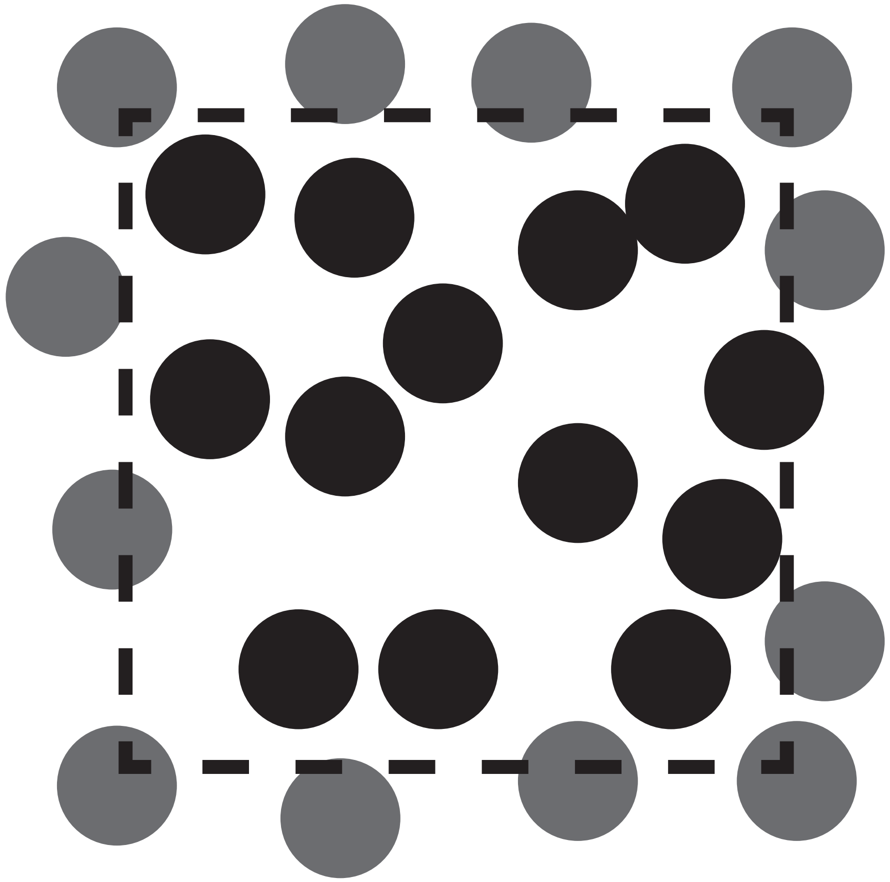
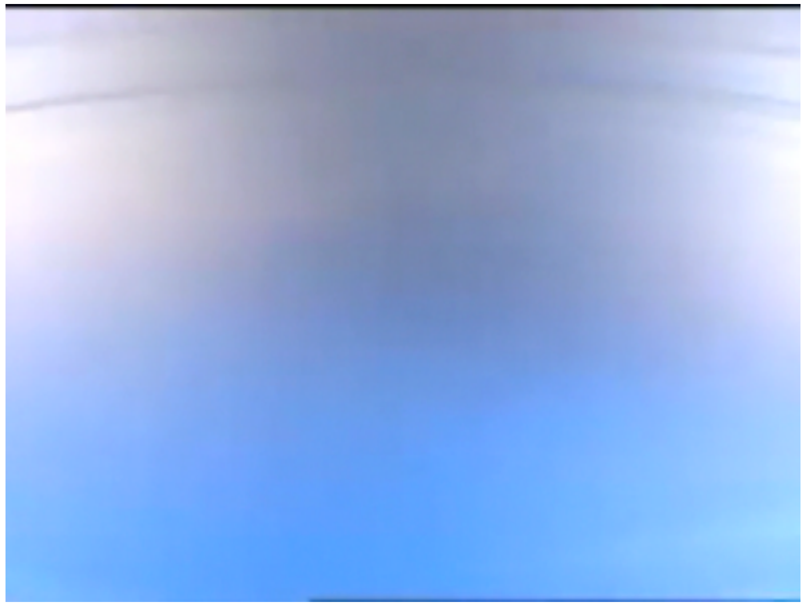
Statistical Mechanics of Liquids

