Ergodic hypothesis and canonical ensemble

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I. Ergodic hypothesis

Mechanics

Newton $$m\frac{d^2\vec{r}_i}{dt^2} = -\frac{\partial\Phi}{\partial\vec{r}_i}$$

Conservation of energy

$$m\sum_i \frac{d^2\vec{r}_i}{dt^2}\cdot\frac{d\vec{r}_i}{dt} = -\sum_i \frac{\partial\Phi}{\partial\vec{r}_i}\cdot\frac{d\vec{r}_i}{dt}$$

$$\frac{d}{dt}\left(\sum_i \frac{1}{2}m\frac{d\vec{r}_i}{dt}\cdot\frac{d\vec{r}_i}{dt}\right) = -\frac{d\Phi}{dt}$$

$$\frac{d}{dt}\left(\sum_i \frac{1}{2}m\frac{d\vec{r}_i}{dt}\cdot\frac{d\vec{r}_i}{dt} + \Phi\right) = 0$$

I. Ergodic hypothesis

Mechanics

Conservation of energy

$$\frac{d}{dt}\left(\underbrace{\sum_i \frac{\vec{p}_i \cdot \vec{p}_i}{2m} + \Phi(r^{3N})}_{H(r^{3N},\, p^{3N})}\right) = 0 \qquad \rightarrow \qquad \boxed{H(r^{3N}(t),\, p^{3N}(t)) = E}$$

An isolated system will move in phase space on a surface of constant energy

I. Ergodic hypothesis

Notation

Probability distribution in phase space

$$\Pr(\vec{r}_1 \le \vec{R}_1 \le \vec{r}_1 + d\vec{r}_1, \ldots, \vec{p}_N \le \vec{P}_N \le \vec{p}_N + d\vec{p}_N) = P(r^{3N}, p^{3N}) \frac{d^{3N} r d^{3N} p}{h^{3N}}$$

$$\frac{1}{h^{3N}} \int d^{3N} r \int d^{3N} p P(r^{3N}, p^{3N}) = 1$$

Averages

$$\langle A \rangle = \frac{1}{h^{3N}} \int d^{3N} r \int d^{3N} p P(r^{3N}, p^{3N}) A(r^{3N}, p^{3N})$$

I. Ergodic hypothesis

Notation

Divide phase space into cubes of size $d^{3N}rd^{3N}p$

Enumerate cubes and define

$$P_i = P(r_i^{3N}, p_i^{3N})\frac{d^{3n}rd^{3N}p}{h^{3N}}$$

$$\sum_i P_i = 1$$

Averages

$$\langle A \rangle = \sum_i P_i A_i \qquad A_i = A(r_i^{3N}, p_i^{3N})$$

This notation can also be used for quantum systems

I. Ergodic hypothesis

Isolated system !!!!!!!

$\Omega(U)$ **= # of cubes in phase space intersecting** $H(r_i^{3N}, p_i^{3N}) = U$

Assume

- **Equal a priori probabilities**

$$P_i = \frac{1}{\Omega(U)}$$

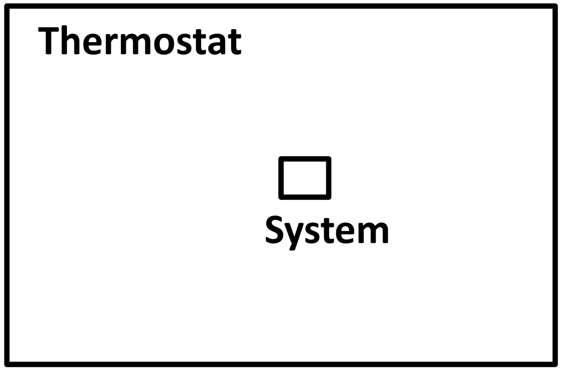
- **Time average equals ensemble average**

$$\frac{1}{T}\int dtA(r^{3N}(t), p^{3N}(t)) = \sum_i A_i P_i$$

II. Canonical ensemble

A. Probabilities

Put system in huge thermostat



Thermostat

System

Treat the total, *i.e.* system plus thermostat, as being isolated !!

