PRESSURE VIA VIRIAL EQUATION [monatomic gas] ①

We work in the canonical ensemble

$$Q = \int \frac{d^{3N}p\, d^{3N}q}{h^{3N} N!} e^{-\beta H} \xrightarrow[\text{over momenta}]{\text{integrating}} \frac{V^N}{\lambda^{3N} N!} \left(\frac{Z}{V^N} \right)$$

$$F = F^{id} + F^{exc} \qquad F^{exc} = -kT \ln \frac{Z}{V^N} \qquad F^{id} = \text{free energy of an ideal gas}$$

$$p = -\frac{\partial F}{\partial V} = -\frac{\partial F^{id}}{\partial V} - \frac{\partial F^{exc}}{\partial V} = \frac{NkT}{V} - \frac{\partial F^{exc}}{\partial V} \equiv p^{(id)} + p^{(exc)}$$

We want to compute the excess part, that depends on the interaction potential

$$\frac{Z}{V^N} = \frac{1}{V^N} \int d^{3N}q\, e^{-\beta U(q_1 \dots q_N)}$$

To compute the derivative we must take into account

i) the explicit dependence of the factor V^{-N}

ii) the implicit dependence of the integration domain

Fix the volume: a cube of size $L \times L \times L$: $V = L^3$

$$p^{(exc)} = -\frac{1}{3L^2} \frac{\partial F^{exc}}{\partial L}$$

Now

$$\frac{Z}{V^N} = \frac{1}{V^N} \int_0^L dq_{1x} \int_0^L dq_{1y} \cdots \int_0^L dq_{Nz}\, e^{-\beta U(\bar{q}_1 \dots \bar{q}_N)}$$

Change variables

$$\begin{cases} \bar{s} = \dfrac{\bar{q}}{L} \\ \bar{q} = L\bar{s} \end{cases} \qquad \begin{array}{l} 0 \le s_x \le 1 \\ 0 \le s_y \le 1 \\ 0 \le s_z \le 1 \end{array}$$

$$\frac{Z}{V^N} = \int_0^1 ds_{1x} \int_0^1 ds_{1y} \cdots \int_0^1 ds_{Nz}\; e^{-\beta U(\bar{s}_1 L, \bar{s}_2 L, \ldots s_N \bar{L})}$$

It follows

$$\frac{\partial}{\partial L}\left(\frac{Z}{V^N}\right) = \int_0^1 d^{3N}s\; e^{-\beta U(\bar{s}_1 L, \bar{s}_2 L, \ldots \bar{s}_N L)} \times$$

$$\times(-\beta)\left(\frac{\partial U}{\partial q_{1x}} \underbrace{\frac{\partial q_{1x}}{\partial L}}_{s_{1x}} + \frac{\partial U}{\partial q_{1y}} \underbrace{\frac{\partial q_{1y}}{\partial L}}_{s_{2x}} + \cdots \frac{\partial U}{\partial q_{Nz}} \underbrace{\frac{\partial q_{Nz}}{\partial L}}_{s_{Nz}}\right)$$

$$= -\beta \int_0^1 d^{3N}s\; e^{-\beta U(\bar{s}_1 L \ldots \bar{s}_N L)} \sum_{i=1}^{N} \frac{\partial U}{\partial \bar{q}_i} \cdot \vec{s}_i$$

Now, let's go back to the original variables $\bar{q}$

$$= -\frac{\beta}{V^N} \int_0^L d^{3N}q\; e^{-\beta U(\bar{q}_1 \cdots \bar{q}_N)} \sum_{i=1}^{N} \frac{\partial U}{\partial \bar{q}_i} \cdot \frac{\bar{q}_i}{L}$$

$$p^{exc} = \frac{kT}{3L^2} \frac{V^N}{Z} \frac{\partial}{\partial L}\left(\frac{Z}{V^N}\right)$$