Johan T. Padding
Université catholique de Louvain, Belgium



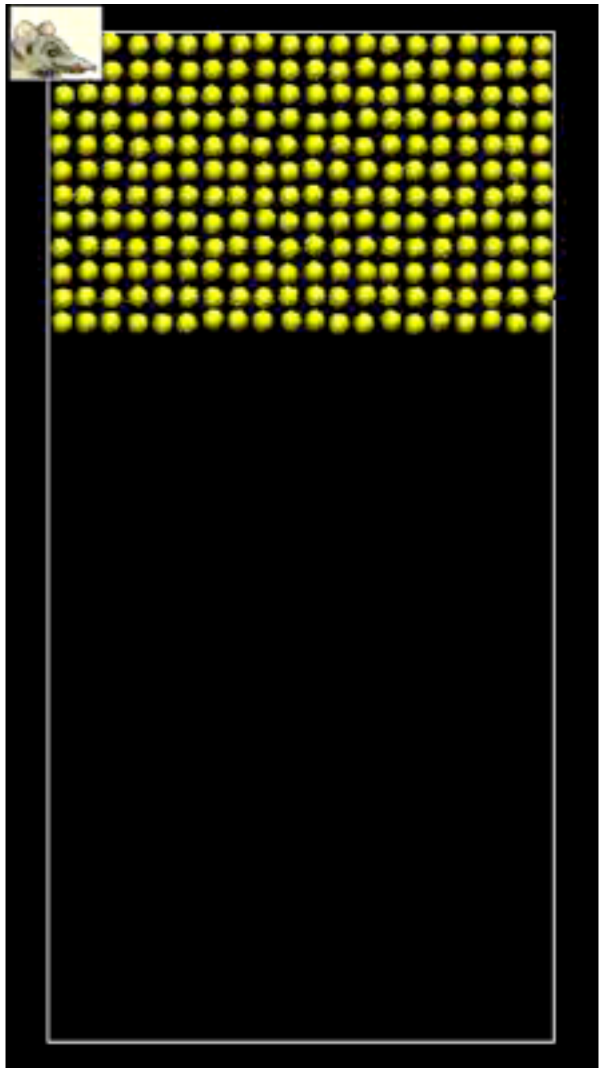
Simple liquids



near-spherical molecules
structure on molecular scale

water, light oils

Colloidal liquids



liquid with embedded particles
structure also on nano/micro scale

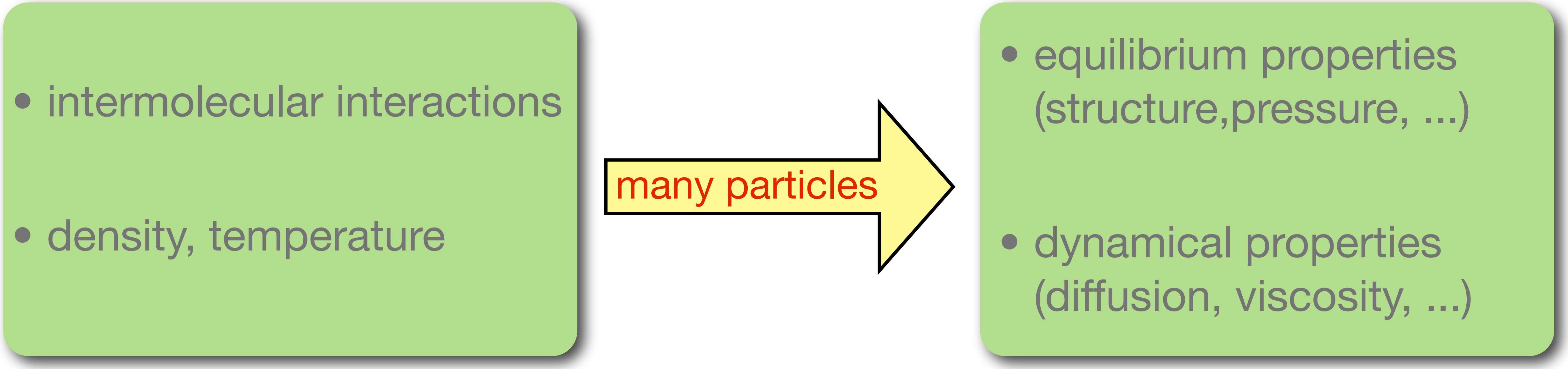
paint, milk, blood

Polymeric liquids

long, stringy molecules
random coils / fibers / helices

silly putty, actin, DNA solution

Statistical mechanics:
bridge between molecular and macroscopic world



- intermolecular interactions
- density, temperature

many particles

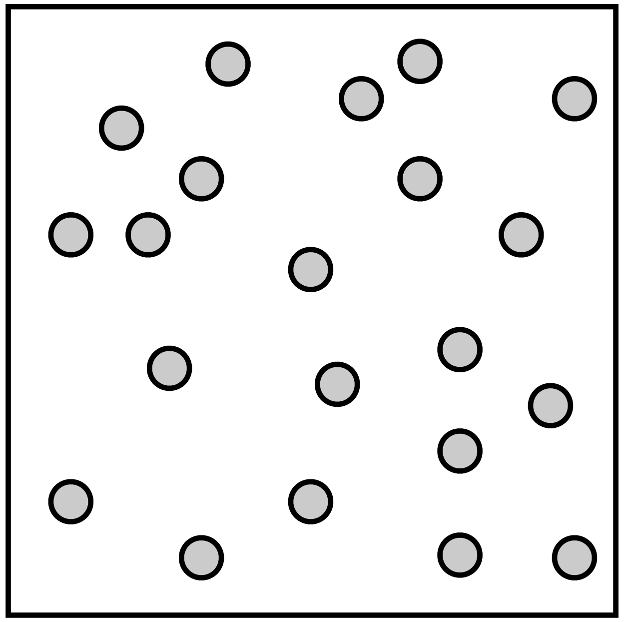
- equilibrium properties (structure,pressure, ...)
- dynamical properties (diffusion, viscosity, ...)

