Gibbs canonical Ensemble: Team-Discussion

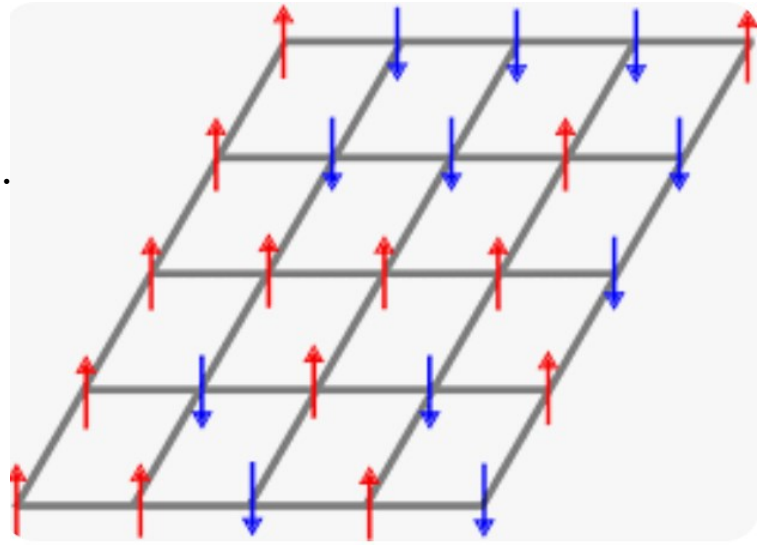
- **Example: spins in magnetic field – classical paramagnetic**

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

Consider a solid lattice which has N magnetic dipoles with two allowed directions - either ↑ or ↓. Under an external magnetic field B that is parallel with the ↑ direction, with the energy

$$\epsilon_\uparrow = -\mu_0 B, \qquad \epsilon_\downarrow = \mu_0 B,$$

where the μ_0 is the magnetic moment per dipole.



Q1: What is the partition function?

Ignore the interactions between magnetic dipoles.

$$\mathbf{J}\cdot\mathbf{x} = \vec{B}\cdot\vec{M}$$

$$\mathcal{Z}(N,T,B) = \sum_{\{\mu\}} \exp(-\beta\mathcal{H} + \beta\vec{B}\cdot\vec{M})]$$

Gibbs canonical Ensemble

- **Example: spins in magnetic field – classical paramagnetic**

Gibbs partition function: $\mathcal{Z}(N,T,B)=\sum_{\{\mu\}}\exp(-\beta\mathcal{H}+\beta\vec{B}\cdot\vec{M})]$

- ✓ Since it is solid, and there are no interactions between spins, thus $\mathcal{H}=0$.
- ✓ The magnetization is given by $\boldsymbol{M}=\mu_0\sum_{i=1}^{N}\boldsymbol{\sigma_i}$, where μ_0 is a microscopic magnetic moment, and $\boldsymbol{\sigma_i}$ is either +1 or -1.

$$\mathcal{Z}(N,T,B)=\sum_{\{\sigma\}}\exp(\beta\vec{B}\cdot\mu_0\sum_{i=1}^{N}\sigma_i)]$$
$$=[e^{\beta\mu_0 B}+e^{-\beta\mu_0 B}]^N=\left[2\cosh\left(\beta\mu_0 B\right)\right]^N$$

$$\sinh x=\frac{e^x-e^{-x}}{2},\qquad \cosh x=\frac{e^x+e^{-x}}{2},$$
$$\tanh x=\frac{\sinh x}{\cosh x}=\frac{e^x-e^{-x}}{e^x+e^{-x}}$$
$$\operatorname{sech} x=\frac{2}{e^x+e^{-x}}\approx 1-\frac{x^2}{2}$$

- ✓ We can calculate the Gibbs free energy.

$$G=-k_BT\ln\mathcal{Z}=-Nk_BT\ln\left[2\cosh\left(\beta\mu_0 B\right)\right]$$

- ✓ The average magnetization is given by

$$M=-\frac{\partial G}{\partial B}=N\mu_0\tanh\left(\beta\mu_0 B\right)$$
$$\chi=\frac{\partial M}{\partial B}=\frac{N\mu_0^2}{k_BT}\operatorname{sech}^2\left(\beta\mu_0 B\right)\approx\frac{N\mu_0^2}{k_BT}$$

Single particle partition function

❑ Single particle partition function

$$\mathcal{Z}(N,T,B)=\left[2\cosh\left(\beta\mu_0 B\right)\right]^N \qquad Z(T,N)=\left(1+\mathrm{e}^{-\beta\epsilon}\right)^N \qquad Z(T,V,N)=\frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N$$

✓ If particles are distinguishable, so each particle has the same set of single particle energy levels. We can write the partition function as (no interactions)

$$Z=\zeta^N$$

✓ ζ is called single particle partition function, ε_r denotes the single particle energy

$$\zeta=\sum_r e^{-\beta\varepsilon_r}$$

The sum over r is a sum over single particle states

✓ Then we can get $\ln Z=N\ln\zeta=N\ln\left(\sum_r e^{-\beta\varepsilon_r}\right)$

✓ Example: Single particle partition function for two-level system

$$\zeta=\sum_r e^{-\beta\varepsilon_r}=\sum_{n=0}^{1} e^{-\beta\epsilon n}=1+e^{-\beta\epsilon}$$

✓ Partition function for the N particle system, $Z=\zeta^N=(1+e^{-\beta\epsilon})^N$

Single particle partition function

- **Single particle partition function: identical particle**
  - ✓ For identical particles, we need to add *N*! permutations.

