Lecture 12

22.02.2018

Virial theorem

Virial term

Let's consider this averaged quantity – virial term

$$\left\langle \frac{d}{dt} \sum_i p_i\, q_i \right\rangle = \left\langle \sum_i \dot{p}_i q_i \right\rangle + \left\langle \sum_i p_i\, \dot{q}_i \right\rangle$$

Use Hamiltonian particle dynamics

$$\left\langle \frac{d}{dt} \sum_i p_i\, q_i \right\rangle = \left\langle \sum_i p_i \frac{\partial H}{\partial p_i} \right\rangle - \left\langle \sum_i q_i \frac{\partial H}{\partial q_i} \right\rangle$$

The ensemble averaged quantity on the lhs vanishes for ergotic systems

(ensemble averages = time averages)

$\left\langle \frac{d}{dt} \sum_i p_i\, q_i \right\rangle \equiv \frac{1}{\tau} \int_0^\tau \frac{d}{dt} \left(\sum_i p_i q_i\right) = \frac{1}{\tau} \left(\sum_i p_i q_i\right)\Big|_0^\tau \xrightarrow[\tau \to \infty]{} 0$

(when phase space volume is finite, $\left(\sum_i p_i q_i\right) < \infty$)

$$\langle \theta \rangle \equiv \left\langle \sum_i q_i \frac{\partial H}{\partial q_i} \right\rangle = \left\langle \sum_i p_i \frac{\partial H}{\partial p_i} \right\rangle = 2\langle K \rangle, \qquad \langle K \rangle = \left\langle \sum_i \frac{p_i^2}{2m} \right\rangle$$

Kinetic energy

Use the equilibrium Maxwell-Boltzmann distribution for the averages in canonical ensemble

$$\langle \theta \rangle \equiv 2\langle K \rangle = \left\langle \sum_i p_i \frac{\partial H}{\partial p_i} \right\rangle = \frac{1}{Z_N} \int d\omega_N \sum_i p_i \frac{\partial H_N}{\partial p_i} \, e^{-\beta H_N}$$

$$\langle \theta \rangle \equiv 2\langle K \rangle = -\frac{kT}{Z_N} \sum_i \int d\omega_N \, p_i \frac{\partial}{\partial p_i} \left(e^{-\beta H_N} \right) =$$

Integration by parts for each $3N$ terms in the sum (identical integral for each term in the sum)

$$2\langle K \rangle = \frac{3NkT}{Z_N} \int d\omega_N \, e^{-\beta H_N} = 3NkT$$

$$\mathbf{2\langle K \rangle = 3NKT}$$

Equipartition of energy $\boldsymbol{\langle K \rangle = \frac{f}{2} kT, \quad e.g. \, f = 3N}$ Each quandratic degreees of freedom that is **freely accessible** gets the same quota of energy $kT/2$

Virial theorem

Now use the other definition

$$3NkT = \langle\theta\rangle = \left\langle \sum_i q_i \frac{\partial H}{\partial q_i} \right\rangle = -\left\langle \sum_i q_i \dot{p}_i \right\rangle = -\left\langle \sum_k \vec{r}_k \cdot \dot{\vec{p}}_k \right\rangle = -\left\langle \sum_k \vec{r}_k \cdot \vec{F}_k \right\rangle, \qquad \dot{\vec{p}} = \vec{F}$$

$$3NkT = \langle\theta^{int}\rangle + \langle\theta^{ext}\rangle, \qquad \vec{F} = \vec{F}^{int} + \vec{F}^{ext} = -\vec{\nabla} U_N - P\mathrm{d}\vec{S}$$

$\vec{F}^{int} = -\nabla U_N$ is the internal force acting on a particle due to its interaction with the other particles in the systems; force generated by the pairwise interaction potential

$\vec{F}^{ext} = -P\mathrm{d}\vec{S}$ is the force acting on a surface element $\mathrm{d}\vec{S}$ of the particle due to the pressure maintained by the equilibrium with the reservoir

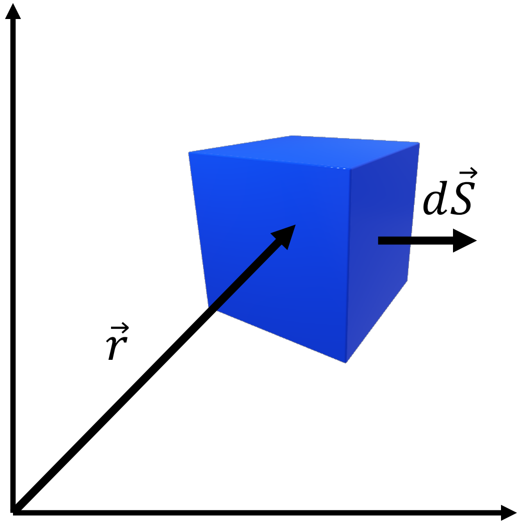
$$3NkT = \left\langle \sum_i \vec{r}_i \cdot \vec{\nabla}_i U_N \right\rangle + P \left\langle \sum_i \vec{r}_i \cdot \mathrm{d}\vec{S}_i \right\rangle$$

$$\vec{r} \cdot \vec{\nabla} = x\frac{\partial}{\partial x} + y\frac{\partial}{\partial y} + \mathrm{z}\frac{\partial}{\partial z}$$