Probability to find the system in state n

$$P_n = \frac{\Omega^{Th}(U^{tot} - E_n)}{\Omega^{tot}} \propto \Omega^{Th}(U^{tot} - E_n)$$

II. Canonical ensemble

A. Probabilities

Probability to find the system in state n

$$P_n \propto \Omega^{Th}(U^{tot} - E_n)$$

$P_n \propto \Omega^{Th}(U^{Th} - \Delta E_n)$ **with** $\Delta E_n = E_n - U$**,** $U^{Th} = U^{tot} - U$

General property

$$\Omega^{Th}(U) = C \cdot U^{cN^{Th}} = C \cdot U^{M}$$

Then

$$P_n \propto (U^{Th} - \Delta E_n)^{M}$$

II. Canonical ensemble

A. Probabilities

Probability to find the system in state n

$$P_n \propto \left(U^{Th} - \Delta E_n\right)^M \propto \left(1 - \frac{\Delta E_n}{U^{Th}}\right)^M$$

Now comes the trick

$$P_n \propto \left(1 - \frac{M}{U^{Th}} \frac{\Delta E_n}{M}\right)^M = \left(1 - \frac{\beta \Delta E_n}{M}\right)^M$$

II. Canonical ensemble

A. Probabilities

Probability to find the system in state n

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$$\boxed{P_n \propto e^{-\beta \Delta E_n} \propto e^{-\beta E_n}}$$

II. Canonical ensemble

B. Thermodynamics

Average energy

$$U = \sum_n E_n P_n \qquad P_n = \frac{e^{-\beta E_n}}{\sum_m e^{-\beta E_m}} = \frac{e^{-\beta E_n}}{Q}$$

Manipulate

$$U = \sum_n E_n \frac{e^{-\beta E_n}}{\sum_m e^{-\beta E_m}} = \frac{\sum_n E_n e^{-\beta E_n}}{\sum_m e^{-\beta E_m}} = -\frac{\frac{\partial}{\partial \beta}\sum_n e^{-\beta E_n}}{\sum_m e^{-\beta E_m}}$$

II. Canonical ensemble

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$$\rightarrow \quad \boxed{U = -\frac{\partial}{\partial \beta} \ln Q}$$

II. Canonical ensemble

B. Thermodynamics, quicky

- **Temperature**

Ideal gas

$$Q = \left(\frac{2\pi m}{\beta h^2}\right)^{3N/2} \frac{V^N}{N!}$$

$$U = -\frac{\partial \ln Q}{\partial \beta} = \frac{3N}{2\beta} \quad \rightarrow \quad \beta = \frac{1}{k_B T}$$

- **Free energy**

$$U = A + TS = A - T\left(\frac{\partial A}{\partial T}\right)_V = \left(\frac{\partial A/T}{\partial 1/T}\right)_V = -k_B\left(\frac{\partial \ln Q}{\partial 1/T}\right)_V$$

II. Canonical ensemble

B. Thermodynamics, quicky

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$$\rightarrow \quad \boxed{\frac{A}{T} = -k_B \ln Q}$$

II. Canonical ensemble

B. Thermodynamics, entropy

Notice

$$E_n = -k_B T \ln P_n - k_B T \ln Q$$

So,

$$\begin{aligned} S &= \frac{1}{T}(U - A) \\ &= \frac{1}{T}\left(\sum_n E_n P_n + k_B T \ln Q\right) \end{aligned} \rightarrow \boxed{S = -k_B \sum_n P_n \ln P_n}$$

Notice that this expression also holds true for the micro-canonical ensemble

II. Canonical ensemble

B. Thermodynamics, classical

$$U = A + TS = A - T\left(\frac{\partial A}{\partial T}\right)_V = \left(\frac{\partial A/T}{\partial 1/T}\right)_V = -k_B\left(\frac{\partial \ln Q}{\partial 1/T}\right)_V$$

$$\rightarrow \qquad \frac{A}{T} = -k_B \ln Q + C_{N,V}$$

Experiments force us to choose $C_{N,V} = k_B \ln N!$

Redefine partition function

$$\boxed{\begin{aligned} &\frac{A}{T} = -k_B \ln Q \\ &Q = \frac{1}{h^{3N} N!}\int d^{3N}r \int d^{3N}p \exp\left(-\frac{H(r^{3N}, p^{3N})}{k_B T}\right) \end{aligned}}$$

