# Computational Soft Matter and Biophysics

# We start at 10:00

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## 3.3.2 Pressure

Virial theorem

$$G(t) = \sum_{i=1}^{N} m_i \underline{r}_i(t) \cdot \ddot{\underline{r}}_i(t)$$

Time average $t^*$

$$\bar{G} = \frac{1}{t^*} \int_0^{t^*} dt \sum_i m_i \underline{r}_i(t) \cdot \ddot{\underline{r}}_i(t)$$

$$= \frac{1}{t^*} \int_0^{t^*} dt \left[ -\underline{r}_i(t) \underline{\nabla} \phi\left(\underline{r}_j(t)\right) \right]$$

On the other hand: partial integration

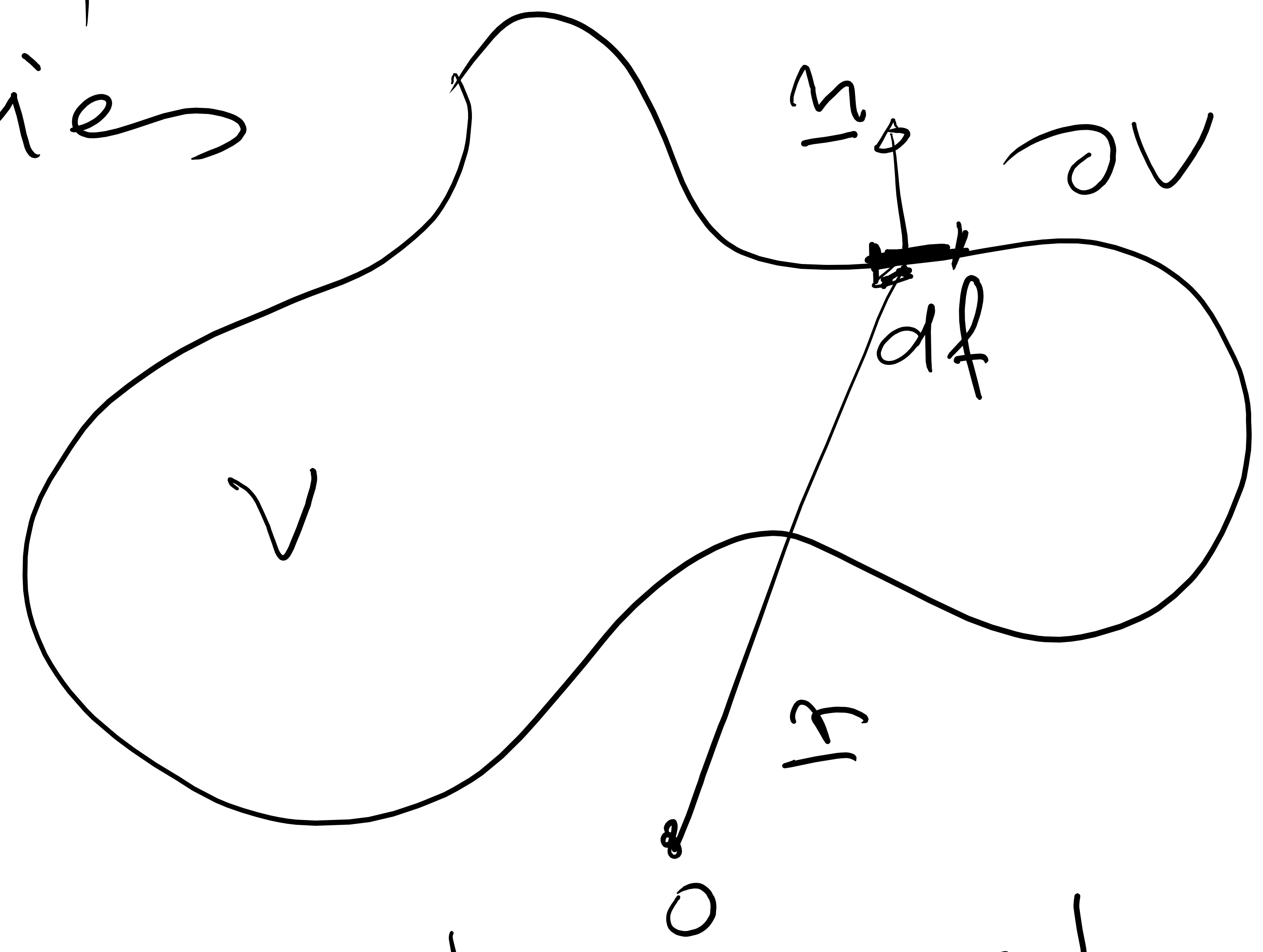
$$\bar{G} = \underbrace{\sum_i m_i \frac{1}{t^*} \left[ \underline{r}_i(t) \cdot \dot{\underline{r}}_i(t) \right]_0^{t^*}}_{\substack{\text{for finite volume} \\ \text{and } t^* \to \infty}} - \frac{1}{t^*} \int_0^{t^*} dt \underbrace{\sum_i m_i \dot{\underline{r}}_i^2}_{E_{kin}}$$