Statistical mechanics:

- does not predict individual molecular trajectories, but
- gives probabilities for large collections of particles, and
- yields measurable quantities as averages over ensembles

Chapter 1: Structure in liquids and gases

Probability density



- box volume *V*, with *N* identical (rigid) particles
- define number density $\rho = N/V$
- probability density to encounter system in configuration

  $$R^{6N} = \{\mathbf{r}_1, \mathbf{\Omega}_1, \ldots, \mathbf{r}_N, \mathbf{\Omega}_N\}$$

  is given by the Boltzmann distribution function:

$$\boxed{P(R^{6N}) = \frac{1}{Z} \exp\left(-\frac{\Phi(R^{6N})}{k_B T}\right),}$$

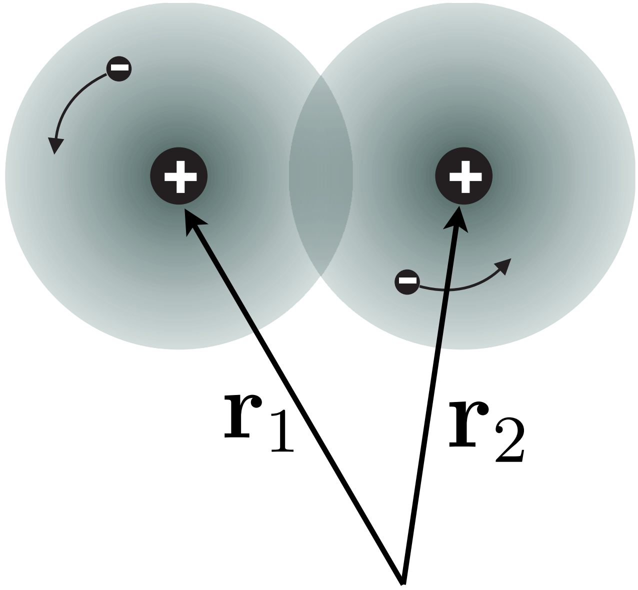
- $\Phi(R^{6N})$ is potential energy of the configuration - contains interactions

Pair interaction between two neutral atoms

- one pair of atoms, fixed nuclei:
  total ground state energy

$$\epsilon_0(\mathbf{r}_1,\mathbf{r}_2) = \epsilon_0(\mathbf{r}_1) + \epsilon_0(\mathbf{r}_2) + \varphi(\mathbf{r}_1,\mathbf{r}_2).$$

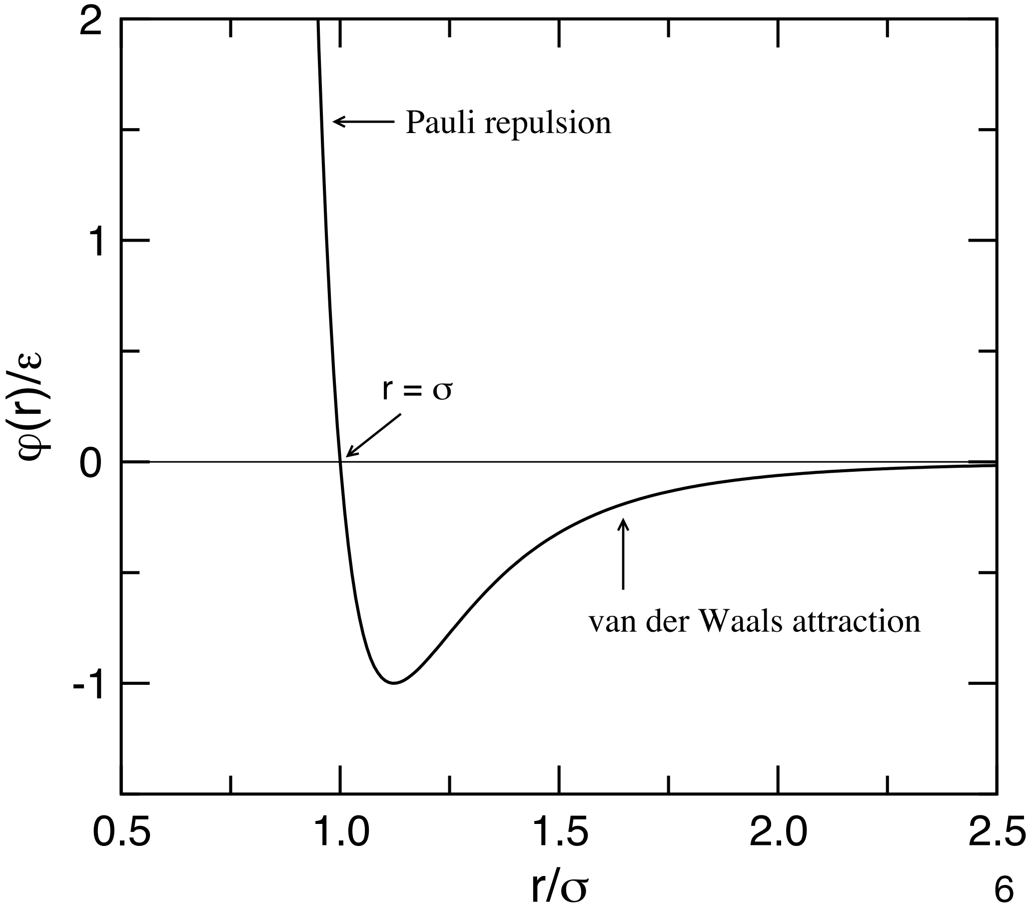
$\varphi(\mathbf{r}_1,\mathbf{r}_2)$ is interatomic interaction / potential