II. Canonical ensemble

C. Fluctuations

Probability to observe E_n :

$$P(E_n) = \Omega(E_n)\frac{e^{-\beta E_n}}{Q}$$

$\Omega(E_n)$ sharply increases with E_n , $e^{-\beta E_n}$ sharply decreases

II. Canonical ensemble

C. Fluctuations

Width of energy distribution

$$\sigma_E^2 = \left\langle \left(E - \langle E \rangle \right)^2 \right\rangle = \langle E^2 \rangle - \langle E \rangle^2$$

$$\sigma_E^2 = \frac{\partial^2 \ln Q}{\partial \beta^2}$$

Estimate

$$\sigma_E^2 = \frac{\partial}{\partial \beta} \frac{\partial \ln Q}{\partial \beta} = -\frac{\partial U}{\partial \beta} = k_B T^2 \frac{\partial U}{\partial T}$$

With $U = \alpha N k_B T$

$$\rightarrow \quad \boxed{\frac{\sigma_E}{U} = \frac{1}{\sqrt{N\alpha}}}$$

II. Canonical ensemble

D. Back to micro canonical ensemble

$$Q=\sum_n \Omega(E_n)e^{-E_n/k_BT}=\Omega(U)e^{-U/k_BT}\sum_n \exp\left[-\frac{(E_n-U)^2}{2\sigma_E^2}\right]\approx\Omega(U)e^{-U/k_BT}\rho_L\sqrt{2\pi\sigma_E^2}$$

$$A=-k_BT\ln Q=U-k_BT\ln\Omega(U)-k_BT\ln\cancel{\left(\rho_L\sqrt{2\pi\sigma_E^2}\right)}$$

$$\rightarrow$$

$$A=U-k_BT\ln\Omega(U)$$

$S(U)=k_B\ln\Omega(U)$ **as before**

III. Interacting systems

Semi classical partition function

$$Q = \frac{1}{h^{3N} N!} \int d^{3N} r \int d^{3N} p \exp\left[-\frac{p_{1,x}^2 + \ldots + p_{3N,z}^2}{2mk_B T} - \frac{\Phi_N(r^{3N})}{k_B T} \right]$$

Integrate over momenta

$$Q = \frac{1}{\Lambda^{3N} N!} Z_N$$

Thermal de Broglie length $\Lambda = \sqrt{\frac{h^2}{2\pi m k_B T}}$

Configuration integral $Z_N = \int d^{3N} r \exp\left[-\frac{\Phi_N(r^{3N})}{k_B T} \right]$

III. Interacting systems

Averages of functions which only depend on configurations:

$$\langle F \rangle = \frac{\int d^{3N} r F(r^{3N}) \exp\left[-\frac{\Phi_N(r^{3N})}{k_B T} \right]}{\int d^{3N} r \exp\left[-\frac{\Phi_N(r^{3N})}{k_B T} \right]}$$

$$\langle F \rangle = \frac{1}{Z_N} \int d^{3N} r F(r^{3N}) \exp\left[-\frac{\Phi_N(r^{3N})}{k_B T} \right]$$

This holds for Cartesian coordinates, otherwise you must introduce Jacobians

III. Interacting systems

A. Chemical potential

$$\mu = \left(\frac{\partial A}{\partial N}\right)_{T,V} = k_B T \ln\left(\frac{N}{V}\Lambda^3\right) - k_B T \ln\frac{1}{V} - k_B T \frac{\partial \ln Z_N}{\partial N}$$

Approximate

$$\frac{\partial \ln Z_N}{\partial N} = \ln Z_{N+1} - \ln Z_N = \ln\frac{Z_{N+1}}{Z_N}$$

$$\rightarrow$$

$$\mu = k_B T \ln\left(\frac{N}{V}\Lambda^3\right) - k_B T \ln\left(\frac{1}{V}\frac{Z_{N+1}}{Z_N}\right)$$

