Application C : Classical Gas and Classical Ideal Gas

C. Classical Gas and Classical Ideal Gas

$$Z(T,V,N) = \sum_{\substack{\text{all } N\text{-particle} \\ \text{states } i}} e^{-\beta E_i}$$

① for the N-particle state i of energy E_i

② weight it by $e^{-\beta E_i}$

③

Classical Physics: N particles in 3D ⇒ 6N Phase space

$$Z(T,V,N) = \frac{1}{h^{3N} N!} \int d\vec{x}_1 \int d\vec{p}_1 \cdots \int d\vec{x}_N \int d\vec{p}_N \; e^{-\beta H(\{p,x\})}$$

(1b) $H(\{p,x\})$ of energy

(1a) an N-particle state is specified by $\underbrace{\{p,x\}}_{6N \text{ of them}}$

turn phase space into states

correct overcounting

integrate over all phase space

② weight it by $e^{-\beta H(\{p,x\})}$

③ summing over all N-particle states (6N integrals)

$$\boxed{Z(T,V,N) = \frac{1}{N!\,h^{3N}} \int d\vec{x}_1 \int d\vec{p}_1 \cdots \int d\vec{x}_N \int d\vec{p}_N \; e^{-\beta H(\{p,x\})}} \qquad (C1)$$

$$H(\{p,x\}) = H(p_{1x}, p_{1y}, p_{1z}, x_1, y_1, z_1;\ p_{2x}, p_{2y}, p_{2z}, x_2, y_2, z_2;\ \cdots,\ p_{Nx}, p_{Ny}, p_{Nz}, x_N, y_N, z_N)$$

= Hamiltonian of N particles (3D) in a volume V)

• Starting Point for interacting (non-ideal) gas/liquid and ideal gas

$$H(\{p,x\}) = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} + \sum_{(ij)\text{ pairs}} U(\vec{x}_i - \vec{x}_j) \qquad (C2)^{+}$$ general interacting case

$$H(\{p,x\}) = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} \qquad (C3)^{+}$$ Classical ideal (Non-interacting) case

+ Both cases have the same k.e. $\left(\sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m}\right)$ term.

$$Z(T,V,N) = \frac{1}{N!}\,\frac{1}{h^{3N}} \int d\vec{x}_1 \int d\vec{p}_1 \cdots \int d\vec{x}_N \int d\vec{p}_N \; \overbrace{e^{-\beta \frac{\vec{p}_1^{\,2}}{2m}} \cdots e^{-\beta \frac{\vec{p}_N^{\,2}}{2m}}}^{e^{-\beta \sum_{i=1}^{N} \vec{p}_i^{\,2}/2m}} \cdot e^{-\beta \sum_{(ij)\,\text{pairs}} \mathcal{U}(\vec{x}_i - \vec{x}_j)} \qquad \text{(general)}$$

$$= \frac{1}{N!}\,\frac{1}{h^{3N}} \underbrace{\underbrace{\left(\int d\vec{p}_1\, e^{-\beta \frac{\vec{p}_1^{\,2}}{2m}}\right)}_{3\ \text{integrals}} \cdots \underbrace{\left(\int d\vec{p}_N\, e^{-\beta \frac{\vec{p}_N^{\,2}}{2m}}\right)}_{3\ \text{integrals}}}_{3N\ \text{integrals}} \cdot \underbrace{\int d\vec{x}_1 \cdots \int d\vec{x}_N\; e^{-\beta \sum_{(ij)\,\text{pairs}} \mathcal{U}(\vec{x}_i - \vec{x}_j)}}_{3N\ \text{integrals}} \qquad \text{(general)} \qquad \text{(C4)}$$

- [starting point of liquid state physics and non-ideal gas physics, and other classical stat. mech. problems]
- Note integrals $\left(\int d\vec{p}_i\, e^{-\beta \frac{\vec{p}_i^{\,2}}{2m}}\right)$ are there

$\Rightarrow$ results coming from these terms are general for interacting and ideal gases