$\to 0$

$$\leadsto \boxed{2 \langle E_{kin} \rangle - \sum_{i=1}^{N} \langle \underline{r}_i \cdot \underline{\nabla}_i \phi \rangle}$$

$$= W_{int} + W_{ext}$$

External virial: interactions of particles with boundaries




short-range interactions

$$W_{ext}\Big|_{df} = \sum_{i=1}^{N} \underline{r}_i\Big|_{df} \cdot \underline{\nabla}\,\phi_{ext} =$$

$$= \underline{r} \underbrace{\sum_i \nabla_i\,\phi_{ext}\Big|_{df}}_{\text{force, which particles exert on } df}$$

$$= \underline{r} \cdot (p \cdot \underline{n})\,df \qquad p: \text{pressure}$$

$$\rightsquigarrow W_{ext} = \int_{\partial V} d\underline{A}\; \underline{r} \cdot (p \cdot \underline{n}) \underset{\text{Gauss}}{=} 3pV$$

$$\boxed{2\langle E_{kin} \rangle = 3p \cdot V + W_{int}}$$

Internal virial:

2 particle interaction

$$\sum_i \underline{r}_i \cdot \underline{F}_i = \sum_i \sum_{j \neq i} \underline{r}_i \cdot \underline{F}_{ij}$$

$$= \frac{1}{2}\sum_i\sum_{j\neq i}\Big(\underline{r}_i\cdot\underline{F}_{ij} + \underline{r}_j\cdot\underbrace{\underline{F}_{ji}}_{-\underline{F}_{ij}\ (\text{Newton})}\Big)$$

$$= \frac{1}{2}\sum_i\sum_{j\neq i}\underline{r}_{ij}\cdot\underline{F}_{ij}$$

$$= \sum_i\sum_{j>i}\underline{r}_{ij}\cdot\underline{F}_{ij} \qquad \text{with } \underline{r}_{ij} = \underline{r}_i - \underline{r}_j$$

$$= -\sum_i\sum_{j>i}\underline{r}_{ij}\cdot\nabla_{ij}\,v_2(r_{ij}) = -\sum_i\sum_{j>i} w(r_{ij})$$

2-particle potential

Thus:

$$\boxed{pV = Nk_BT + \frac{1}{3}\sum_i \sum_{j>i} \langle w(r_{ij}) \rangle}$$

with interaction potential

$$\phi(\underline{r}_1, \ldots, \underline{r}_N) = \sum_i \sum_{j>i} v_2(|\underline{r}_i - \underline{r}_j|)$$

and

$$w(r) = r \frac{d}{dr} v_2(r)$$

Remark:

With calculation of $p$ and $T$, eq. of state $p = \Gamma(\rho, T)$ can be obtained, with density $\rho = \frac{N}{V}$

## 3.3.3. Transport Coefficients

Consider diffusion of a particle in a fluid, with diffusion coeff. D

$$\lim_{t\to\infty} \left\langle \left(\underline{r}_i(t) - \underline{r}_i(0)\right)^2 \right\rangle = 6Dt \quad (\text{in } 3 \text{ dim})$$

Now: $\underline{r}_i(t) = \underline{r}_i(0) + \int_0^t dt' \, \underline{v}_i(t')$

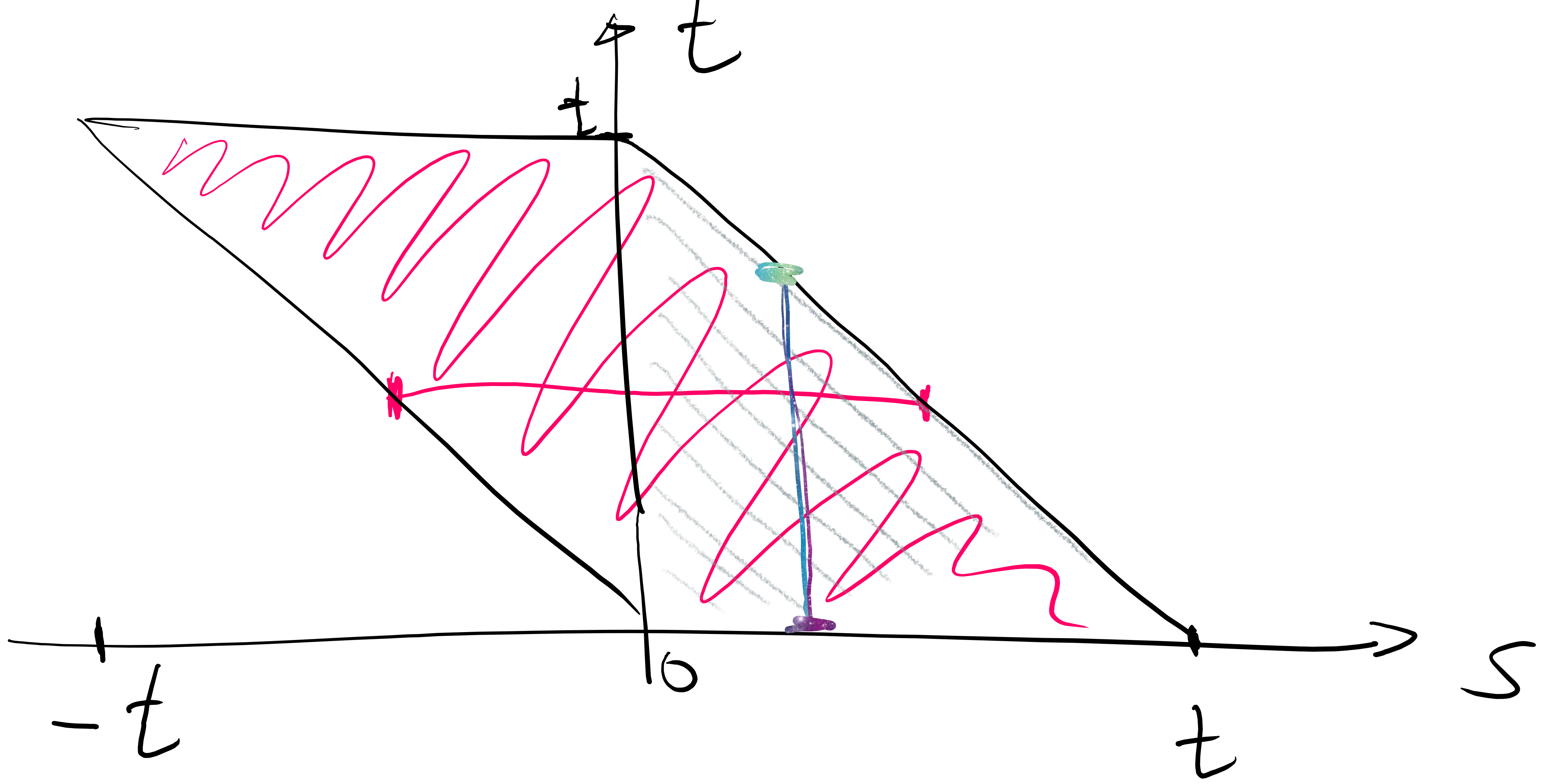
$$6Dt = \int_0^t dt' \int_0^t dt'' \langle \underline{v}_i(t') \cdot \underline{v}_i(t'') \rangle$$

$$\underset{\text{temp. homogeneity}}{=} \int_0^t dt' \int_0^t dt'' \langle \underline{v}_i(t''-t') \cdot \underline{v}_i(0) \rangle$$

