Statistical Mechanics

Week 4

Microcanonical Ensemble

- ☐ **Ideal gas:** continuous microstates
  - ✓ Hamiltonian is $\mathcal{H}(p,q) = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m}$, and $E < \mathcal{H}(p,q) < E + \Delta$
  - ✓ Ideal gas, no '*q*' term in $\mathcal{H}(p,q)$, so

$$\Omega(E) = \int_{E<\mathcal{H}(p,q)<E+\Delta} d^{3N}p\,d^{3N}q = V^N \int_{E<\mathcal{H}(p,q)<E+\Delta} d^{3N}p$$

  - ✓ We have identified the integral as the volume of a 3*N*-dimensional spherical shell with radius $(2mE)^{1/2}$ and thickness Δ.
  - ✓ The calculation of the integral is complicated (not required), the final result is

$$\Omega(E) = V^N \frac{2\pi^{3N/2}}{\left(\frac{3N}{2} - 1\right)!} (2mE)^{(3N-1)/2}$$

  - ✓ Using Stirling's formula, and neglecting terms of order of 1 or $\ln E \sim \ln N$ in the large *N* limit, results in

$$S(E,V,N) = k_B\left[N\ln V + \frac{3N}{2}\ln(2\pi mE) - \frac{3N}{2}\ln\frac{3N}{2} + \frac{3N}{2}\right] = Nk_B \ln\left[V\left(\frac{4\pi emE}{3N}\right)^{3/2}\right]$$

Gibbs paradox: Team-Discussion

- **Entropy:**

$$S(E,V,N) = Nk_B \ln\left[V \left(\frac{4\pi e m E}{3N} \right)^{3/2} \right]$$

[1] The above entropy is the one we obtained for ideal gas using microcanonical ensemble method. Any problem?

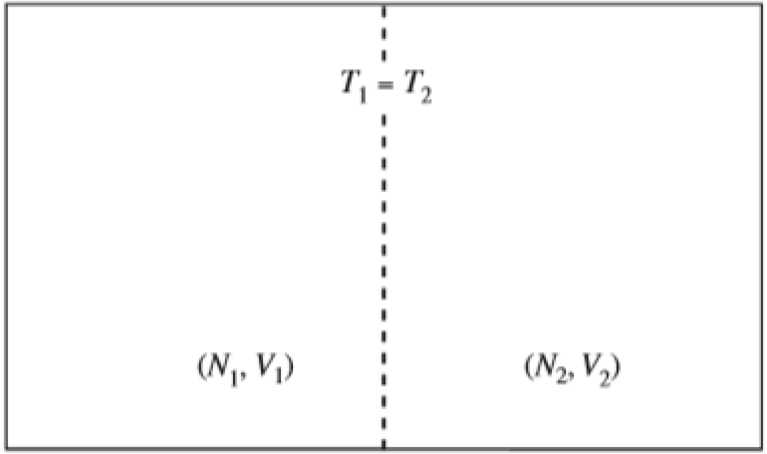
[2] Consider two distinct gases, initially occupying volumes V_1 and V_2 at the **same temperature** $\boldsymbol{T}$. The partition between them is removed, and they are allowed to expand and occupy the combined volume $V = V_1 + V_2$. Consider the following questions:

(a) What is the initial entropy before mixing?

(b) What is the final entropy after mixing?

(c) What is the difference: $S_f - S_i$?

[3] Two gases are *identical* with same density, $n = N_1/V_1 = N_2/V_2$. What is the the difference: $S_f - S_i$?



Gibbs paradox

❑ **Mixing Entropy:**

$$S(E,V,N) = Nk_B \ln\left[V \left(\frac{4\pi e m E}{3N} \right)^{3/2} \right]$$

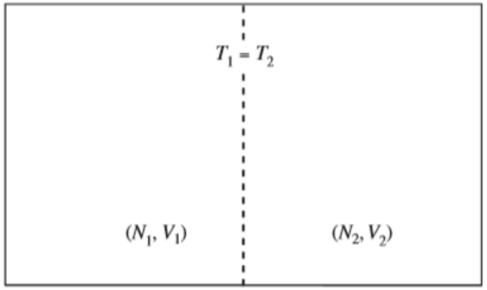
✓ The entropy is non-additive, i.e., $S(E,V,N) = Ns(\frac{E}{N},\frac{V}{N})$. E is normalized by N, but V is not. This difficulty is related to the *mixing entropy*.