Classical Ideal Gas

$\mathcal{U}(\vec{x}) = 0$ [non-interacting particles], $e^{-\beta \mathcal{U}} = 1$

$$Z(T,V,N) = \frac{1}{N!\,h^{3N}} \left(\int d\vec{p}_1 \int d\vec{x}_1\, e^{-\beta \frac{\vec{p}_1^{\,2}}{2m}} \right) \cdots \left(\int d\vec{p}_N \int d\vec{x}_N\, e^{-\beta \frac{\vec{p}_N^{\,2}}{2m}} \right) \quad \text{(ideal gas)}$$

$$= \frac{1}{N!} \underbrace{\left(\frac{1}{h^3} \int d\vec{p}_1 \int d\vec{x}_1\, e^{-\beta \frac{\vec{p}_1^{\,2}}{2m}} \right)}_{\text{particle \#1's partition function}} \cdots \underbrace{\left(\frac{1}{h^3} \int d\vec{p}_N \int d\vec{x}_N\, e^{-\beta \frac{\vec{p}_N^{\,2}}{2m}} \right)}_{\text{particle \#N's partition function}}$$

the same

$$= \frac{1}{N!} z^N \qquad \text{(C5)}$$

→ (factorized for ideal gas)

where

$$z(T,V,1) = \frac{1}{h^3} \int d\vec{p} \underbrace{\int d\vec{x}}_{V}\, e^{-\beta \frac{\vec{p}^{\,2}}{2m}} = \frac{1}{h^3} V \int d\vec{p}\, e^{-\beta \frac{\vec{p}^{\,2}}{2m}} \qquad \text{(C6)}$$

single-particle (so formally "N=1") OR just $z(T,V)$

$$z = \frac{V}{h^3}\int d\vec{p}\, e^{-\beta\frac{\vec{p}^2}{2m}} = \frac{V}{h^3}\int_{-\infty}^{\infty} dp_x \int_{-\infty}^{\infty} dp_y \int_{-\infty}^{\infty} dp_z\, e^{-\beta\frac{p_x^2}{2m}}\, e^{-\beta\frac{p_y^2}{2m}}\, e^{-\beta\frac{p_z^2}{2m}}$$

single-particle partition function

(Using Cartesian Coordinates)

[can use other coordinates]

$$= \frac{V}{h^3}\underbrace{\left[\int_{-\infty}^{\infty} dp\, e^{-\beta\frac{p^2}{2m}}\right]^3}_{}$$

this is a Gaussian Integral† $\int_{-\infty}^{\infty} e^{-ax^2}dx = \sqrt{\frac{\pi}{a}}$

$$= \frac{V}{h^3}\left(\sqrt{\frac{2m\pi}{\beta}}\right)^3 = \underbrace{\frac{V}{h^3}\left(\sqrt{2\pi mkT}\right)^3}_{\text{answer}} = V\,\frac{1}{\left(\frac{h}{\sqrt{2\pi mkT}}\right)^3} = \frac{V}{\lambda_{th}^3(T)} \quad \text{(C7)}$$

saw this before

de Broglie thermal wavelength

<u>Interpreting z</u>

- a number
- $\frac{V}{\lambda_{th}^3}$ ← dividing volume V by a box of volume λ_{th}^3 (temp.-dependent), each box is a single-particle state
  ← # ways the particle will pick to be in one of $\frac{V}{\lambda_{th}^3}$ states

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† Gaussian Integrals are a class of integrals important in stat. mech. If you know the given one, you also know, e.g. $\int_{-\infty}^{\infty} x^2 e^{-ax^2}dx$, by taking a derivative w.r.t. a.

$$Z = \frac{1}{N!} z^N = \frac{1}{N!}\left(\frac{V}{\lambda_{th}^3}\right)^N$$

Interpreting Z : z^N → each particle has z ways → distinguishable particles

then $\frac{1}{N!}$ correct over-counting

$$\langle E\rangle = -\left(\frac{\partial}{\partial\beta}\ln Z\right)_{N,V} \quad ; \quad \ln Z = N\ln z - N\ln N + N$$

"β" in z only as $z = \frac{V}{h^3}\left(\frac{2m\pi}{\beta}\right)^{3/2}$

$$= -N\frac{\partial}{\partial\beta}\left[\frac{3}{2}\ln\left(\frac{2m\pi}{\beta}\right)\right]$$

(the $\ln\left[\frac{V}{h^3}\right]$ term won't contribute)

$$= -\frac{3}{2}N\frac{1}{\left(\frac{2m\pi}{\beta}\right)}(2m\pi)\frac{\partial}{\partial\beta}\left(\frac{1}{\beta}\right) = \frac{3}{2}\frac{N}{\beta} = \frac{3}{2}NkT \quad (C8)$$

Nothing Surprising!

$$F(T,V,N) = -kT\ln Z = -NkT\left[\ln z - \ln N + 1\right]$$

$$= -\underset{\substack{\uparrow \\ \text{Make } F \text{ Extensive}}}{N}kT\left[\ln\left[\underbrace{\left(\frac{V}{N}\right)}_{\text{intensive}}\left(\frac{\sqrt{2\pi mkT}}{h}\right)^3\right] + 1\right] \quad (C9)$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = -\frac{\partial}{\partial V}\left(-NkT\ln(\mathcal{A}V)\right) = NkT\frac{1}{\mathcal{A}V}\cdot\mathcal{A} = \frac{NkT}{V}$$

$$\Rightarrow PV = NkT \qquad \text{(C10)}$$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = -kT\ln\left[\frac{V}{N}\left(\frac{\sqrt{2\pi mkT}}{h}\right)^3 + 1\right] \overbrace{-NkT\frac{\partial}{\partial N}\left(\ln\left(\frac{\mathcal{A}}{N}\right)\right)}^{+kT\ (\text{Ex.})} = \underbrace{-kT\ln\left[\frac{V}{N}\left(\frac{\sqrt{2\pi mkT}}{h}\right)^3\right]}_{\text{saw this before}} \qquad \text{(C11)}$$

Ex: $S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = ?$ or $S = \frac{\langle E\rangle - F}{T} = ?$

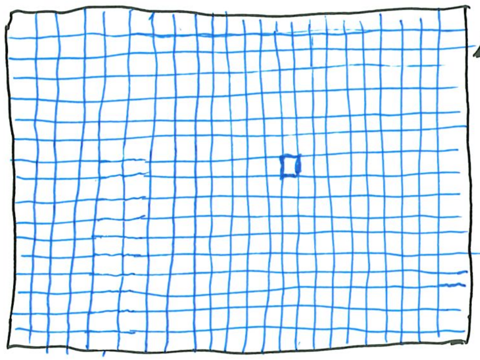
$\langle E^2\rangle = ?$; $\sigma_E^2 = \langle E^2\rangle - \langle E\rangle^2 = ?$; $\sigma_E = ?$

You can compare the microcanonical and canonical ensemble approaches in two-level particles, oscillator problems, and ideal classical gas, and think over the concepts behind the two methods, as well as which way is more convenient.

Picture of z: $\quad z = V/\lambda_{th}^3$

Temperature T, mass of particle m: $\lambda_{th}(T) = \dfrac{h}{\sqrt{2\pi m k T}}$ a length $\Rightarrow \lambda_{th}^3$ a "volume"

high temp. (when gases are ideal gases) λ_{th} is small



"V" (think 3D)

"box" (volume λ_{th}^3)

$$\underbrace{\frac{V}{\lambda_{th}^3}}_{z} = \#\text{ boxes of size } \lambda_{th}^3 \text{ in Volume } V$$

allowing particle to pick a box to be in, z is the number of ways (it is T-dependent)

Picture of Z: $\frac{1}{N!} z^N$

- same picture for each of N particles
  if particles were distinguishable, then z^N ways (also T-dependent)
- But particles are indistinguishable, AND # boxes are MANY in ideal gas, $\frac{1}{N!}$ can correct for overcounting