Virial theorem $\langle\theta^{ext}\rangle$

$$\sum_i \vec{r}_i \cdot \vec{F}_i = -P \oint_S \vec{r} \cdot d\vec{S} = -P \int_V \vec{\nabla} \cdot \vec{r}\, dv = -3PV$$

$$\langle\theta^{ext}\rangle = P \sum_{i=1}^{N} \langle \vec{r}_i \cdot \mathrm{d}\vec{S}_i \rangle = 3PV$$



Virial theorem $\langle \theta^{int} \rangle$

$$\langle \theta^{int} \rangle = \left\langle \sum_i \vec{r}_i \cdot \vec{\nabla}_i U_N \right\rangle, \qquad U_N = \sum_k \sum_{j\neq k} u(\vec{r}_{kj}), \qquad \vec{r}_{kj} = \vec{r}_k - \vec{r}_j$$

$$\langle \theta^{int} \rangle = \sum_i^N \sum_{j\neq i} \langle \vec{r}_i \cdot \vec{\nabla}_i u(\vec{r}_{ij}) \rangle = \sum_i^N \sum_{j\neq i} \left\langle \vec{r}_i \cdot \frac{\partial}{\partial \vec{r}_{ij}} u(\vec{r}_{ij}) \right\rangle = \sum_i^N \sum_{j<i} \left\langle \vec{r}_i \cdot \frac{\partial}{\partial \vec{r}_{ij}} u(\vec{r}_{ij}) \right\rangle + \sum_i^N \sum_{j>i} \left\langle \vec{r}_i \cdot \frac{\partial}{\partial \vec{r}_{ij}} u(\vec{r}_{ij}) \right\rangle$$

$$= \sum_i^N \sum_{j<i} \left[\left\langle \vec{r}_i \cdot \frac{\partial}{\partial \vec{r}_{ij}} u(\vec{r}_{ij}) \right\rangle + + \left\langle \vec{r}_j \cdot \frac{\partial}{\partial \vec{r}_{ji}} u(\vec{r}_{ji}) \right\rangle \right], \qquad \vec{r}_{ji} = -\vec{r}_{ij}, u(\vec{r}_{ji}) = u(\vec{r}_{ij})$$

$$= \sum_i^N \sum_{j<i} \left\langle \vec{r}_{ij} \cdot \frac{\partial}{\partial \vec{r}_{ij}} u(\vec{r}_{ij}) \right\rangle =_{isotropy} \sum_i^N \sum_{j<i} \left\langle r_{ij} \cdot \frac{\partial}{\partial r_{ij}} u(r_{ij}) \right\rangle, \qquad r_{ij} = |\vec{r}_{ij}|$$

$$\langle \theta^{int} \rangle = \frac{N(N-1)}{2} \sum_{j<i} \left\langle r_{12} \cdot \frac{\partial}{\partial r_{12}} u(r_{12}) \right\rangle$$

Virial theorem $\langle \theta^{int} \rangle$

The virial related to internal forces is

$$\langle \theta^{int} \rangle = \frac{N(N-1)}{2} \left\langle r_{12} \frac{du(r_{12})}{dr_{12}} \right\rangle$$

$$\langle \theta^{int} \rangle = \frac{N(N-1)}{2} \frac{1}{Q_N} \int d\vec{r}_1 \cdots d\vec{r}_N \; r_{12} \frac{du(r_{12})}{dr_{12}} \;\; e^{-\beta U_N}$$

$$\langle \theta^{int} \rangle = \frac{1}{2} \int d\vec{r}_1 d\vec{r}_2 \; r_{12} \frac{du(r_{12})}{dr_{12}} \left(\frac{N(N-1)}{Q_N} \int d\vec{r}_3 \cdots d\vec{r}_N \; e^{-\beta U_N} \right)$$

$$\langle \theta^{int} \rangle = \frac{1}{2} \int d\vec{r}_1 d\vec{r}_2 \; r_{12} \frac{du(r_{12})}{dr_{12}} \;\; \rho^2 g(r_{12})$$

Relative coordinates $\vec{r} = \vec{r}_1 - \vec{r}_2, \vec{z} = (\vec{r}_1 + \vec{r}_2)/2$ and using isotropy $d\vec{r} \rightarrow 4\pi r^2 dr$

$$\langle \theta^{int} \rangle = \frac{1}{2} \int d\vec{r}_1 d\vec{r}_2 \; r_{12} \frac{du_{12}}{dr_{12}} \;\; \rho^2 g(r_{12}) = \frac{\rho^2}{2} \int d\vec{z} \int d\vec{r} \, r \frac{du(r)}{dr} \;\; g(r)$$

$$\boldsymbol{\langle \theta^{int} \rangle = \frac{N\rho}{2} \, 4\pi \int dr \, r^3 \, u'(r) \, g(r)}$$