III. Interacting systems

A. Chemical potential

Potential energy

$$\Phi_N(r^{3(N+1)}) = u(r^{3N}, \vec{r}_{N+1}) + \Phi_N(r^{3N})$$

$$\rightarrow$$

$$\frac{1}{V}\frac{Z_{N+1}}{Z_N} = \frac{1}{V}\int d^3 r_{N+1} \frac{\int d^{3N} r e^{-\beta u(r^{3N}, \vec{r}_{N+1})} e^{-\beta \Phi_N(r^{3N})}}{\int d^{3N} r e^{-\beta \Phi_N(r^{3N})}} = \left\langle e^{-\beta u} \right\rangle$$

Average of $e^{-\beta u(r^{3N}, \vec{r}_{N+1})}$ over all configurations r^{3N} , and all positions $\vec{r}_{N+1}$

III. Interacting systems

A. Chemical potential

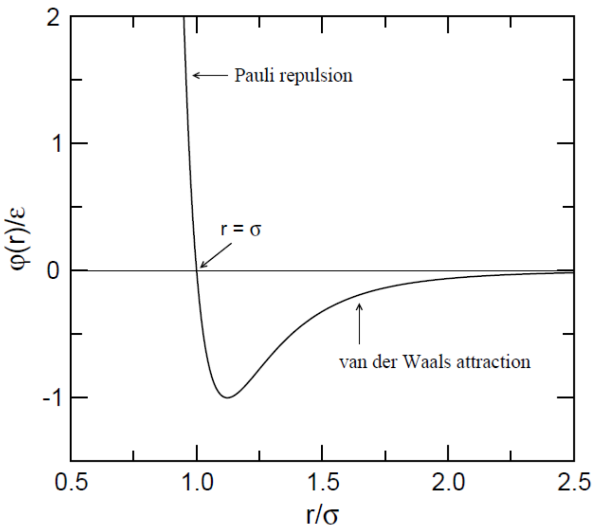
$$\mu = k_B T \ln\left(\rho\Lambda^3\right) \underbrace{- k_B T \ln\left\langle e^{-u/k_B T}\right\rangle}$$

Work performed to bring a particle from infinity into the system

III. Interacting systems

B. Van der Waals

Interaction potential



$$\varphi(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

Diameter σ

III. Interacting systems

B. Van der Waals

Divide space into little cubes of size $\Delta = \sigma^3$

$$Z_N = \sum_{conf} e^{-\beta\Phi_N(conf)}\Delta^N$$

Approximate Lennard-Jones by square well with diameter σ , and interaction range less than 2σ

→
- Only configurations with zero or one particle per cube
- Only nearest neighbour interactions

Still too difficult !!

III. Interacting systems

B. Van der Waals

Mean field approximation:
Every allowed configuration has the same, average energy

$$\overline{\Phi}_N = \frac{1}{2} Nz \frac{N}{M}(-\varepsilon)$$

Configuration integral

$$Z_N = \Omega e^{-\beta \overline{\Phi}_N} \Delta^N$$

Number of allowed states ($M = V/\Delta$)

$$\Omega = \frac{M!}{(M-N)!}$$

(Distinguishable particles)

III. Interacting systems

B. Van der Waals

$$A = -Nk_BT\ln\Lambda^3 - k_BT\ln\left(\frac{M!}{N!(M-N)!}\right) - \frac{1}{2}Nz\frac{N}{M}\varepsilon - Nk_BT\ln\Delta$$

$$p = -\frac{k_BT}{\Delta}\ln\left(1-\frac{N\Delta}{V}\right) - \frac{1}{2}z\varepsilon\Delta\frac{N^2}{V^2}$$

$$\ln(1+x) = \cfrac{1}{1+\cfrac{x}{2+\cfrac{x}{3+\cfrac{4x}{4+\ldots}}}} \approx \frac{1}{1+x/2}$$

$$\rightarrow$$

III. Interacting systems

B. Van der Waals

$$p = \frac{Nk_B T}{V - Nb} - a\frac{N^2}{V^2}$$

$$a = z\varepsilon\Delta / 2 \qquad b = \Delta / 2$$

Thank you

Brrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrriels