field gradient to exert a force: $\mathbf{F} = \nabla (\mu \cdot \mathbf{B})$.
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- Need a field gradient to exert a force: \( \mathbf{F} = \nabla (\mu \cdot \mathbf{B}) \).
- Assume a field profile

\[
B(z) = \frac{B_0}{2} \left( \frac{2z}{L} \right)
\] (25)
Magnetic potential

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\[
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\]

- Thus for spin 1/2 particles (He\(_3\))

\[
\mu_{\text{ext}} = \mu \cdot \mathbf{B} \tag{26}
\]

\[
\mu_{\mp,\text{ext}} = \pm \mu_B B_0 \frac{z}{L} \tag{27}
\]
Magnetic potential

- Remember: no magnetic monopoles \( \nabla \cdot \mathbf{B} = 0 \)
- On a dipole, only a torque (no force) in \( \mathbf{B} \) const
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(25)

- Thus for spin 1/2 particles (He\(_3\))

\[
\mu_{\text{ext}} = \mu \cdot \mathbf{B}
\]

(26)

\[
\mu_{\pm, \text{ext}} = \pm \mu_B B_0 \frac{z}{L}
\]

(27)

\[
n^\uparrow = n_0 \exp \frac{z}{\lambda} \quad n^\downarrow = n_0 \exp -\frac{z}{\lambda} \quad \lambda \equiv \frac{\tau L}{\mu_B B_0}
\]

(28)
Magnetic potential

\[ \mu_B \cdot 1 \, \text{T} \sim 0.66 \, \text{K}; \text{ for a high field gradient of } L = 1 \, \text{mm}, \]
\[ \lambda = 45 \, \text{cm} \text{ (not much separation)} \]
Gibbs factor / Gibbs sum

- Again, two systems: $S$

$S_1$  $S_2$

**Figure:** Isolated systems $S_1, S_2$
Gibbs factor / Gibbs sum

- Again, two systems: \( S \)

\[ S_1 \quad S_2 \]

Figure: Isolated systems \( S_1, S_2 \)

- Energies \( U_1, U_2 \) fixed.
Gibbs factor / Gibbs sum

- Again, two systems: $S$
- Energies $U_1, U_2$ fixed.
- Particles: $N_1, N_2$ fixed

Figure: Isolated systems $S_1, S_2$
Open Systems

Definition

The chemical potential $\mu$

Internal $\mu$

External $\mu$

Gravity

Magnetic

Gibbs factor and Gibbs sum

Again, two systems: $S$

$S_1$

$S_2$

Figure: Isolated systems $S_1, S_2$

- Energies $U_1, U_2$ fixed.
- Particles: $N_1, N_2$ fixed
- What happens?
Again, two systems: $S$

$S_1 + S_2$

Figure: Joined system $S = S_1 + S_2$
Gibbs factor / Gibbs sum

- Again, two systems: $S$

\[ S_1 \quad S_2 \]

Figure: Joined system $S = S_1 + S_2$

- Can exchange energy: $U = U_1 + U_2$ fixed.
Gibbs factor / Gibbs sum

- Again, two systems: $S$

\[
S_1 \quad S_2
\]

Figure: Joined system $S = S_1 + S_2$

- Can exchange energy: $U = U_1 + U_2$ fixed.
- **Now can** exchange particles: $N = N_1 + N_2$ fixed, $N_1$, $N_2 = N - N_1$ variable.
Gibbs factor / Gibbs sum

- Again, two systems: $S$

  \[
  S = S_1 + S_2
  \]

- Can exchange energy: $U = U_1 + U_2$ fixed.
- **Now can** exchange particles: $N = N_1 + N_2$ fixed, $N_1, N_2 = N - N_1$ variable.
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*Figure:* Joined system $S = S_1 + S_2$
Known / unknown

- We know direction of energy flow (from high T to low T)
Known / unknown

- We know direction of energy flow (from high $T$ to low $T$)
- We know direction of particle flow (from high $\mu$ to low $\mu$)
Known / unknown

- We know direction of energy flow (from high $T$ to low $T$)
- We know direction of particle flow (from high $\mu$ to low $\mu$)
- Don’t know: relative probability of large $N$ compared with small $N$
Two regions:

- **Universe**
  - $U = U_o$
  - $N = N_o$

- **Reservoir R**
  - $U = U_o - \varepsilon$
  - $N = N_o - N$

**Figure:** Universe: tiny system, big reservoir.
Dividing universe (again)

- **Two regions:**
  - **Universe**
    - $U = U_0$
    - $N = N_0$
  - **Reservoir $R$**
    - $U = U_0 - \varepsilon$
    - $N = N_0 - N$

**System $S$**

*Figure: Universe: tiny system, big reservoir.*
Dividing universe (again)

- **Two regions:**

  ![Diagram showing Universe and Reservoir](image)

  - **Universe**
    - $U = U_o$
    - $N = N_o$

  - **Reservoir $R$**
    - $U = U_o - \varepsilon$
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**Figure:** Universe: tiny system, big reservoir.