General equation of state

Virial theorem

$$2\langle K\rangle = \left\langle \theta^{int} \right\rangle + \langle \theta^{ext} \rangle$$

$$3NkT = 2\pi N\rho \int dr\, r^3\, u'(r)\, g(r) + 3PV$$

$$P = \rho\left[kT - \frac{\rho}{6}\int d\vec{r}\, r\, u'(r) g(r)\right], \qquad r = |\vec{r}|$$

Low-density limit $g(r) \approx e^{-\beta u(r)}$

$$P = \rho\left[kT - \frac{2\pi}{3}\,\rho\int dr\, r^3\, u'(r) g(r)\right] = \rho\left[kT - \frac{2\pi}{3}\,\rho\int dr\, r^3\, u'(r) e^{-\beta u(r)}\right]$$

$$\frac{P}{kT} = \rho - \frac{2\pi}{3}\,\rho^2\int dr\, r^3\,\frac{d}{dr}\left(1 - e^{-\beta u(r)}\right)$$

Integration by parts

$$\frac{P}{kT} = \rho\left[1 + \frac{\rho}{2}\int d\vec{r}\left(1 - e^{-\beta u(r)}\right)\right]$$

Virial expansion

$$P = \rho\left[kT - \frac{2\pi}{3}\ \rho\int dr\, r^3\, u'(r) g(r)\right]$$

Perturbative expansion: $g(r) = e^{-\beta u(r)}[1 + \sum_{n=1}^{\infty} \rho^n y_n(r)]$

$$P = \rho\left[kT - \frac{2\pi}{3}\ \rho\int dr\, r^3\, u'(r) e^{-\beta u(r)}\left[1 + \sum_{n=1}^{\infty} \rho^n y_n(r)\right]\right]$$

$$\frac{P}{kT} = \rho + \sum_{n=2} B_n(T)\rho^n,$$

$$B_2(T) = \frac{1}{2}\int d\vec{r}\left(1 - e^{-\beta u(r)}\right)$$

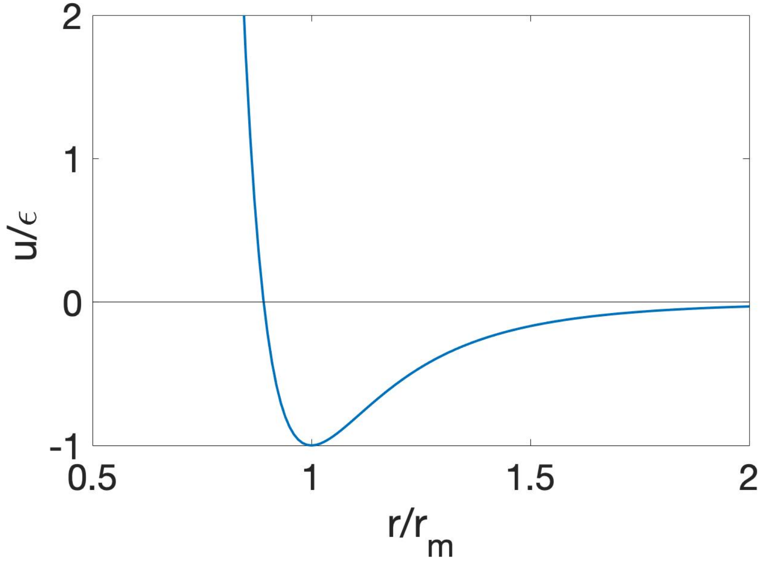
Van der Waals equation of state

$$\frac{P}{kT} = \rho + B_2(T)\rho^2$$

$$B_2 = \frac{1}{2}\int_0^{r_m} dr\ 4\pi r^2 + \frac{1}{2}\int_{r_m}^{\infty} dr\ 4\pi r^2 \left(1 - e^{-\beta u(r)}\right)$$

$$B_2 = \frac{1}{2}\frac{4\pi r_m^3}{3} + \frac{1}{kT}\frac{1}{2}\int_{r_m}^{\infty} dr\ 4\pi r^2\, u(r)$$

$$B_2(T) = b - \frac{a}{kT}, \qquad a, b > 0$$



Van der Waals in the low density limit

$$\frac{P}{kT} = \rho + \rho^2 \left(b - \frac{a}{kT}\right)$$

$$B_2(T) = b - \frac{a}{kT}$$

Boyle's temperature $\mathrm{T_B} = \frac{\mathrm{a}}{\mathrm{kb}}$ is defined as the finite temperature at which the Van der Waals gas behaves as the ideal ideal gas

$$P_B = \rho k T_B$$

T_B is the temperature at which attraction and repulsive forces balance each other out, and the gas behaves effectively as an ideal gas