$\boxed{\text{Remember } \beta kT = 1}$

$\boxed{V^N \cdot \frac{1}{V^N} = 1}$ $\boxed{\frac{1}{L^2} \cdot \frac{1}{L} = \frac{1}{V}}$

$$= -\frac{1}{3V} \frac{1}{Z} \int d^{3N}q\; e^{-\beta U} \sum_{i=1}^{N} \frac{\partial U}{\partial \bar{q}_i} \cdot \bar{q}_i$$

$$= \frac{1}{3V} \Big\langle \underbrace{-\sum_{i=1}^{N} \frac{\partial U}{\partial \bar{q}_i} \cdot \bar{q}_i}_{\text{Virial}} \Big\rangle$$

$\langle \quad \rangle =$ average with $e^{-\beta U}/Z$

Now assume: a) NO EXTERNAL FORCES

b) pair interactions only

$$U(\bar q_1, \dots \bar q_N) = \underbrace{\sum_{1 = i < j = N}}_{\text{sum over all pairs of molecules.}} V(|\bar q_i - \bar q_j|)$$

Now note that

$$\frac{\partial}{\partial x_i} |\bar q_i - \bar q_j| = \frac{\partial}{\partial x_i}\left[(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2\right]^{1/2} = \frac{x_i - x_j}{|\bar q_i - \bar q_j|} = \frac{q_{xij}}{|q_{ij}|}$$

$$\frac{\partial}{\partial \bar q_i} |q_i - q_j| = \frac{\bar q_{ij}}{|q_{ij}|}$$

$$\frac{\partial}{\partial \bar q_i}\left(\sum_{j<k} V(|q_{jk}|)\right) = \frac{\partial}{\partial \bar q_i} \sum_{\substack{j=1 \\ j \neq i}}^{N} V(|q_{ij}|)$$

[$\sum_{j<k}$ is a sum over all pairs of molecules]

we only keep the term corresponding to molecule i interacting with all the others

$$= \sum_{\substack{j=1 \\ j \neq i}}^{N} \frac{\partial V}{\partial |q_{ij}|} \frac{\bar q_{ij}}{|q_{ij}|}$$

Thus

$$\sum_{i=1}^{N} \frac{\partial U}{\partial \bar q_i} \cdot \bar q_i = \sum_{i=1}^{N} \sum_{\substack{j=1 \\ j \neq i}}^{N} \frac{\partial V}{\partial |q_{ij}|} \frac{\bar q_{ij}}{|q_{ij}|} \cdot \vec q_i$$

To understand how the sum simplifies, set $N=3$ Explicitly

$$(i=1) \quad \frac{\partial V}{\partial|q_{12}|}\frac{\bar{q}_{12}}{|q_{12}|}\cdot\bar{q}_1+\frac{\partial V}{\partial|q_{13}|}\frac{\bar{q}_{13}}{|q_{13}|}\cdot\bar{q}_1 + \qquad (j=2,3)$$

$$(i=2) \quad \frac{\partial V}{\partial|q_{12}|}\frac{\bar{q}_{21}}{|q_{12}|}\cdot\bar{q}_2+\frac{\partial V}{\partial|q_{23}|}\frac{\bar{q}_{23}}{|q_{23}|}\cdot\bar{q}_2 + \qquad (j=1,3)$$

$$(i=3) \quad \frac{\partial V}{\partial|q_{13}|}\frac{\bar{q}_{31}}{|q_{13}|}\cdot q_3+\frac{\partial V}{\partial|q_{23}|}\frac{\bar{q}_{32}}{|q_{23}|}\cdot\bar{q}_3 \qquad (j=1,2)$$

[we always use $|q_{ji}|=|q_{ij}|$]

Now the term proportional to $\frac{\partial V}{\partial|q_{12}|}$ are

$$\frac{\partial V}{\partial|q_{12}|}\frac{\bar{q}_{12}\cdot q_1}{|q_{12}|}+\frac{\partial V}{\partial|q_{12}|}\frac{\bar{q}_{21}\cdot\bar{q}_2}{|q_{12}|}=$$

$$=\frac{\partial V}{\partial|q_{12}|}\frac{1}{|q_{12}|}\Big[(\bar{q}_1-\bar{q}_2)\cdot\bar{q}_1+(\bar{q}_2-\bar{q}_1)\cdot q_2\Big]=$$

$$(q_1-q_2)^2$$

$$=\frac{\partial V}{\partial|q_{12}|}\frac{1}{|q_{12}|}|q_{12}|^2=|q_{12}|\frac{\partial V}{\partial|q_{12}|}$$