- **System $S$**
- **Reservoir $R$**
Dividing universe (again)

- **System**

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Dividing universe (again)

- **System**
  
  Interested in understanding the system.
Dividing universe (again)

- **System $S$**
  
  Interested in understanding the system.

  Energy: $U_S = \epsilon$; Particles: $N$
Dividing universe (again)

- **System $S$**
  Interested in understanding the system.
  Energy: $U_S = \epsilon$; Particles: $N$

- **Reservoir $R$**
Dividing universe (again)

- **System** $S$
  
  Interested in understanding the system.

  Energy: $U_S = \epsilon$; Particles: $N$

- **Reservoir** $R$
  
  All parts of the universe which are not the system.
Dividing universe (again)

- **System** $\mathcal{S}$
  Interested in understanding the system.
  Energy: $U_\mathcal{S} = \epsilon$; Particles: $N$

- **Reservoir** $\mathcal{R}$
  All parts of the universe which are not the system.
  Energy: $U_\mathcal{R}$. 
Dividing universe (again)

- **System** $\mathbb{S}$
  - Interested in understanding the system.
  - Energy: $U_\mathbb{S} = \epsilon$; Particles: $N$

- **Reservoir** $\mathbb{R}$
  - All parts of the universe which are not the system.
  - Energy: $U_\mathbb{R}$.

- Total energy $U_0 = U_\mathbb{S} + U_\mathbb{R}$
Dividing universe (again)

- **System** $S$
  Interested in understanding the system.
  
  Energy: $U_S = \epsilon$; Particles: $N$

- **Reservoir** $R$
  All parts of the universe which are not the system.
  
  Energy: $U_R$.

- Total energy $U_0 = U_S + U_R$
  
  $\Rightarrow U_R = U_0 - \epsilon$, $N_R = N_0 - N$
Evaluating multiplicity

- multiplicity of the whole universe

\[ g_{\text{tot}} = g^S g^R \]  (29)
Evaluating multiplicity

- multiplicity of the whole universe

\[ g_{\text{tot}} = g^S g^R \]  \hspace{1cm} (29)

- Taking \$ as a single state:

\[ g^S = 1. \]
Evaluating multiplicity

- multiplicity of the whole universe

\[ g_{tot} = g^S g^R \]  \hfill (29)

- Taking $S$ as a single state:

\[ g^S = 1. \]

- Total multiplicity is multiplicity of reservoir $R$

\[ g_{tot} = g^R \]  \hfill (30)
Differential relation

- For entropy, expand

\[
d\sigma = \left( \frac{\partial \sigma}{\partial U} \right)_{V,N} \, dU + \left( \frac{\partial \sigma}{\partial V} \right)_{U,N} \, dV + \left( \frac{\partial \sigma}{\partial N} \right)_{V,N} \, dN
\]

(31)
Differential relation

- For entropy, expand

\[
d\sigma = \left( \frac{\partial \sigma}{\partial U} \right)_{V,N} dU + \left( \frac{\partial \sigma}{\partial V} \right)_{U,N} dV + \left( \frac{\partial \sigma}{\partial N} \right)_{V,N} dN
\]

(31)

- At constant volume, constant entropy

\[
0 = \frac{1}{\tau} dU + \left( \frac{\partial \sigma}{\partial N} \right)_{V,N} dN
\]

(32)
Differential relation

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\[
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(32)

- Thus

\[
\left( \frac{\partial \sigma}{\partial N} \right)_{V,N} = -\frac{1}{\tau} \left( \frac{\partial U}{\partial N} \right)_{\sigma,V}
\]

(33)
Differential relation

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0 = \frac{1}{\tau} dU + \left( \frac{\partial \sigma}{\partial N} \right)_{V,N} dN
\]

(32)

- Thus

\[
\left( \frac{\partial \sigma}{\partial N} \right)_{V,N} = -\frac{1}{\tau} \left( \frac{\partial U}{\partial N} \right)_{\sigma,V}
\]