✓ The initial entropy $S_i = S_1 + S_2 = N_1 k_B(lnV_1 + \sigma_1) + N_2 k_B(lnV_2 + \sigma_2)$

momentum contribution to the entropy of the αth gas $\sigma_\alpha = \ln\left(\frac{4\pi e m_\alpha}{3} \cdot \frac{E_\alpha}{N_\alpha} \right)^{3/2}$

✓ The temperature is unchanged by mixing, since

$$\frac{3}{2}k_B T_f = \frac{E_1 + E_2}{N_1 + N_2} = \frac{E_1}{N_1} = \frac{E_2}{N_2} = \frac{3}{2}k_B T.$$



✓ The final entropy of the mixed gas is

$$S_f = N_1 k_B ln(V_1 + V_2) + N_2 k_B ln(V_1 + V_2) + k_B(N_1\sigma_1 + N_2\sigma_2)$$

✓ Mixing entropy $S_f - S_i = N_1 k_B ln\frac{V}{V_1} + N_2 k_B ln\frac{V}{V_2} = -Nk_B[\frac{N_1}{N} ln\frac{V_1}{V} + \frac{N_2}{N} ln\frac{V_2}{V}]$

Gibbs paradox

- **Gibbs paradox:**
  - ✓ Mixing entropy $S_f - S_i = N_1 k_B ln\frac{V}{V_1} + N_2 k_B ln\frac{V}{V_2} = -N k_B[\frac{N_1}{N} ln\frac{V_1}{V} + \frac{N_2}{N} ln\frac{V_2}{V}]$
  - ✓ Solely from the contribution of the coordinates.
  - ✓ ***The Gibbs paradox***: the two gases are *identical* with same density, $n = N_1/V_1 = N_2/V_2$. Since removing or inserting the partition does not change the state of the system, there should be no entropy of mixing?!
  - ✓ While the exchange of *distinct* particles leads to two configurations, a similar exchange has no effect on *identical* particles.

  - ✓ We over-counted the phase space associated with N identical particles by the number of possible permutations (i.e., $N!$). We make the correction to the microstate number

$$\Omega(E) = V^N \frac{2\pi^{3N/2}}{(3N/2-1)!}(2mE)^{(3N-1)/2} \quad \rightarrow \quad \frac{V^N}{N!}\frac{2\pi^{3N/2}}{(3N/2-1)!}(2mE)^{(3N-1)/2}$$

$$S = k_B \ln\Omega = k_B[N\ln V - N\ln N + N\ln \mathrm{e}] + Nk_B\sigma = Nk_B\left[\ln\frac{\mathrm{e}V}{N} + \sigma\right]$$

Use Stirling’s formula

Gibbs paradox

- ☐ **Corrected entropy:**

$$S = Nk_B\left[\ln(eV/N) + \sigma\right]$$

- ✓ *V* has been changed to *V/N*, the entropy is now properly extensive. The mixing entropies can be recalculated.

Mixing of distinct gases

$$\begin{aligned} S_f - S_i &= N_1k_B\ln\frac{V}{N_1} + N_2k_B\ln\frac{V}{N_2} - \left(N_1k_B\ln\frac{V_1}{N_1} + N_2k_B\ln\frac{V_2}{N_2}\right) \\ &= N_1k_B\ln\left(\frac{V}{N_1}\cdot\frac{N_1}{V_1}\right) + N_2k_B\ln\left(\frac{V}{N_2}\cdot\frac{N_2}{V_2}\right) \\ &= -Nk_B\left[\frac{N_1}{N}\ln\frac{V_1}{V} + \frac{N_2}{N}\ln\frac{V_2}{V}\right] > 0 \end{aligned}$$

Mixing of identical gases

$$S_f - S_i = \left(N_1 + N_2\right)k_B\ln\frac{V_1 + V_2}{N_1 + N_2}$$

$$-\left(N_1k_B\ln\frac{V_1}{N_1} + N_2k_B\ln\frac{V_2}{N_2}\right) = 0.$$

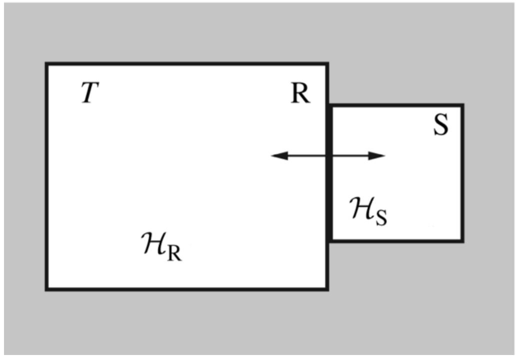
$$N_1/V_1 = N_2/V_2 = \left(N_1 + N_2\right)/\left(V_1 + V_2\right)$$

The canonical Ensemble

❑ Canonical ensemble

- ✓ Canonical ensemble: the macrostates, specified by $M \equiv (T, x)$, allow the input of heat into the system, but no external work.
- ✓ The system *S* is maintained at a constant temperature through contact with a reservoir *R*. The reservoir is another macroscopic system that is sufficiently large so that its temperature does not change.
- ✓ The combined system belongs to a microcanonical ensemble of $E_{Tot} >> E_s$.
- ✓ The joint probability of microstates $p(S \otimes R)$ is

$$p(S \otimes R) = \frac{1}{\Omega_{S \oplus R}\left(E_{\text{Tot}}\right)} \cdot \begin{cases} 1 & \text{for } E_S + E_R = E_{\text{Tot}} \\ 0 & \text{otherwise} \end{cases}$$