$$\underset{s = t''-t'}{=} \int_0^t dt' \int_{-t'}^{t-t'} ds \, \underbrace{\langle \underline{v}_i(s) \cdot \underline{v}_i(0) \rangle}_{\text{symm. function of } s}$$

$$\int_0^t dt' \int_{-t'}^{t-t'} ds = 2 \int_0^t ds \int_0^{t-s} dt'$$

Area of integration:




$$6Dt = 2 \int_0^t ds\,(t-s) \cdot \langle \underline{v}_i(s) \cdot \underline{v}_i(0) \rangle$$

$$= 2t \int_0^t ds \left(1 - \frac{s}{t}\right) \underbrace{\langle \underline{v}_i(s) \cdot \underline{v}_i(0) \rangle}_{\xrightarrow[s\to\infty]{} s^{-\alpha} \text{ with } \alpha \geq (1)\, 2}$$

For $t \to \infty$

$$\boxed{D = \frac{1}{3} \int_0^\infty dt \, \langle \underline{v}_i(t) \cdot \underline{v}_i(0) \rangle}$$

## 3.3.4 Correlation functions

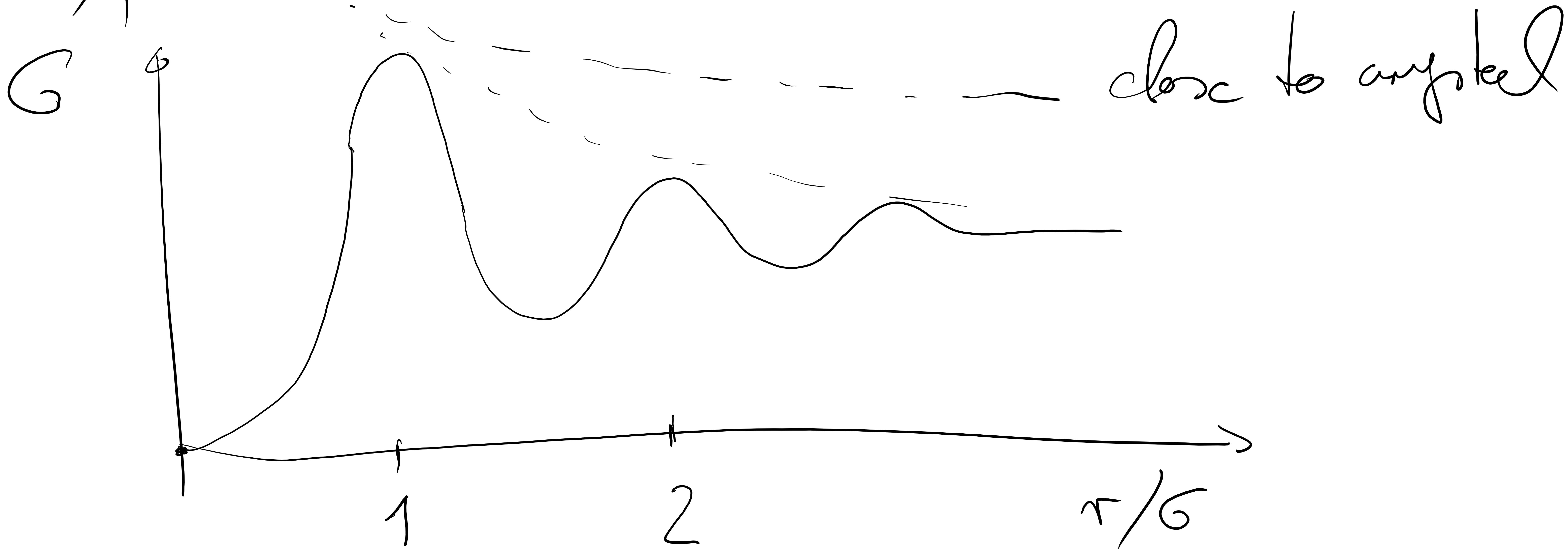
2-point correlation function

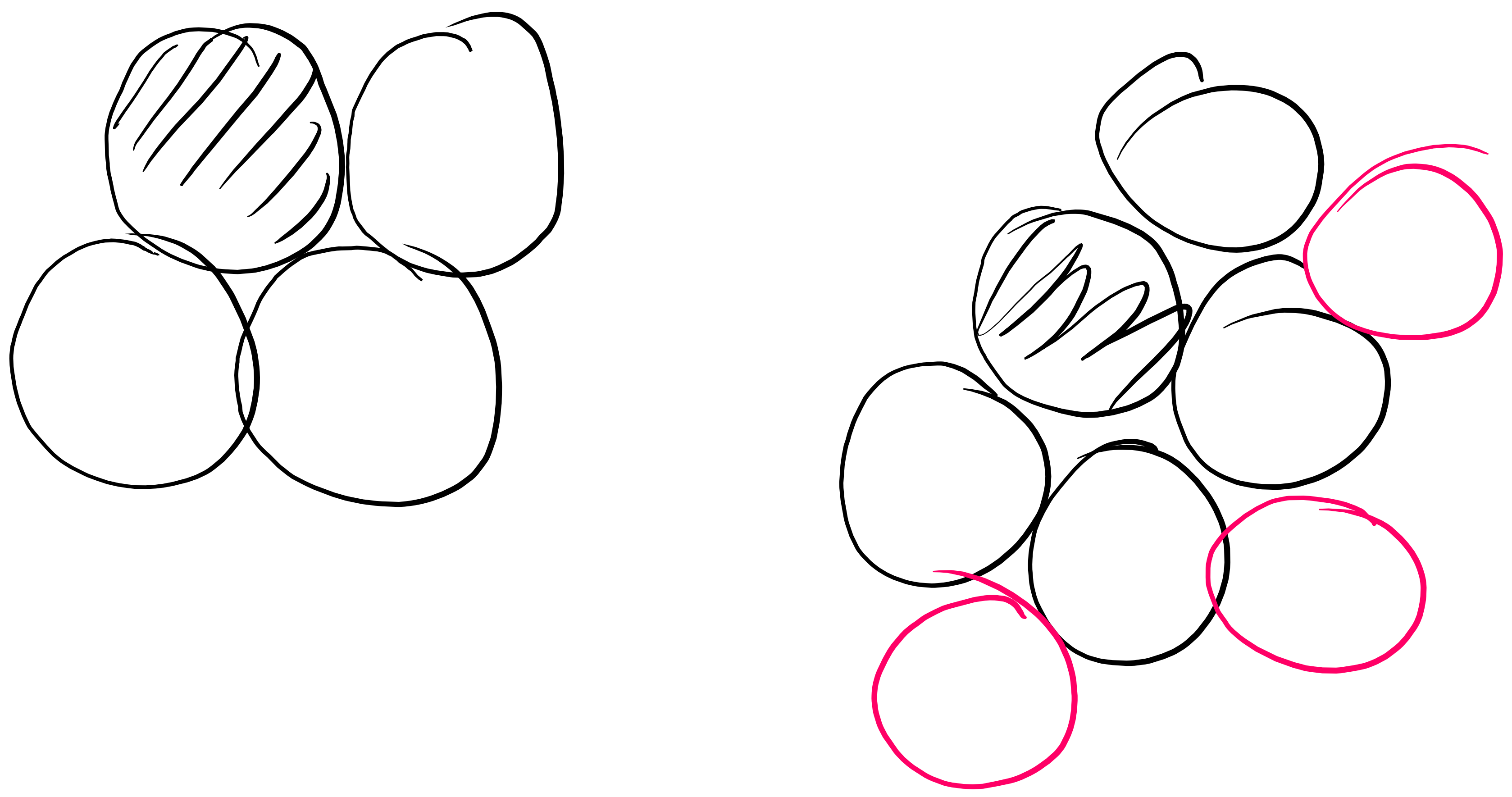
$$G(\underline{r}) = \frac{1}{\rho^2} \sum_i \sum_{j \neq i} \langle \delta(\underline{r}_i)\, \delta(\underline{r}_j - \underline{r}) \rangle$$

$$= \frac{V}{N^2} \sum_i \sum_{j \neq i} \langle \delta(\underline{r} - (\underline{r}_j - \underline{r}_i)) \rangle$$

Conditional probability to find a particle at $\underline{r}$, when other particle at origin j uses translational invariance of homogeneous systems

# Typical form for LJ-fluids





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