(33)

\[
\left( \frac{\partial \sigma}{\partial N} \right)_{V,N} = -\frac{\mu}{\tau}
\]

(34)
Entropy of reservoir

- Taylor-expand the reservoir entropy

\[
\sigma_R = \sigma_0 + \left( \frac{\partial \sigma}{\partial U} \right)_{V,N} (U_0 - \epsilon) + \left( \frac{\partial \sigma}{\partial N} \right)_{V,N} (N_0 - N) \tag{35}
\]
Entropy of reservoir

- Taylor-expand the reservoir entropy

\[ \sigma_R = \sigma_0 + \left( \frac{\partial \sigma}{\partial U} \right)_{V,N} (U_0 - \epsilon) + \left( \frac{\partial \sigma}{\partial N} \right)_{V,N} (N_0 - N) \] (35)

\[ \sigma_R = \sigma_0 + \frac{1}{\tau} (U_0 - \epsilon) \frac{-\mu}{\tau} (N_0 - N) \] (36)
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- Taylor-expand the reservoir entropy

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$$\sigma_R = \sigma_0 + \frac{1}{\tau} (U_0 - \epsilon) \frac{-\mu}{\tau} (N_0 - N) \quad (36)$$

- So,

$$\frac{P(N_1, E_1)}{P(N_2, E_2)} = \frac{\exp(\sigma_R(N_1, E_1))}{\exp(\sigma_R(N_2, E_2))} \quad (37)$$
Entropy of reservoir

- Taylor-expand the reservoir entropy

\[ \sigma_R = \sigma_0 + \left( \frac{\partial \sigma}{\partial U} \right)_{V,N} (U_0 - \epsilon) + \left( \frac{\partial \sigma}{\partial N} \right)_{V,N} (N_0 - N) \]  

(35)

\[ \sigma_R = \sigma_0 + \frac{1}{\tau} (U_0 - \epsilon) - \frac{\mu}{\tau} (N_0 - N) \]  

(36)

- So,

\[ \frac{P(N_1, E_1)}{P(N_2, E_2)} = \frac{\exp(\sigma_R(N_1, E_1))}{\exp(\sigma_R(N_2, E_2))} \]  

(37)

\[ \frac{P(N_1, E_1)}{P(N_2, E_2)} = \exp \left[ \frac{E_2 - E_1}{\tau} - \frac{\mu}{\tau} (N_2 - N_1) \right] \]  

(38)
For reference, take $N_2 = 0, E_2 = 0$

\[ P(N, E) = \exp \left( \frac{N\mu - E}{\tau} \right) \] (39)
Gibbs factor and Gibbs sum

- For reference, take $N_2 = 0, E_2 = 0$

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P(N, E) = \exp \left( \frac{N\mu - E}{\tau} \right)
\]

(39)

- Gibbs factor!
Gibbs factor and Gibbs sum

- For reference, take $N_2 = 0$, $E_2 = 0$

$$P(N, E) = \exp \left( \frac{N\mu - E}{\tau} \right)$$  \hspace{1cm} (39)

- Gibbs factor!

- Plays same role as Boltzmann factor for systems which can exchange particles.
Gibbs factor and Gibbs sum

- For reference, take \( N_2 = 0, \ E_2 = 0 \)

\[
P(N, E) = \exp\left(\frac{N\mu - E}{\tau}\right)
\]  

(39)

- Gibbs factor!
- Plays same role as Boltzmann factor for systems which can exchange particles.
- Analogue of partition function \( Z \): Gibbs sum

\[
\zeta = \sum_{N=0}^{\infty} \sum_{s(N)} \exp\left(\frac{N\mu - \epsilon_s}{\tau}\right)
\]

(40)
Gibbs factor and Gibbs sum

- For reference, take $N_2 = 0$, $E_2 = 0$

\[ P(N, E) = \exp \left( \frac{N\mu - E}{\tau} \right) \]  \hspace{1cm} (39)

- Gibbs factor!

- Plays same role as Boltzmann factor for systems which can exchange particles.

- Analogue of partition function $Z$: Gibbs sum

\[ \zeta = \sum_{N=0}^{\infty} \sum_{s(N)} \exp \left[ (N\mu - \epsilon_s)/\tau \right] \]  \hspace{1cm} (40)

a.k.a. grand canonical sum
Number of particles

- Not hard to verify (like for $U$)

\[
\langle N \rangle = \tau \frac{\partial \ln \zeta}{\partial \mu}
\]  

(41)