- ✓ The probability for microstates of *S* can be obtained from the sum all reservoir microstates. The $p(S)$ is related to the entropy of the reservoir,

$$p(S) = \sum_{\{R\}} p(S \otimes R) = \frac{\Omega_R\left(E_{\text{Tot}} - E_S\right)}{\Omega_{S \oplus R}\left(E_{\text{Tot}}\right)} \qquad S_R = k \ln \Omega_R\left(E_{\text{Tot}} - E_S\right)$$

The canonical Ensemble

☐ Canonical ensemble

- ✓ We now exam S_R. Since only the values near $E_S = \overline{E_S}$ are expected to be important, and $\overline{E_S} \ll E_{Tot}$, we may perform the expansion near $E_R = E_{Tot}$

$$k \ln \Omega_R \left(E_{Tot} - E_S\right) = S_R\left(E_{Tot} - E_S\right)$$

$$= S_R\left(E_{Tot}\right) - E_S\left[\frac{\partial S_R\left(E_R\right)}{\partial E_R}\right]_{E_R = E_{Tot}} + \cdots$$

$$= S_R\left(E_{Tot}\right) - \frac{E_S}{T} \qquad T = T_R$$

- ✓ Therefore, $\Omega_R(E_{Tot} - E_s) \approx \exp[S_R(E_{Tot})/k]\exp(-E_s/kT)$
- ✓ The first factor is independent of E_s and is thus a constant as far as the small subsystem is concerned.
- ✓ The probability for microstates of S is (use $E_S = \mathcal{H}_s(p_s, q_s)$),

$$p(S) = \frac{\Omega_R(E_{Tot} - E_s)}{\Omega_{S\oplus R}(E_{Tot})} = \frac{\exp[S_R(E_{Tot})/k]}{\Omega_{S\oplus R}(E_{Tot})} \exp\left[\frac{-\mathcal{H}_s(p_s, q_s)}{kT}\right] = \frac{\exp[-\mathcal{H}_s(p_s, q_s)/k\,T]}{Z(T, x)}$$

The canonical Ensemble

☐ **Partition function**

$$p(s) = \frac{\exp[-\beta\mathcal{H}(s)]}{Z(T,x)} \qquad \beta = 1/kT$$

- ✓ We drop the subscript *s*, since we may now forget about the larger subsystem, apart from the information that its temperature is *T*.
- ✓ Boltzmann factor: $\exp[-\beta\mathcal{H}(s)]$, it quantifies how the probability of a particular energy state of a system depends on both the energy of that state and the temperature of the system.
- ✓ The normalization factor $Z(T,x)$ is called *partition function*. Since $\sum_s p(s) = 1$, we get $Z(T,x) = \sum_s \exp[-\beta\mathcal{H}(s)]$, sum of Boltzmann factor. It summarizes all possible ways a system can distribute its total energy among its constituent particles, and accounts for all the possible microstates.
- ✓ In other words, partition function *Z* "contains" all information. Many physical quantities can be derived from *Z*. No need to calculate entropy *S* first.

Q: Physical meaning of Boltzmann factor?

Team Discussion: Boltzmann factor

☐ **Boltzmann factor**

$$p(s) = \frac{\exp[-\beta\mathcal{H}(s)]}{Z(T,x)} \qquad \beta = 1/kT$$

✓ The normalization factor $Z(T,x)$ is called *partition function*. Since $\sum_s p(s) = 1$, we get $Z(T,x) = \sum_s \exp[-\beta\mathcal{H}(s)]$, sum of Boltzmann factor.

Q1: What is the value Boltzmann factor at $T = 0$? Why?

Q2: T increases from 0 to higher?

$T = 0$ K, Boltzmann factor = 0 for all states except the one with the lowest energy.

When T increases, higher energy levels have non-zero Boltzmann factor and they can be occupied.

The canonical Ensemble

- ☐ **Partition function** $p(s) = \dfrac{\exp[-\beta\mathcal{H}(s)]}{Z(T,x)}$ $\beta = 1/kT$

✓ $Z(T,x) = \sum_s \exp[-\beta\mathcal{H}(s)]$, but for continuous case, such as the ideal gas

$$Z(T,V,N) = \int \frac{d^{3N}p\,d^{3N}q}{N!\,h^{3N}} \exp[-\beta\mathcal{H}(p,q)]$$

✓ **Partition function** is very useful since it is linked to **free energy**.

✓ Let's look at the energy probability distribution $p(\varepsilon)$, we need to change s (represents a microstate) to $\mathcal{H}$ in probability p, sum all s states with $\mathcal{H} = \varepsilon$,

$$p(\mathcal{E}) = \sum_{\{s\}} p(s)\delta(\mathcal{H}(s) - \mathcal{E}) = \frac{\mathrm{e}^{-\beta\mathcal{E}}}{Z}\sum_{\{s\}}\delta(\mathcal{H}(s) - \mathcal{E}) = \frac{\Omega(\mathcal{E})\mathrm{e}^{-\beta\mathcal{E}}}{Z}$$

$\Omega(\mathcal{E}) = \sum_{\{s\}}\delta(\mathcal{H}(s) - \mathcal{E})$: just the number of microstates with energy $\mathcal{E}$

$$S(\mathcal{E}) = k\ln\Omega(\mathcal{E}) \qquad p(\mathcal{E}) = \frac{1}{Z}\exp\left[\frac{S(\mathcal{E})}{k_B} - \frac{\mathcal{E}}{k_B T}\right] = \frac{1}{Z}\exp\left[-\frac{F(\mathcal{E})}{k_B T}\right]$$

where we have set $F = \varepsilon - TS$, it is the *Helmholtz free energy*.