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

  - ✓ Let's exam the ideal gas using single particle partition function

$$\zeta = \int \frac{d^3 p d^3 q}{h^3} \exp[-\beta \frac{p^2}{2m}] = \frac{V}{\lambda^3}$$

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

$$Z = \frac{\zeta^N}{N!} = \frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N$$

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

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

Qualifying exam problem

Consider a system of N_0 non-interacting quantum mechanical oscillators in thermal equilibrium with a heat bath at temperature T. The energy levels of a single oscillator are $\epsilon_m = (m + 1/2)\gamma/V$ with $m = 0, 1, 2$ ... etc. (γ is a constant, the oscillators and volume V are one dimensional.)

(a) Find internal energy E and heat capacity C_v, as functions of T.

Solutions:

(a) The partition function is $Z = Z_1^{N_0}$, where z_1 is the single particle partition function,

$$z_1 = \sum_{m=0}^{\infty} e^{-\beta(m+\frac{1}{2})\gamma V^{-1}} = \frac{1}{2} csch \frac{\gamma\beta}{2V} \qquad \frac{d}{dx}\operatorname{csch} x = -\coth x \operatorname{csch} x$$

The internal energy is

$$E = -N_0 \frac{\partial}{\partial\beta} lnz_1 = \frac{N_0\gamma}{2V} coth \frac{\gamma\beta}{2V} = \frac{N_0\gamma}{2V} coth \frac{\gamma}{2VkT}$$

The heat capacity $C_v = \left(\frac{\partial E}{\partial T}\right)_v = N_0 k \left(\frac{\gamma}{2VkT}\right)^2 csch^2(\frac{\gamma}{2VkT})$ $\qquad \frac{d}{dx}\coth x = -\operatorname{csch}^2 x$

Interacting gas: Team Discussion

❑ Phase transition

✓ Let's examine the density fluctuations in a grand canonical ensemble. (Two phases can exchange particles.)

$$\begin{cases} \left\langle N^2 \right\rangle_c = \dfrac{\partial^2 (\ln \mathcal{Q})}{\partial(\beta\mu)^2} = \dfrac{\partial \langle N \rangle}{\partial(\beta\mu)}, & (1) \\ \langle N \rangle = N = \dfrac{\partial(\ln \mathcal{Q})}{\partial(\beta\mu)}, & (2) \end{cases}$$

$$\ln \mathcal{Q} = -\beta \mathcal{G} = \beta P V$$

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

$$E = TS - PV + \mu N$$

✓ Dividing the two equations (1) and (2), and using the chain rule,

$$\frac{\left\langle N^2 \right\rangle_c}{N} = \frac{\partial \langle N \rangle}{\partial(\ln \mathcal{Q})} = \frac{\partial \langle N \rangle}{\partial(\beta P V)} = \frac{k_B T}{V} \left. \frac{\partial N}{\partial P} \right|_{T,V}$$

$$= -\frac{k_B T}{V} \left. \frac{\partial N}{\partial V} \right|_{P,T} \left. \frac{\partial V}{\partial P} \right|_{N,T} = n k_B T \kappa_T$$

For ideal gas? $\kappa_T = \dfrac{1}{P} > 0$

$$\frac{\left\langle N^2 \right\rangle_c}{N} = \frac{N k_B T}{V P} = 1$$

Does not change with T or P

How about interacting gas?

Interacting gas

❑ **Phase transition**

$$P = \frac{Nk_BT}{V-b} - \frac{a}{V^2} \qquad \kappa_T = -\frac{1}{V}\frac{\partial V}{\partial P}\bigg|_T \qquad \frac{\langle N^2 \rangle_c}{N} = nk_BT\kappa_T$$

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{Nk_BT}{(V-b)^2} + \frac{2a}{V^3}$$

$$\kappa_T = -\frac{1}{V}\frac{1}{-\dfrac{Nk_BT}{(V-b)^2} + \dfrac{2a}{V^3}} = \frac{(V-b)^2/V}{Nk_BT - 2a(V-b)/V^3}$$

- ✓ The mechanical stability of a gas requires the positivity of the isothermal compressibility.
- ✓ But κ_T can diverge at T_c and become negative at lower temperatures: an instability toward density fluctuations, phase instability and transition.

Fluctuations in particle number corresponds to compressibility is the result of a general "fluctuation-dissipation" theorem: fluctuation is related to one susceptibility.

Team Discussion: Phase diagram

❑ **Phase transition**

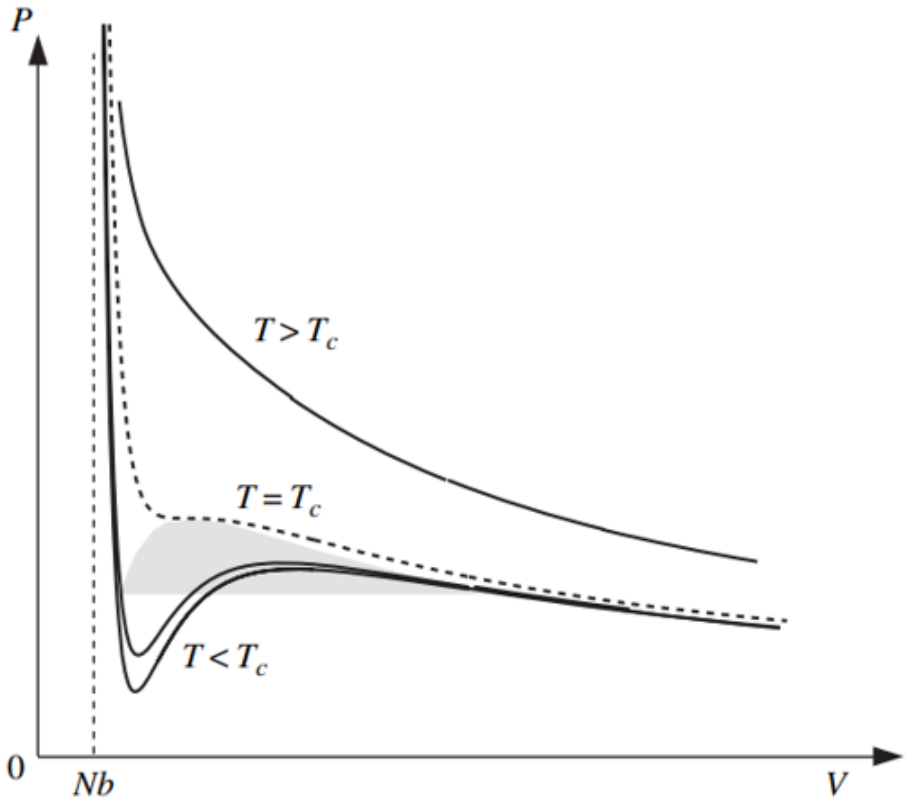
✓ How does P-V look like when T is very large, T close to T_c, and T well below T_c?

$$P = \frac{Nk_BT}{V-b} - \frac{a}{V^2}$$

$$\frac{\langle N^2 \rangle_c}{N} = nk_BT\kappa_T$$

$$\kappa_T = \frac{(V-b)^2 / V}{Nk_BT - 2a(V-b)/V^3}$$

$$\kappa_T = -\frac{1}{V}\frac{\partial V}{\partial P}\bigg|_T$$



Interacting gas

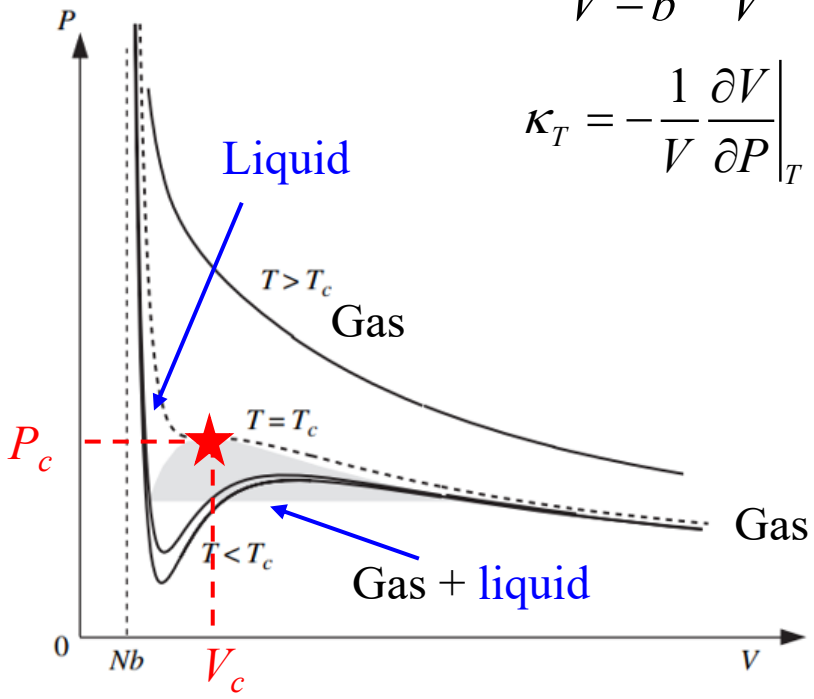
$$P = \frac{Nk_BT}{V-b} - \frac{a}{V^2}$$

$$\kappa_T = -\frac{1}{V}\frac{\partial V}{\partial P}\bigg|_T$$

❑ Critical point

At low temperatures, the $P(V)$ equation exhibit a maximum and a minimum at two points. At a particular temperature, the maximum and minimum merge into a single point.

This point is called the *critical point* (T_c, V_c, P_c). Q: How to determine (T_c, V_c, P_c)?



Using $\frac{\partial P}{\partial V} = 0$, and $\frac{\partial^2 P}{\partial V^2} = 0$, we get $-\frac{RT}{(V-b)^2} + \frac{2a}{V^3} = 0$ and $\frac{2RT}{(V-b)^3} - \frac{6a}{V^4} = 0$.

Eliminate RT/a from these two equations, we find the critical volume $V_c = 3b$.

Substitute this into the above two equations, we obtain the critical $T_c = \frac{8a}{27Rb}$.

Substitute the V_c and T_c to the Van der Waals equation,

we obtained the critical pressure: $P_c = \frac{a}{27b^2}$, so $\frac{P_cV_c}{RT_c} = \frac{3}{8}$

Interacting gas

❑ Partition function

✓ The Hamiltonian of interaction gas? (Can you try?)

$$H(q,p)=\sum_{i=1}^{N}\frac{p_i^2}{2m}+\sum_{i<j}\mathcal{V}\left(\vec{q}_i-\vec{q}_j\right)$$

✓ The partition function of interaction gas:

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

✓ The kinetic energy part can be calculated:

$$Z(T,N,V)=\frac{1}{N!}\frac{1}{\lambda^{3N}}\int\prod_{i=1}^{N}\mathrm{d}^3\vec{q}_i\exp\left[-\beta\sum_{i<j}\mathcal{V}\left(\vec{q}_i-\vec{q}_j\right)\right]$$

✓ The coordinate part is not easy to calculate…

Interacting gas: Team Discussion

❑ **Approximation: Mean-field theory**

$$Z(T,N,V)=\frac{1}{N!}\frac{1}{\lambda^{3N}}\int\prod_{i=1}^{N}\mathrm{d}^3\vec{q}_i\,\exp\left[-\beta\sum_{i<j}\mathcal{V}\left(\vec{q}_i-\vec{q}_j\right)\right]$$

✓ We can consider the "hard-core gas" at low densities (weak interactions).

✓ Like before, we treat the contributions of the **hard core** and **attractive portions** of the potential separately.

✓ "Hard core" will induce excluded volume effect. Can you guess it?

$$Z(T,N,V)=\frac{1}{N!}\frac{1}{\lambda^{3N}}V^N \quad\rightarrow Z(T,N,V)=\frac{1}{N!}\frac{1}{\lambda^{3N}}\{f(V)\}\ \{\text{attractive potential}\}$$

$$\rightarrow Z(T,N,V)=\frac{1}{N!}\frac{1}{\lambda^{3N}}\underbrace{V(V-\Omega)\cdots(V-(N-1)\Omega)}_{\text{Excluded volume effects}}\{\text{attractive potential}\}$$

✓ Next, we use the **mean-field $\bar{U}$** to represent an **average attraction energy**,

$$\sum_{i<j}\mathcal{V}\left(\vec{q}_i-\vec{q}_j\right)\rightarrow\bar{U} \qquad \exp\left[-\beta\sum_{i<j}\mathcal{V}\left(\vec{q}_i-\vec{q}_j\right)\right]\rightarrow\exp\left[-\beta\bar{U}\right]$$

Interacting gas

- **Mean-field theory**

$$Z(T,N,V) \approx \frac{1}{N!}\frac{1}{\lambda^{3N}} \underbrace{V(V-\Omega)\cdots(V-(N-1)\Omega)}_{\text{Excluded volume effects}} \exp(-\beta\bar{U}) \qquad \bar{U} = \sum_{i<j} \mathcal{V}\left(\vec{q}_i - \vec{q}_j\right)$$

- ✓ Replace $\sum_{i<j}$ by $(1/2)\sum_{i,j}$, $\bar{U} = \frac{1}{2}\sum_{i,j} \mathcal{V}_{\text{attr.}}\left(\vec{q}_i - \vec{q}_j\right)$

- ✓ Instead of counting each particle, we consider the attractive potential between **local clusters** with **local density**:

$$\bar{U} = \frac{1}{2}\sum_{i,j} \mathcal{V}_{\text{attr.}}\left(\vec{q}_i - \vec{q}_j\right) = \frac{1}{2}\int \mathrm{d}^3\vec{r}_1\, \mathrm{d}^3\vec{r}_2 n\left(\vec{r}_1\right) n\left(\vec{r}_2\right) \mathcal{V}_{\text{attr.}}\left(\vec{r}_1 - \vec{r}_2\right)$$

Particle number at $\vec{r}_1$ is $\Delta N(\vec{r}_1) = \mathrm{d}^3\vec{r}_1 n\left(\vec{r}_1\right)$