The other terms are analogous. We obtain

$$|q_{12}|\frac{\partial V}{|q_{12}|}+|q_{13}|\frac{\partial V}{\partial|q_{13}|}+|q_{23}|\frac{\partial V}{\partial|q_{23}|}$$

For N particles

$$\sum_{i=1}^{N}\frac{\partial U}{\partial\bar{q}_i}\cdot\bar{q}_i=\sum_{i<j}|q_{ij}|\frac{\partial V}{\partial|q_{ij}|}$$

↑
sum over all pairs of molecules

$$p^{exc} = \frac{1}{3V}\left\langle - \sum_{i<j} |r_{ij}| \frac{\partial V}{\partial |r_{ij}|} \right\rangle$$

This formula shows that the excess pressure depends on the forces $-\frac{\partial V}{\partial |r_{ij}|}$ that occur among pairs of molecules

The same formula holds in other ensembles

EXAMPLE: grandcanonical ensemble

$$\Xi = \sum_N e^{\beta\mu N} Q(N,V,T) = \sum_N e^{\beta\mu N} e^{-\beta F(N,V,T)}$$

$$\frac{\partial \Xi}{\partial V} = -\sum_N e^{\beta\mu N} e^{-\beta F} \beta \frac{\partial F}{\partial V} = -\beta \sum_N e^{\beta\mu N} Q \frac{\partial F}{\partial V}$$

$$-\frac{\partial F}{\partial V} = \frac{NkT}{V} - \frac{1}{Q}\frac{1}{3V} \int \frac{dp\,dq}{h^{3N} N!} e^{-\beta H} \sum_{i<j} |r_{ij}| \frac{\partial V}{\partial |r_{ij}|}$$

It follows

$$\frac{\partial \Xi}{\partial V} = \cancel{\beta} \sum_N e^{\beta\mu N} Q \left(\frac{N\cancel{kT}}{V}\right)$$

$$- \beta \frac{1}{3V} \sum_N e^{\beta\mu N} \int \frac{dp\,dq}{h^{3N} N!} e^{-\beta H} \sum_{i<j} |r_{ij}| \frac{\partial V}{\partial r_{ij}}$$

$$\frac{1}{\Xi}\frac{\partial \Xi}{\partial V} = \left\langle \frac{N}{V} \right\rangle_{GC} - \frac{\beta}{3V} \left\langle \sum_{i<j} |r_{ij}| \frac{\partial V}{\partial |r_{ij}|} \right\rangle_{GC}$$

$\langle \; \rangle_{GC}$ is the grandcanonical average

$$p = -\left(\frac{\partial \Omega}{\partial V}\right)_{T,\mu} = kT \frac{\partial \Xi}{\partial V} \frac{1}{\Xi}$$

$$= \frac{\langle N \rangle_{GC} kT}{V} - \frac{1}{3V} \left\langle \sum_{i<j} |r_{ij}| \frac{\partial V}{\partial |r_{ij}|} \right\rangle_{GC}$$

Of course

$$\langle A \rangle_{GC} = \frac{1}{\Xi} \sum_N e^{\beta \mu N} \int \frac{d^{3N}p \, d^{3N}q}{h^{3N} N!} e^{-\beta H} A$$

ONE FINAL COMMENT:
In the canonical ensemble we obtained

$$p^{exc} = \frac{1}{3V} \left\langle - \sum_{i<j} |r_{ij}| \frac{\partial V}{\partial r_{ij}} \right\rangle$$ average over the configurational part

$$= \frac{1}{3V} \frac{1}{Z} \int d^{3N}q \, e^{-\beta U} \left(- \sum_{i<j} |r_{ij}| \frac{\partial V}{\partial r_{ij}} \right)$$

However, since there is no momentum dependence we can also write

$$p^{exc} = \frac{1}{3V} \frac{1}{Q} \int \frac{d^{3N}p \, d^{3N}q}{h^{3N} N!} e^{-\beta H} \left(- \sum_{i<j} |r_{ij}| \frac{\partial V}{\partial r_{ij}} \right)$$