The canonical Ensemble

- **Partition function**

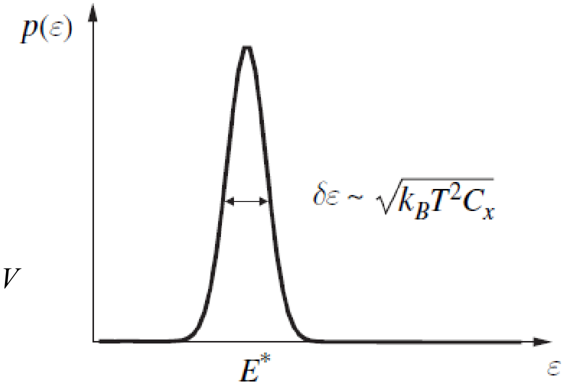
$$p(\mathcal{E}) = \frac{1}{Z}\exp\left[-\frac{F(\mathcal{E})}{k_B T}\right] \qquad Z = \sum_{\mathcal{E}} \mathrm{e}^{-\beta F(\mathcal{E})}$$

Q: For what condition, the probability $p(\varepsilon)$ is a maximum?

When the *Helmholtz free energy F* is a minimum, $p(\varepsilon)$ is a maximum.

- The probability $p(\varepsilon)$ is sharply peaked at a E^* which minimizes *F*.
- Thus, in the sum of *Z*, we only need to keep the largest term

$$Z = \sum_{\mathcal{E}} \mathrm{e}^{-\beta F(\mathcal{E})} \approx \mathrm{e}^{-\beta F\left(E^*\right)} \qquad F(T, \mathbf{x}) = -k_B T \ln Z$$



$$\mathrm{d}F = -S\mathrm{d}T - p\mathrm{d}V + \mu\mathrm{d}N. \qquad p = -\left(\frac{\partial F}{\partial V}\right)_{T,N} \qquad S = -\frac{\partial F}{\partial T}\bigg|_{N,V}$$

The internal energy

$$E = \langle \mathcal{H} \rangle = \sum_{s} \mathcal{H}(s)\frac{\mathrm{e}^{-\beta \mathcal{H}(s)}}{Z} = -\frac{1}{Z}\frac{\partial}{\partial \beta}\sum_{s} \mathrm{e}^{-\beta \mathcal{H}} = -\frac{\partial \ln Z}{\partial \beta}$$

The canonical Ensemble: Team-Discussion

❑ **Example: ideal gas**

Q: Can you solve the partition function for ideal gas using canonical ensemble?

$$Z(T,V,N) = \int \frac{d^{3N}p\, d^{3N}q}{N!\, h^{3N}} \exp[-\beta \mathcal{H}(p,q)]$$

$$Z(T,V,N) = \int \frac{1}{N!} \prod_{i=1}^{N} \frac{\mathrm{d}^3\vec{q}_i\, \mathrm{d}^3\vec{p}_i}{h^3} \exp\left[-\beta \sum_{i=1}^{N} \frac{p_i^2}{2m}\right] = \frac{V^N}{N!} \int \prod_{i=1}^{N} \frac{\mathrm{d}^3\vec{p}_i}{h^3} \exp\left[-\beta \sum_{i=1}^{N} \frac{p_i^2}{2m}\right]$$

$$= \frac{V^N}{N!} \int \prod_{i=1}^{N} \frac{4\pi p_i^2 \mathrm{d}p_i}{h^3} \exp\left[-\beta \sum_{i=1}^{N} \frac{p_i^2}{2m}\right] = \frac{V^N}{N!} \left(\frac{2\pi m k_B T}{h^2}\right)^{3N/2} = \frac{1}{N!} \left(\frac{V}{\lambda^3}\right)^N$$

$$\int_0^\infty x^2 e^{-\alpha x^2} dx = \frac{\sqrt{\pi}}{4\alpha^{3/2}} \qquad \lambda = \frac{h}{\sqrt{2\pi m k_B T}}$$

$$F(T,N) = -k_B T \ln Z = -k_B T[N \ln V - 3N \ln \lambda - \ln N!]$$

$$= -k_B T[N \ln V - 3N \ln \lambda - N \ln \frac{N}{e}] = -N k_B T \ln\left[\frac{eV}{N}\left(\frac{2\pi m k T}{h^2}\right)^{3/2}\right] = -N k_B T \ln[\frac{V}{A}]$$

$$\ln N! = N \ln(N/e)$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = -(-N k_B T)\frac{1}{V} = \frac{N k_B T}{V}$$

The canonical Ensemble: Team-Discussion

- **Example: two-level system**
  - ✓ The N impurities are described by a macrostate $M \equiv (T, N)$. Subject to the Hamiltonian $\mathcal{H} = \epsilon \sum_{i=1}^{N} n_i$, the microstates $\mu = \{n_i\}$.