- ✓ **Key approximation**: replacing the local density $n(\vec{r})$ with the uniform density n.

$$\bar{U} = \frac{n^2}{2}\int \mathrm{d}^3\vec{r}_1\, \mathrm{d}^3\vec{r}_2 \mathcal{V}_{\text{attr.}}\left(\vec{r}_1 - \vec{r}_2\right) \approx \frac{n^2}{2} V \int \mathrm{d}^3\vec{r}\, \mathcal{V}_{\text{attr.}}(\vec{r})$$

$$d^3\vec{r}_1\, \mathrm{d}^3\vec{r}_2 \left\{\mathcal{V}_{\text{attr.}}\left(\vec{r}_1 - \vec{r}_2\right)\right\} = d^3(\vec{r} + \vec{r}_2)\left\{\mathcal{V}_{\text{attr.}}\left(\vec{r}\right)\right\} \mathrm{d}^3\vec{r}_2$$

Interacting gas

❑ Mean-field theory

✓ Use the uniform density $n = N/V$ and parameter u describes the net effect of the attractive interactions.

$$\bar{U} \approx \frac{n^2}{2} V \int \mathrm{d}^3\vec{r}\, \mathcal{V}_{\text{attr.}}(\vec{r}) \equiv -\frac{N^2}{2V} u$$

$$Z(T,N,V) \approx \frac{1}{N!}\frac{1}{\lambda^{3N}} \underbrace{V(V-\Omega)\cdots(V-(N-1)\Omega)}_{\text{Excluded volume effects}} \exp(-\beta\bar{U})$$

$$\approx \frac{1}{N!}\frac{1}{\lambda^{3N}} \underbrace{V(V-\Omega)\cdots(V-(N-1)\Omega)}_{\text{Excluded volume effects}} \exp\left[\frac{\beta u N^2}{2V}\right]$$

✓ **Approximation:** At low densities, the overall effect is a reduction of the volume available to each particle by approximately $N\Omega/2$.

$$Z(T,N,V) \approx \frac{(V - N\Omega/2)^N}{N!\lambda^{3N}} \exp\left[\frac{\beta u N^2}{2V}\right]$$

Interacting gas

- **Mean-field theory**

$$Z(T,N,V) \approx \frac{(V - N\Omega/2)^N}{N!\lambda^{3N}} \exp\left[\frac{\beta u N^2}{2V}\right]$$

✓ The free energy,

$$F = -k_B T \ln Z = -Nk_B T \ln(V - N\Omega/2) + Nk_B T \ln(N/\mathrm{e}) + 3Nk_B T \ln\lambda - \frac{uN^2}{2V}$$

✓ We obtain the expression for the pressure

$$P = -\left.\frac{\partial F}{\partial V}\right|_{T,N} = \frac{Nk_B T}{V - N\Omega/2} - \frac{uN^2}{2V^2} \qquad P = \frac{Nk_B T}{V - b} - \frac{a}{V^2}$$

✓ Remarkably, the uniform density approximation reproduces the **van der Waals equation of state**.

Interacting gas

❑ Virial expansion

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

- ✓ Another way to derive the equation of state for interaction gas: *virial expansion*
- ✓ We can write the corrections to the ideal gas equation of state as a series of powers of the **density** ***N/V***: *virial expansion*.

$$\beta P=\frac{N}{V}\rightarrow\qquad\beta P=\frac{N}{V}\left[1+B_2(T)\frac{N}{V}+B_3(T)\left(\frac{N}{V}\right)^2+\cdots\right].$$

The temperature-dependent parameters, $B_i(T)$, are known as the *virial coefficients* and originate from the interparticle interactions.

Usually *the second virial coefficients* is the most important one.

$$B_2=-\frac{1}{2}\int\mathrm{d}^3\vec{q}\left(\mathrm{e}^{-\beta\mathcal{V}(\vec{q})}-1\right)$$

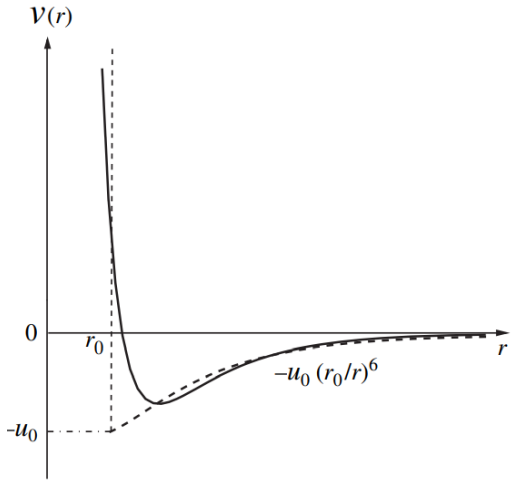
Interacting gas

❑ Virial expansion

$$B_2 = -\frac{1}{2}\int \mathrm{d}^3\vec{q}\left(\mathrm{e}^{-\beta\mathcal{V}(\vec{q})} - 1\right)$$

The interaction potential can be characterized by a hard-core repulsion at short distances and a van der Waals attraction at large distances.

$$\mathcal{V}(r) = \begin{cases} +\infty & \text{for } r < r_0 \\ -u_0\left(r_0 / r\right)^6 & \text{for } r > r_0 \end{cases},$$



$$B_2 = -\frac{1}{2}\left\{\int_0^{r_0} 4\pi r^2\,\mathrm{d}r(-1) + \int_{r_0}^{\infty} 4\pi r^2\,\mathrm{d}r\left[\mathrm{e}^{+\beta u_0 (r_0/r)^6} - 1\right]\right\}$$

The second integrand can be approximated by $\beta u_0 (r_0/r)^6$ in the high T limit, $1 >> \beta u_0$

$$B_2 = -\frac{1}{2}\left[-\frac{4\pi r_0^3}{3} + 4\pi\beta u_0 r_0^6\left(-\frac{r^{-3}}{3}\right)\Bigg|_{r_0}^{\infty}\right] = \frac{2\pi r_0^3}{3}\left(1-\beta u_0\right) = \frac{\Omega}{2}\left(1-\frac{u_0}{k_B T}\right)$$

We can define an *excluded volume* of $\Omega = 4\pi r_0^3/3$, which is 8 times the atomic volume (the distance of minimum approach r_0 is twice an atomic radius).

Interacting gas

❑ Second virial coefficients

$$B_2 = \frac{\Omega}{2}\left(1 - \frac{u_0}{k_B T}\right) \qquad \beta P = \frac{N}{V}\left[1 + B_2(T)\frac{N}{V} + B_3(T)\left(\frac{N}{V}\right)^2 + \cdots\right].$$

$$\frac{P}{k_B T} = n + \frac{\Omega}{2}\left(1 - \frac{u_0}{k_B T}\right)n^2 + \cdots$$

$$\frac{1}{k_B T}\left(P + \frac{u_0\Omega}{2}n^2\right) = n\left(1 + n\frac{\Omega}{2} + \cdots\right) \approx n\frac{1}{1 - n\Omega/2} = \frac{N}{V - N\Omega/2}$$

$$\left[P + \frac{u_0\Omega}{2}\left(\frac{N}{V}\right)^2\right]\left[V - \frac{N\Omega}{2}\right] = Nk_B T \qquad P = \frac{Nk_B T}{V - b} - \frac{a}{V^2}$$

Mean field and from partition function:

$$P = -\left.\frac{\partial F}{\partial V}\right|_{T,N} = \frac{Nk_B T}{V - N\Omega/2} - \frac{uN^2}{2V^2}$$

Quantum statistics

Heat capacity, phonons, and photons

Quantum statistics

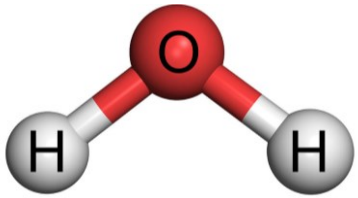
Quantum effects we would have in a physical system:

- **Quantized energy levels:**
  - ✓ Such as the two-level system: we have considered the quantized energy levels in classical statistics.
  - ✓ Many physical systems do exhibit quantized energy levels: molecule, phonons of solid, photons and spins in magnetic field.
- **Identical particles:** all particles are same; we can not distinguish them.
  - ✓ This effect has been considered by introducing $N!$. (Otherwise, entropy is non-additive.)
  - ✓ The identical-particle effect affect the **occupation number**, giving rise to many interesting quantum effects, such as the Bose-Einstein condensation and Fermi-Dirac statistics.

Quantum statistics

- We have calculated the ideal gas several times using different ensembles, such as the microcanonical, canonical, grand canonical and Gibbs canonical. In all these calculations, we supposed that the gas is consisted of *monoatomic elements*, for example, Helium, Argon *et al*.

- But most of the gas in nature is consisted of polyatomic elements, for example, air is consisted of O_2, N_2, CO_2 and H_2O vapor. Monoatomic model is not sufficient.



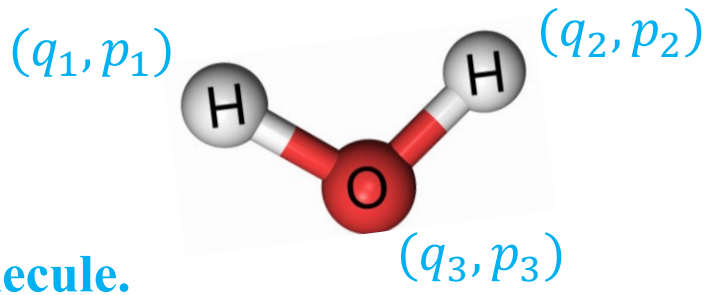
- New model:
  - ✓ Ideal gas: ignore the interactions between polyatomic molecules.
  - ✓ Strong interactions between the atoms inside of each molecule.

- Interactions (in each molecule): like spring, vibrations of harmonic oscillator.
  - ✓ Now let's use statistical method and take account into the effect of quantized energy levels.

Quantum statistics

- Consider a dilute gas of polyatomic molecules, the Hamiltonian for *each* molecule of n atoms is

$$\mathcal{H}_1 = \sum_{i=1}^{n} \frac{\vec{p}_i^{\,2}}{2m} + \mathcal{V}(\vec{q}_1, \ldots, \vec{q}_n),$$



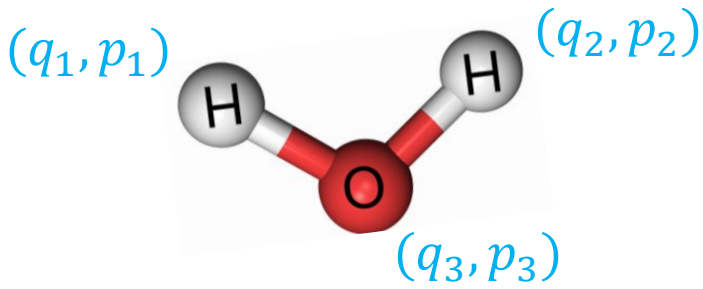
Here we sum over all the atoms inside of one molecule.

- The potential $\mathcal{V}$ describes the interactions between atoms inside of the molecule. For simplicity, we assumed that all atoms in the molecule have the same mass.
- If the masses are different, the Hamiltonian can be still brought into the above form by rescaling the coordinates q_1 by $\sqrt{m_i/m}$ (and the momenta by $\sqrt{m/m_i}$), where m_i is the mass of the ith atom.
- **Ignoring the interactions between different molecules**, the partition function of the ideal gas is (much simpler than that of the interacting gas):

$$Z(N) = \frac{Z_1^N}{N!} = \frac{1}{N!}\left\{\int \prod_{i=1}^{n} \frac{\mathrm{d}^3\vec{p}_i\,\mathrm{d}^3\vec{q}_i}{h^3} \exp\left[-\beta \sum_{i=1}^{n} \frac{\vec{p}_i^{\,2}}{2m} - \beta \mathcal{V}(\vec{q}_1, \ldots, \vec{q}_n)\right]\right\}^N$$

Quantum statistics: Discussion

$$\mathcal{H}_1 = \sum_{i=1}^{n} \frac{\vec{p}_i^{\,2}}{2m} + \mathcal{V}(\vec{q}_1, \ldots, \vec{q}_n),$$



$$Z(N) = \frac{Z_1^N}{N!}$$

$$= \frac{1}{N!}\left\{\int \prod_{i=1}^{n} \frac{\mathrm{d}^3\vec{p}_i\,\mathrm{d}^3\vec{q}_i}{h^3} \exp\left[-\beta \sum_{i=1}^{n} \frac{\vec{p}_i^{\,2}}{2m} - \beta \mathcal{V}(\vec{q}_1, \ldots, \vec{q}_n)\right]\right\}^N$$

- The difference of potential $\mathcal{V}$ from that of the Van der Waals gas?
- What kind of approximation can we use for the potential $\mathcal{V}$?
- The possible solutions to the single molecule Hamiltonian?

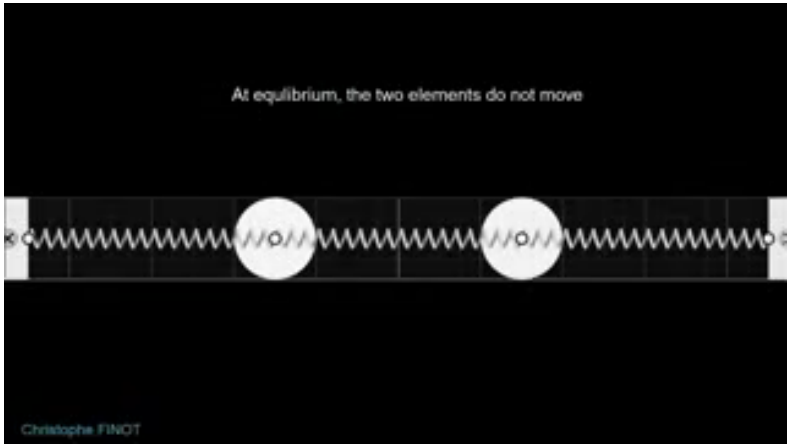
Quantum statistics

- An arbitrary potential $\mathcal{V}$ can be expanded near minimum/equilibrium using Tayler series. Assume $\vec{q}_i^*$ is the equilibrium position and $\vec{u}_i$ is a small deformation:

$$\vec{q}_i = \vec{q}_i^* + \vec{u}_i$$

$$\mathcal{V} = \mathcal{V}^* + \frac{1}{2}\sum_{i,j=1}^{n}\sum_{\alpha,\beta=1}^{3}\frac{\partial^2 \mathcal{V}}{\partial q_{i,\alpha}\partial q_{j,\beta}}u_{i,\alpha}u_{j,\beta} + \mathcal{O}\left(u^3\right).$$

$i, j = 1, \ldots, n$ identify the atoms, and $\alpha, \beta =$ 1,2,3 label a particular component (x, y, z)



- $\mathcal{V}(u) \approx \mathcal{V}^* + (1/2)\kappa u^2$, this potential is parabolic. The solutions are normal modes (review classical mechanics). We can change coordinate variables from the original deformations $\{u_i\}$ to the amplitudes $\{\tilde{u}_s\}$ of the normal modes. In the new coordinate, the deformation Hamiltonian is then (***n* atoms, 3*n* normal modes**)

$$\mathcal{H}_1 = \sum_{i=1}^{n}\frac{\vec{p}_i^{\,2}}{2m} + \mathcal{V}\left(\vec{q}_1, \ldots, \vec{q}_n\right), \quad \Rightarrow \quad \mathcal{H}_1 = \mathcal{V}^* + \sum_{s=1}^{3n}\left[\frac{1}{2m}\tilde{p}_s^2 + \frac{K_s}{2}\tilde{u}_s^2\right]$$

$\{\tilde{p}_s = m\dot{\tilde{u}}_s\}$: Each normal mode has a conjugate momenta
(so, 6*n* degree of freedom)

Quantum statistics

- The average energy of each molecule is the expectation value of the Hamiltonian. Value?

$$\mathcal{H}_1 = \mathcal{V}^* + \sum_{s=1}^{3n}\left[\frac{1}{2m}\tilde{p}_s^2 + \frac{K_s}{2}\tilde{u}_s^2\right]$$

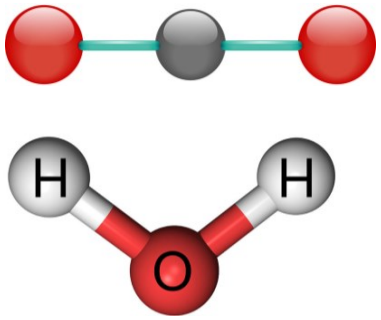
- The Hamiltonian has constant and quadratic terms. Since each quadratic degree of freedom classically contributes a factor of $k_BT/2$ to the energy, expectation value is

$$\langle \mathcal{H}_1 \rangle = \mathcal{V}^* + \frac{3n+m}{2}k_BT$$

conjugate momenta: $3n$

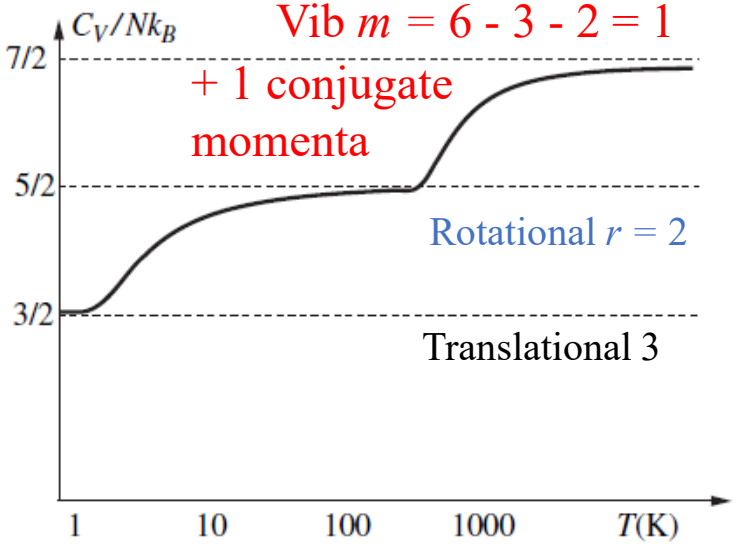
- *m is the* number of the normal modes with non-zero K_s (pure vibrational modes). The value of *m*? Need to remove rotation and zeros.

  - ✓ total normal modes: $3n$
  - ✓ translation modes (zero K_s): 3
  - ✓ rotation modes (zero K_s): r
    $r = 2$ for liner molecule,
    $r = 3$ for non-linear molecule
  - ✓ $m = 3n - 3 - r$.



$$\langle \mathcal{H}_1 \rangle = \frac{6n-3-r}{2}k_BT. \qquad C_V = \frac{6n-3-r}{2}k_B$$

$n = 2,\ C_V = (7/2)k_B$



Quantum statistics: Discussion

- Let's calculate the exact heat capacity coming from vibrational and rotational modes, respectively. First calculate the **vibrational mode**.
- A diatomic molecule has **one** vibrational mode with stiffness $K \equiv m\omega^2$, where ω is the frequency of oscillations. First, let's look at the single particle ***classical*** partition function for this mode.

- Can you write down the single particle partition function?

$$Z_{\text{vib}}^{c} = \int \frac{\mathrm{d}p\,\mathrm{d}q}{h} \exp\left[-\beta\left(\frac{p^2}{2m} + \frac{m\omega^2 q^2}{2}\right)\right]$$

- This is the **classical** case. Can you guess the energy related to this mode?