Q: What is the partition function?

$$Z(T,\mathbf{x}) = \sum_{\{s\}} \mathrm{e}^{-\beta \mathcal{H}(s)}$$

$$Z(T,N) = \sum_{\{n_i\}} \exp\left[-\beta\epsilon \sum_{i=1}^{N} n_i\right] = \left(\sum_{n_1=0}^{1} \mathrm{e}^{-\beta\epsilon n_1}\right)\cdots\left(\sum_{n_N=0}^{1} \mathrm{e}^{-\beta\epsilon n_N}\right) = \left(1+\mathrm{e}^{-\beta\epsilon}\right)^{N}$$

$$F(T,N) = -k_B T \ln Z = -N k_B T \ln\left[1+\mathrm{e}^{-\epsilon/(k_B T)}\right]$$

$$S = -\left.\frac{\partial F}{\partial T}\right|_{N} = \underbrace{N k_B \ln\left[1+\mathrm{e}^{-\epsilon/(k_B T)}\right]}_{-F/T} + N k_B T \left(\frac{\epsilon}{k_B T^2}\right) \frac{\mathrm{e}^{-\epsilon/(k_B T)}}{1+\mathrm{e}^{-\epsilon/(k_B T)}}$$

$$E = F + TS = \frac{N\epsilon}{1+\mathrm{e}^{\epsilon/(k_B T)}}, \qquad E = -\frac{\partial \ln Z}{\partial \beta} = \frac{N\epsilon \mathrm{e}^{-\beta\epsilon}}{1+\mathrm{e}^{-\beta\epsilon}}$$

The canonical Ensemble

❑ Energy fluctuations

$$\left\langle \mathcal{H}^2 \right\rangle_c = \left\langle \mathcal{H}^2 \right\rangle - \langle \mathcal{H} \rangle^2 = \frac{1}{Z}\sum_\mu \mathcal{H}^2 \mathrm{e}^{-\beta\mathcal{H}} - \frac{1}{Z^2}\left(\sum_\mu \mathcal{H}\mathrm{e}^{-\beta\mathcal{H}}\right)^2 = \frac{\partial^2 \ln Z}{\partial\beta^2} = -\frac{\partial\langle\mathcal{H}\rangle}{\partial\beta}$$

$$Z(T,\mathbf{x}) = \sum_{\{s\}} \mathrm{e}^{-\beta\mathcal{H}(s)} \qquad \langle\mathcal{H}\rangle = -\frac{\partial \ln Z}{\partial\beta}$$

$$-\frac{\partial Z}{\partial\beta} = \sum_\mu \mathcal{H}\mathrm{e}^{-\beta\mathcal{H}}, \quad and \quad \frac{\partial^2 Z}{\partial\beta^2} = \sum_\mu \mathcal{H}^2\mathrm{e}^{-\beta\mathcal{H}}$$

$$\left\langle \mathcal{H}^2 \right\rangle_c = -\frac{\partial\langle\mathcal{H}\rangle}{\partial\left(1/k_BT\right)} = k_BT^2 \left.\frac{\partial\langle\mathcal{H}\rangle}{\partial T}\right|_{\mathbf{x}}, \qquad \Rightarrow \quad \left\langle \mathcal{H}^2 \right\rangle_c = k_BT^2C_{\mathbf{x}}$$

- ➢ Energy fluctuation corresponds to heat capacity (one kind of "susceptibility"): this is the result of a general "fluctuation-dissipation" theorem. Others, like the particle number fluctuation corresponds to compressibility.
- ➢ Fluctuations (*E* or *N*) are very important for phase transitions. Near phase transitions, either the compressibility or heat capacity diverge, due to severe fluctuations.

The grand canonical Ensemble: Team-Discussion

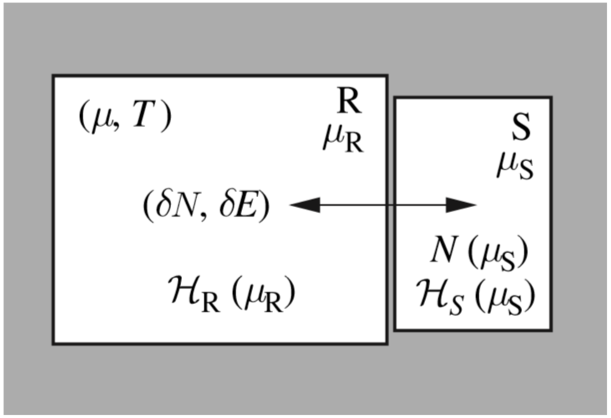
☐ Grand partition function

- ✓ Allow chemical work (by fixing the chemical potential μ, rather than at a fixed number of particles), but no mechanical work. The resulting macrostates $M \equiv (T, \mu, x)$ are described by the grand canonical ensemble.

Q: Can you guess the possibility and grand partition function?

For canonical ensemble:

$$p(s) = \frac{\exp[-\beta\mathcal{H}(s)]}{Z(T,x)} \qquad Z(T,x) = \sum_s \exp[-\beta\mathcal{H}(s)] \, .$$



- ✓ As in the case of canonical ensemble, the system S can be maintained at a constant chemical potential through contact with a reservoir R, at temperature T and chemical potential μ.

grand partition function

$$p(s) = \exp\left[\beta\mu N(s) - \beta\mathcal{H}(s)\right] / \mathcal{Q} \qquad \mathcal{Q}(T, \mu, \mathbf{x}) = \sum_s e^{\beta\mu N(s) - \beta\mathcal{H}(s)}$$

Grouping together all microstates with a given number of particles

$$\mathcal{Q}(T, \mu, \mathbf{x}) = \sum_{N=0}^{\infty} e^{\beta\mu N} \sum_{(s\,N} \text{[redacted]} \, e^{-\beta\mathcal{H}_N(s)}$$

The grand canonical Ensemble

- ☐ **Grand potential**

  - ✓ Because of the sharpness of the distribution for N, the sum in grand partition function can be approximated by its largest term at $N = N^* \approx \langle N \rangle$, that is,

$$\mathcal{Q}(T,\mu,\mathbf{x}) = \lim_{N\to\infty} \sum_{N=0}^{\infty} \mathrm{e}^{\beta\mu N} Z(T,N,\mathbf{x}) = \mathrm{e}^{\beta\mu N^*} Z\left(T,N^*,\mathbf{x}\right) = \mathrm{e}^{\beta\mu N^* - \beta F}$$

$$= \mathrm{e}^{-\beta\left(-\mu N^* + E - TS\right)} = \mathrm{e}^{-\beta\mathcal{G}}$$

$$\mathcal{G}(T,\mu,\mathbf{x}) = E - TS - \mu N = -k_B T \ln \mathcal{Q}$$

grand potential

  - ✓ Thermodynamic information is obtained by using

$$-S = \left.\frac{\partial\mathcal{G}}{\partial T}\right|_{\mu,\mathbf{x}}, \qquad N = -\left.\frac{\partial\mathcal{G}}{\partial \mu}\right|_{T,\mathbf{x}}, \qquad J_i = \left.\frac{\partial\mathcal{G}}{\partial x_i}\right|_{T,\mu} \qquad P = -\left.\frac{\partial\mathcal{G}}{\partial V}\right|_{\mu,T}$$

$$\mathrm{d}\mathcal{G} = -S\,\mathrm{d}T - N\,\mathrm{d}\mu + \mathbf{J}\cdot\mathrm{d}\mathbf{x}$$

The grand canonical Ensemble: Team-Discussion

- ❑ **Example: ideal gas**
  - ✓ The macrostate is $M \equiv (T, \mu, x)$, and the microstates $\{\vec{p}_1,\ \vec{q}_1,\ \vec{p}_2,\ \vec{q}_2,\ \ldots\}$ have indefinite particle number (*N* not fixed).
  - ✓ Can you derive the grand partition function of ideal gas system?

$$\mathcal{Q}(T, \mu, \mathbf{x}) = \sum_{\mu_S} \mathrm{e}^{\beta\mu N(\mu_S) - \beta\mathcal{H}(\mu_S)}$$

$$Z(T, V, N) = \int \frac{d^{3N}p\,d^{3N}q}{N!\,h^{3N}} \exp[-\beta\mathcal{H}(p, q)]$$

The grand canonical Ensemble

❑ **Example: ideal gas**

✓ The macrostate is $M \equiv (T, \mu, x)$, and the microstates $\{\vec{p}_1, \vec{q}_1, \vec{p}_2, \vec{q}_2, \ldots\}$ have indefinite particle number (N not fixed). The grand partition function is given by

$$\mathcal{Q}(T,\mu,V) = \sum_{N=0}^{\infty} \mathrm{e}^{\beta\mu N} \frac{1}{N!}\int\left(\prod_{i=1}^{N}\frac{\mathrm{d}^3\vec{q}_i\,\mathrm{d}^3\vec{p}_i}{h^3}\right)\exp\left[-\beta\sum_i \frac{p_i^2}{2m}\right] = \sum_{N=0}^{\infty}\frac{\mathrm{e}^{\beta\mu N}}{N!}\left(\frac{V}{\lambda^3}\right)^N = \exp\left[\mathrm{e}^{\beta\mu}\frac{V}{\lambda^3}\right]$$

Gaussian functions $\int_0^{\infty} x^2 e^{-\alpha x^2}dx = \frac{\sqrt{\pi}}{4\alpha^{3/2}}$ $\quad e^x = \sum_{n=0}^{\infty}\frac{x^n}{n!} = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \frac{x^4}{4!} + \cdots$ $\quad \lambda = \frac{h}{\sqrt{2\pi m k_B T}}$

✓ The grand potential is $\mathcal{G}(T,\mu,V) = -k_B T \ln \mathcal{Q} = -k_B T \mathrm{e}^{\beta\mu}\frac{V}{\lambda^3}$

✓ The gas pressure can be obtained directly as $P = -\left.\frac{\partial \mathcal{G}}{\partial V}\right|_{\mu,T} = k_B T\frac{\mathrm{e}^{\beta\mu}}{\lambda^3}$

✓ The particle number and chemical potential are related: $N = -\left.\frac{\partial \mathcal{G}}{\partial \mu}\right|_{T,V} = \frac{\mathrm{e}^{\beta\mu}V}{\lambda^3}$

✓ By comparing P and N, we get $P = k_B T N/V$. The chemical potential is given by

$$\mu = k_B T\ln\left(\lambda^3\frac{N}{V}\right) = k_B T\ln\left(\lambda^3 n\right) = k_B T\ln\left(\frac{P\lambda^3}{k_B T}\right)$$

The grand canonical Ensemble

❑ **Fluctuation of number of particles**

$$p(s) = \exp\left[\beta\mu N(s) - \beta\mathcal{H}(s)\right]/\mathcal{Q} \qquad \mathcal{Q}(T,\mu,\mathbf{x}) = \sum_{N=0}^{\infty} e^{\beta\mu N} \sum_{(s\,N} \text{[redacted]}\, e^{-\beta\mathcal{H}_N(s)}$$

✓ The particle number (by average) in the system

$$\langle N\rangle = \left\langle N * p(s)\right\rangle = \langle N * \exp[\mu\beta N - \beta H]/\mathcal{Q}\rangle = \frac{1}{\mathcal{Q}}\frac{\partial}{\partial(\beta\mu)}\mathcal{Q} = \frac{\partial}{\partial(\beta\mu)}\ln\mathcal{Q} = N$$

✓ The number fluctuations are related to the variance

$$\left\langle N^2\right\rangle_C = \left\langle N^2\right\rangle - \langle N\rangle^2 = \frac{1}{\mathcal{Q}}\frac{\partial^2}{\partial(\beta\mu)^2}\ln\mathcal{Q} - \left(\frac{\partial}{\partial(\beta\mu)}\ln\mathcal{Q}\right)^2 = \frac{\partial^2}{\partial(\beta\mu)^2}\ln\mathcal{Q} = \frac{\partial\langle N\rangle}{\partial(\beta\mu)}$$

Compare with the energy fluctuations in canonical ensemble

$$\left\langle \mathcal{H}^2\right\rangle_c = \left\langle \mathcal{H}^2\right\rangle - \langle\mathcal{H}\rangle^2 = \frac{1}{Z}\sum_{\mu}\mathcal{H}^2 e^{-\beta\mathcal{H}} - \frac{1}{Z^2}\left(\sum_{\mu}\mathcal{H}e^{-\beta\mathcal{H}}\right)^2 = \frac{\partial^2\ln Z}{\partial\beta^2} = -\frac{\partial\langle\mathcal{H}\rangle}{\partial\beta}$$

Gibbs canonical Ensemble

- ☐ **Gibbs partition function:** involving work done by/on the system
  - ✓ We can also define a generalized canonical ensemble in which the internal energy changes by the addition of both heat and work. T fixed, the macrostates $M \equiv (T, \boldsymbol{J})$ are specified in terms of the external temperature and generalized forces acting on the system; the thermodynamic coordinates $\boldsymbol{x}$ appear as additional random variables. (position for mechanical force $\boldsymbol{F}$.)
  - ✓ The system is maintained at constant force through external elements (e.g., pistons or magnets). Including the work done against the forces, the energy of the combined system that includes these elements is $\mathcal{H}-\boldsymbol{J}\cdot\boldsymbol{x}$. (Note that while the work done on the system is $+\boldsymbol{J}\cdot\boldsymbol{x}$).
  - ✓ The microstates of this combined system occur with the (canonical) probabilities

$$p(s,\mathbf{x}) = \exp\left[-\beta\mathcal{H}(s) + \beta\mathbf{J}\cdot\mathbf{x}\right] / \mathcal{Z}(T,N,\mathbf{J})$$

  - ✓ Gibbs partition function $$\mathcal{Z}(N,T,\mathbf{J}) = \sum_{s,\mathbf{x}} \mathrm{e}^{\beta\mathbf{J}\cdot\mathbf{x}-\beta\mathcal{H}(s)}$$

Gibbs canonical Ensemble

- ☐ **Grand potential: Gibbs free energy**

$$\mathcal{Z}(N,T,\mathbf{J}) = \sum_{s,\mathbf{x}} \mathrm{e}^{\beta \mathbf{J}\cdot\mathbf{x} - \beta\mathcal{H}(s)}$$

We defined and calculated the Grand potential

$$\mathcal{G}(T,\mu,\mathbf{x}) = E - TS - \mu N = -k_B T \ln \mathcal{Q}$$

- ✓ We define Gibbs free energy, similar to the grand potential

$$G(N,T,\mathbf{J}) = -k_B T \ln \mathcal{Z}, \quad G = E - TS - \mathbf{x}\cdot\mathbf{J}$$

- ✓ In grand canonical ensemble we calculated the average number of particle. Here we can consider the expectation value of the coordinates

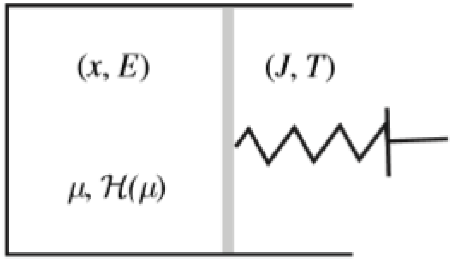
$$\langle N \rangle = \frac{\partial}{\partial(\beta\mu)} \ln \mathcal{Q} \qquad \langle \mathbf{x} \rangle = \frac{\partial \ln \mathcal{Z}}{\partial \beta \mathbf{J}} = k_B T \frac{\partial \ln \mathcal{Z}}{\partial \mathbf{J}}$$

- ✓ We can also define the enthalpy $H \equiv E - \mathbf{x}\cdot\mathbf{J}$

$$H = \langle \mathcal{H} - \mathbf{x}\cdot\mathbf{J} \rangle = -\frac{\partial \ln \mathcal{Z}}{\partial \beta}$$

Gibbs canonical Ensemble: Team-Discussion

- ☐ **Example: ideal gas**
  - ✓ We have established the theoretical framework of Gibbs canonical ensemble, now let's try some examples. The simplest example is ideal gas.



A system in contact with a reservoir at temperature T , and maintained at a fixed force J.

Q: Isothermal? Isobaric? Adiabatic? Free expansion?

- ✓ The ideal gas in the isobaric ensemble is described by the macrostate $M \equiv (N, T, P)$. A microstate $\mu \equiv \{\overrightarrow{p_i}, \overrightarrow{q_i}\}$ with a volume V.

Q: The partition function?

$$\mathcal{Z}(N,T,\mathbf{J}) = \sum_{s,\mathbf{x}} \mathrm{e}^{\beta \mathbf{J}\cdot\mathbf{x} - \beta\mathcal{H}(s)}$$

$$\mathbf{J} \cdot \mathbf{x} = -PV$$

$$\mathcal{Z}(N,T,P) = \sum_{s,V} \mathrm{e}^{-\beta PV - \beta\mathcal{H}(s)}$$

Gibbs canonical Ensemble

- **Example: ideal gas**

$$\lambda = \frac{h}{\sqrt{2\pi m k_B T}}$$

$$\mathcal{Z}(N,T,P) = \int_0^\infty \mathrm{d}V \mathrm{e}^{-\beta PV} \int \frac{1}{N!} \prod_{i=1}^{N} \frac{\mathrm{d}^3\vec{q}_i\, \mathrm{d}^3\vec{p}_i}{h^3} \exp\left[-\beta \sum_{i=1}^{N} \frac{p_i^2}{2m}\right]$$

$$\int_0^\infty x^2 e^{-\alpha x^2} dx = \frac{\sqrt{\pi}}{4\alpha^{3/2}}$$

$$= \int_0^\infty \mathrm{d}V V^N \mathrm{e}^{-\beta PV} \frac{1}{N!\lambda^{3N}} \quad = \frac{1}{(\beta P)^{N+1}\lambda^{3N}}$$

$$\int_0^\infty \frac{x^n}{\exp(x)} dx = n!$$

✓ Now we have the partition function, let's consider the Gibbs free energy

$$G = -k_B T \ln \mathcal{Z} \approx N k_B T \left[\ln P - \frac{5}{2} \ln(k_B T) + \frac{3}{2} \ln\left(\frac{h^2}{2\pi m}\right) \right]$$

Starting from $\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}P + \mu \mathrm{d}N,$ the volume of the gas is obtained as

$$V = \left.\frac{\partial G}{\partial P}\right|_{T,N} = \frac{N k_B T}{P}, \qquad \Rightarrow \quad PV = N k_B T$$

The *enthalpy* $H = \langle E + PV \rangle$ is easily calculated from

$$H = -\frac{\partial \ln \mathcal{Z}}{\partial \beta} = \frac{5}{2} N k_B T \qquad \text{we get } C_P = \mathrm{d}H / \mathrm{d}T = 5/2 N k_B$$

$\mathrm{d}H = \mathrm{d}Q + V\mathrm{d}p + \mu \mathrm{d}N,$ $\quad$ $\mathrm{d}E = \mathrm{d}Q - p\mathrm{d}V + \mu \mathrm{d}N$ $\quad$ $C_P = \mathrm{d}H / dT$ $\quad$ $C_V = dE / dT$