- Lennard-Jones potential describes both Van der Waals attraction and short range Pauli repulsion

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

argon: $\epsilon/k_B \;=\; 117.7\ \mathrm{K} \quad \sigma \;=\; 0.3504\ \mathrm{nm}$
krypton: $\epsilon/k_B \;=\; 164.0\ \mathrm{K} \quad \sigma \;=\; 0.3827\ \mathrm{nm}$



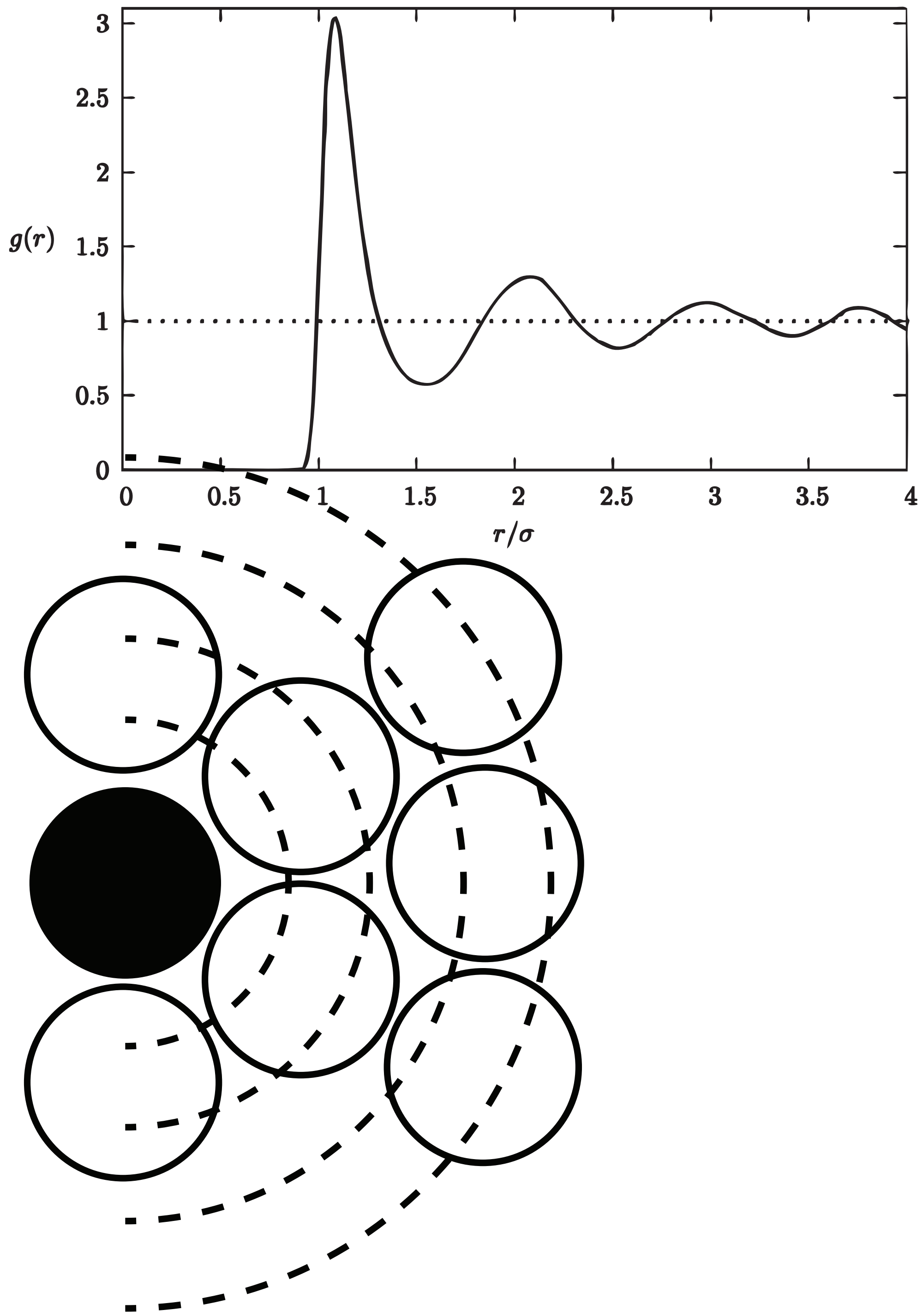
Pair sum approximation

- when >2 particles are present:

$$\Phi\left(\mathbf{r}_1, \ldots, \mathbf{r}_N\right) = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \varphi(r_{ij}). \qquad (1.5)$$

- in practice often a reasonable assumption

The radial distribution function *g(r)*



- molecular interactions cause correlations in their positions

- number of particles at a distance between *r* and *r*+d*r* from a given particle:

$$4\pi r^2 \frac{N}{V} g(r) \mathrm{d}r$$

- *N/V g(r)* is average number density at distance *r* from a given particle

- easy to see that

$$g(0) = 0$$
$$g(\infty) = 1$$

Statistical formulas for *g(r)*

- integrate Boltzman distribution function over all coordinates except first 2

$$P_{12}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{Z} \int \mathrm{d}^3 r_3 \ldots \int \mathrm{d}^3 r_N \exp\left(-\frac{\Phi(r^{3N})}{k_B T}\right), \tag{1.7}$$

$$P_{12}(\mathbf{r}, \mathbf{r}') = \frac{1}{Z} \int \mathrm{d}^3 r_3 \ldots \int \mathrm{d}^3 r_N \exp\left(-\frac{\Phi(r^{3N})}{k_B T}\right)\bigg|_{\mathbf{r}_1=\mathbf{r}, \mathbf{r}_2=\mathbf{r}'}. \tag{1.8}$$

- all particles are equal; prob. to have particle 1 at **r** and any other at **r**':

$$\sum_{j \neq 1} P_{1j}(\mathbf{r}, \mathbf{r}') = (N-1) P_{12}(\mathbf{r}, \mathbf{r}') \tag{1.9}$$

$$\frac{1}{V} \rho g(|\mathbf{r} - \mathbf{r}'|) = (N-1) P_{12}(\mathbf{r}, \mathbf{r}') \tag{1.10}$$

$$\rho^2 g(|\mathbf{r} - \mathbf{r}'|) = N(N-1) P_{12}(\mathbf{r}, \mathbf{r}'). \tag{1.11}$$

How do we get *g(r)* and what can we do with it?

- *g(r)* can be obtained from
  - modern liquid theory
  - computer simulation
  - experimentally, through microscopy (for large particles) or scattering

- knowing *g(r)* we can calculate non-entropic thermodynamic functions, *e.g.*
  - energy
  - compressibility
  - pressure

Relation between *g(r)* and energy

$$U = U^{\text{int}} + \frac{3}{2} N k_B T + \frac{1}{2} N \frac{N}{V} \int_0^\infty \mathrm{d}r 4\pi r^2 g(r) \varphi(r). \tag{1.12}$$

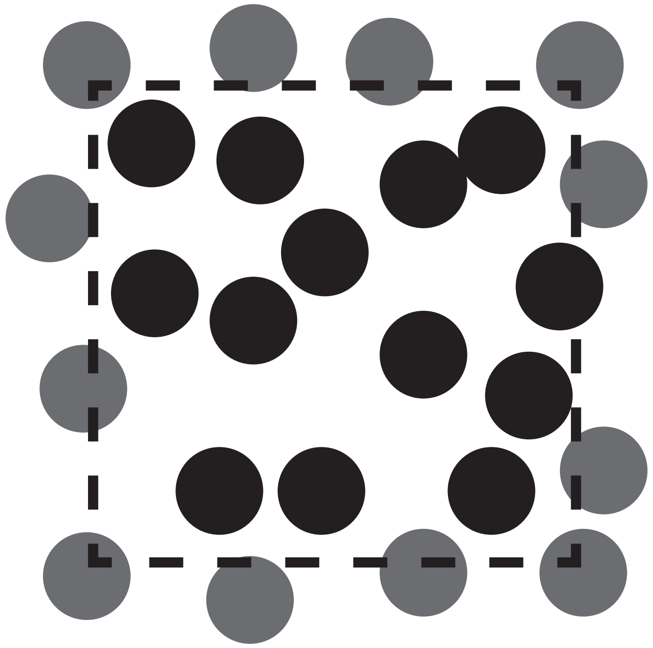
internal energies
of the molecules

average interaction energy
of one particular molecule
with all other molecules

translations
of the molecules

Relation between *g(r)* and compressibility [1/2]

- definition of isothermal compressibility: $\kappa_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,N}$



- compressibility is linked to spontaneous fluctuations in number of particles in an open volume *V*:

$$\langle N\rangle \rho k_B T \kappa_T = \left\langle (N - \langle N\rangle)^2 \right\rangle = \left\langle N^2 \right\rangle - \langle N\rangle^2$$

- assuming that *g(r)* is known, Eq. (1.11) gives us *almost* the needed expression:

$$\int_V \mathrm{d}^3 r_1 \int_V \mathrm{d}^3 r_2 \rho^2 g(r_{12}) = \langle N(N-1)\rangle = \left\langle N^2 \right\rangle - \langle N\rangle \,. \qquad (1.15)$$

Relation between *g(r)* and compressibility [2/2]

- correct by adding $\langle N \rangle$ and subtracting $\langle N \rangle^2$

$$\begin{aligned}\langle N \rangle \rho k_B T \kappa_T &= \rho \int_V \mathrm{d}^3 r_1 \rho \int_V \mathrm{d}^3 r_2 g(r_{12}) + \langle N \rangle - \rho \int_V \mathrm{d}^3 r_1 \rho \int_V \mathrm{d}^3 r_2 \\ &= \rho \int_V \mathrm{d}^3 r_1 \rho \int_V \mathrm{d}^3 r_2 \left(g(r_{12}) - 1\right) + \langle N \rangle \\ &= \rho \int_V \mathrm{d}^3 r_1 \rho \int_{\mathbb{R}^3} \mathrm{d}^3 r \left(g(r) - 1\right) + \langle N \rangle \qquad (1.16)\end{aligned}$$

- dividing by $\langle N \rangle$ we find the compressibility equation

$$\boxed{\rho k_B T \kappa_T = 1 + \rho \int_{\mathbb{R}^3} \mathrm{d}^3 r \left(g(r) - 1\right).} \qquad (1.17)$$

Relation between *g(r)* and pressure

- if density is not high, correlations between >2 particles may be ignored. Then

$$g(r) \approx \exp\{-\beta\varphi(r)\}$$

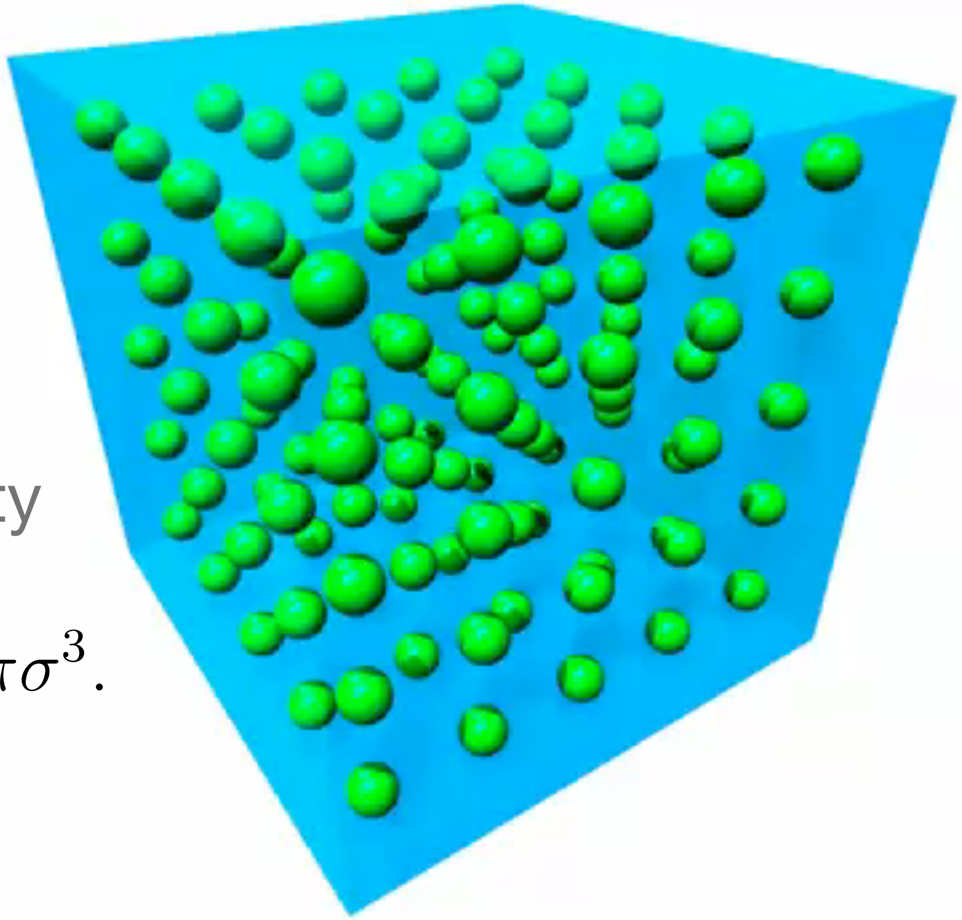
- at low density, virial equation is an accurate expression for pressure

$$PV = Nk_BT\left(1 + B_2(T)\frac{N}{V}\right)$$

- using simple mathematics (see Eq. 1.20) and the compressibility equation, we arrive at a microscopic expression for the second virial coefficient

$$\boxed{B_2(T) = -\frac{1}{2}\int_{\mathbb{R}^3} \mathrm{d}^3r\,\left(\mathrm{e}^{-\beta\varphi(r)} - 1\right).} \tag{1.21}$$

Example: hard-sphere fluid [1/2]



- Pair interaction $$\varphi(r) = \begin{cases} \infty & \text{for } r \le \sigma \\ 0 & \text{for } r > \sigma \end{cases}$$
- *g(r)* at low density $$g(r) \approx \begin{cases} 0 & \text{for } r \le \sigma \\ 1 & \text{for } r > \sigma \end{cases}$$
- second virial coefficient and pressure at low density

$$B_2 = -\frac{1}{2}\int \mathrm{d}^3 r \left(\mathrm{e}^{-\beta\varphi(r)} - 1\right) = 2\pi \int_0^\sigma \mathrm{d}r r^2 = \frac{2}{3}\pi\sigma^3.$$

$$P = \rho k_B T\,(1+4\eta) \qquad \eta = \tfrac{1}{6}\pi\rho\sigma^3$$

- pressure at more general densities (from simulations)

$$\frac{P}{\rho k_B T} = 1 + 4\eta + 10\eta^2 + 18.365\eta^3 + 28.24\eta^4 + 39.5\eta^5 + 56.6\eta^6 + \ldots$$

Example: hard sphere fluid [2/2]

- Carnahan and Starling noticed that the series

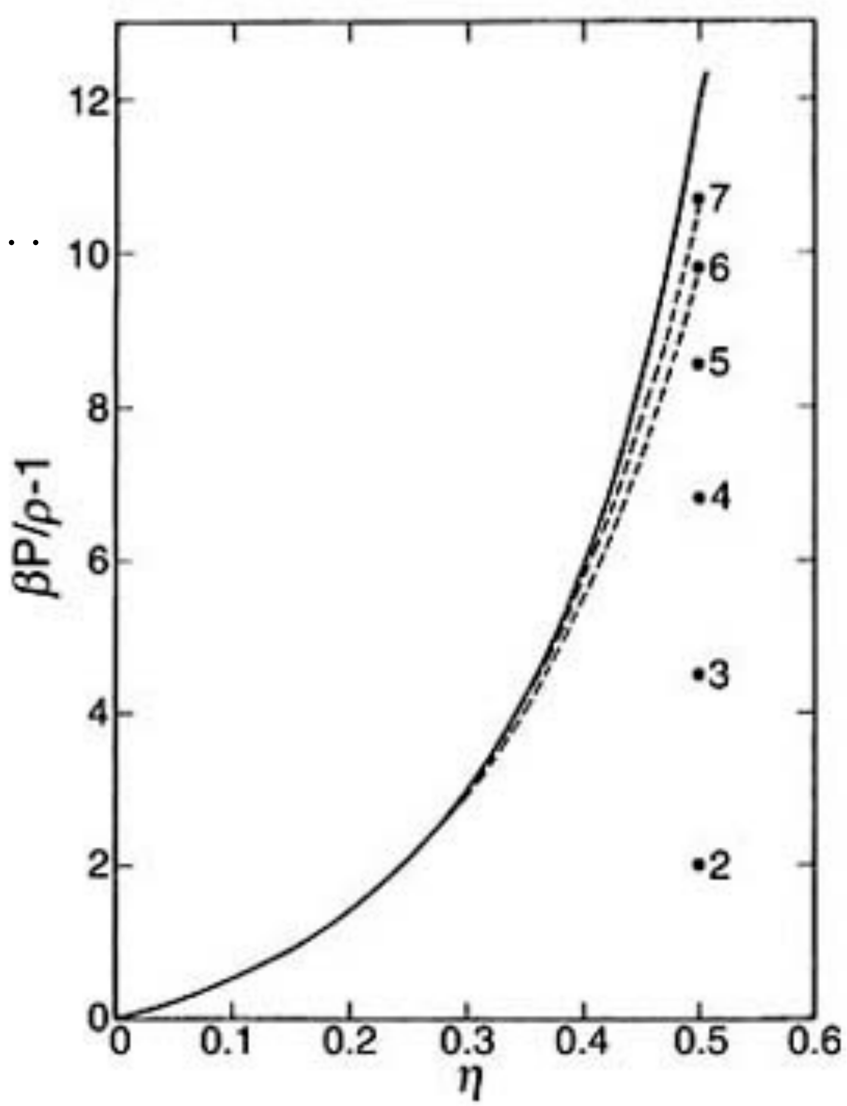
$$\frac{P}{\rho k_B T} \quad = \quad 1 + 4\eta + 10\eta^2 + 18.365\eta^3 + 28.24\eta^4 + 39.5\eta^5 + 56.6\eta^6 + \ldots$$

is quite close to

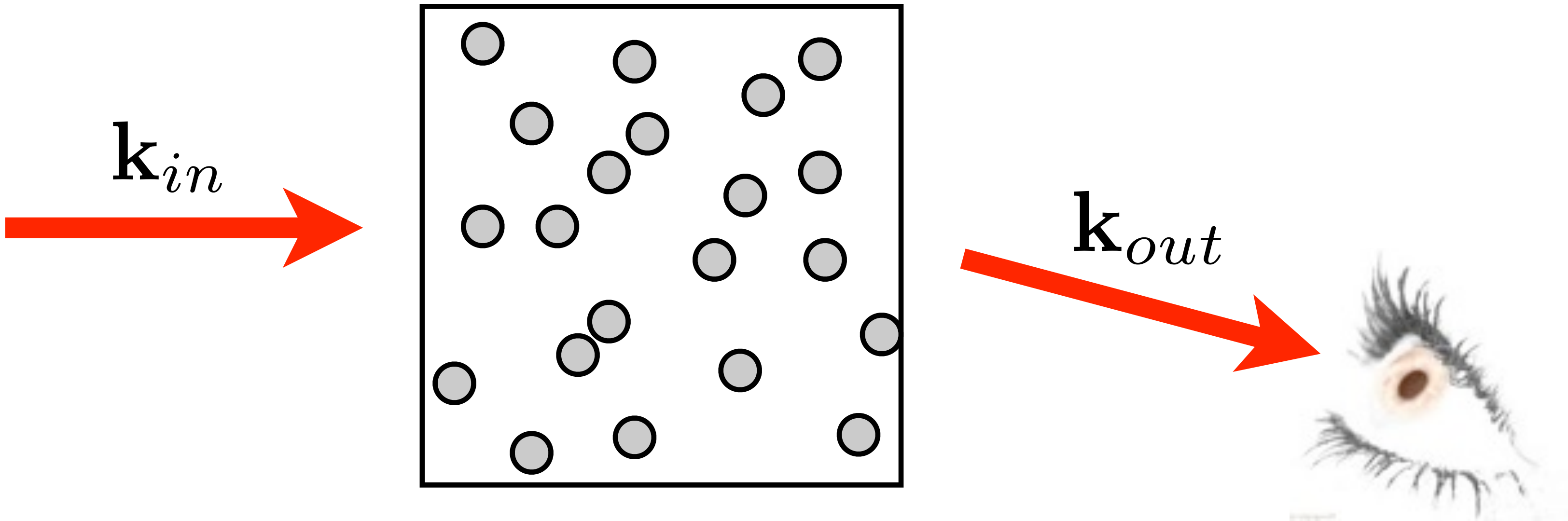
$$\frac{P}{\rho k_B T} = 1 + 4\eta + 10\eta^2 + 18\eta^3 + 28\eta^4 + 40\eta^5 + 54\eta^6 + \ldots$$

which can be summed analytically to

$$\frac{P}{\rho k_B T} = 1 + \sum_{n=1}^{\infty}(n^2 + 3n)\eta^n = \frac{1 + \eta + \eta^2 - \eta^3}{(1-\eta)^3}$$



Scattering and the structure factor



- illuminate a fluid containing spherical particles by a wave (wavevector $\mathbf{k}_{in}$)
  - X-ray or neutron scattering for atomic liquids
  - small-angle X-ray, small-angle neutron or light scattering for colloids
- measured intensity in the direction $\mathbf{k}_{out}$ depends on density fluctuations in the fluid, as probed by the structure factor $S(\mathbf{k})$, with $\mathbf{k} = \mathbf{k}_{out} - \mathbf{k}_{in}$

  N.B. intensity also depends on other factors such as wave polarization, scattering strength and form factor, i.e. internal particle structure

Fourier analysis of density fluctuations

- describe density fluctuations in fluid by means of Fourier components:

$$\begin{aligned}\rho(\mathbf{r}) &= \rho + \frac{1}{(2\pi)^3}\int \mathrm{d}^3k\ \hat{\rho}(\mathbf{k}) \exp\{-\mathrm{i}\mathbf{k}\cdot\mathbf{r}\}\,, \\ \hat{\rho}(\mathbf{k}) &= \int \mathrm{d}^3r\ \{\rho(\mathbf{r})-\rho\} \exp\{\mathrm{i}\mathbf{k}\cdot\mathbf{r}\}\,.\end{aligned}$$

- corresponding microscopic variable

$$\hat{\rho}(\mathbf{k}) = \int \mathrm{d}^3r \left\{\sum_{j=1}^{N} \delta\left(\mathbf{r}-\mathbf{r}_j\right) - \rho\right\} \exp\{\mathrm{i}\mathbf{k}\cdot\mathbf{r}\}$$

$$= \sum_{j=1}^{N} \exp\{\mathrm{i}\mathbf{k}\cdot\mathbf{r}_j\} - \rho\int \mathrm{d}^3r \exp\{\mathrm{i}\mathbf{k}\cdot\mathbf{r}\}$$

$$= \sum_{j=1}^{N} \exp\{\mathrm{i}\mathbf{k}\cdot\mathbf{r}_j\} - (2\pi)^3\rho\delta(\mathbf{k}).$$

Relation between structure factor and *g*(*r*)

- (static) scattering experiments measure amplitudes of density fluctuations:

$$\boxed{S(\mathbf{k}) \equiv \frac{1}{N}\left\langle \hat{\rho}(\mathbf{k})\hat{\rho}^*(\mathbf{k})\right\rangle .}$$

- the structure factor *S*(**k**) is essentially a Fourier transform of *g*(*r*)

$$\begin{aligned} S(\mathbf{k}) &= \frac{1}{N}\left\langle \sum_{j=1}^{N}\sum_{k=1}^{N} \exp\left\{i\mathbf{k}\cdot(\mathbf{r}_j-\mathbf{r}_k)\right\}\right\rangle - \frac{\rho^2}{N}\int \mathrm{d}^3r \int \mathrm{d}^3r' \exp\left\{\mathrm{i}\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')\right\} \\ &= 1+\frac{1}{N}\left\langle \sum_{j=1}^{N}\sum_{k\neq j}^{N} \exp\left\{i\mathbf{k}\cdot(\mathbf{r}_j-\mathbf{r}_k)\right\}\right\rangle - \rho\int \mathrm{d}^3r \exp\left\{\mathrm{i}\mathbf{k}\cdot\mathbf{r}\right\} \\ &= 1+\rho\int \mathrm{d}^3r\,[g(r)-1]\exp\left\{\mathrm{i}\mathbf{k}\cdot\mathbf{r}\right\}. \qquad (1.34) \end{aligned}$$

- so you can measure the compressibility of a fluid without touching it!

$$\rho k_B T \kappa_T = \lim_{k\to 0} S(k).$$

Summary of chapter 1

- the structure of fluids is determined by the interparticle interactions

$$\boxed{P(R^{6N}) = \frac{1}{Z} \exp\left(-\frac{\Phi(R^{6N})}{k_B T}\right) ,} \tag{1.1}$$

- radial distribution function *g*(*r*): density at distance *r* from a given particle, normalised by the average density *N*/*V*. Knowing *g*(*r*), we can calculate e.g.
  - total energy
  - pressure
  - compressibility

$$\boxed{\rho k_B T \kappa_T = 1 + \rho \int_{\mathbb{R}^3} \mathrm{d}^3 r \, (g(r) - 1) \, .}$$

- scattering experiments probe Fourier components of density fluctuations

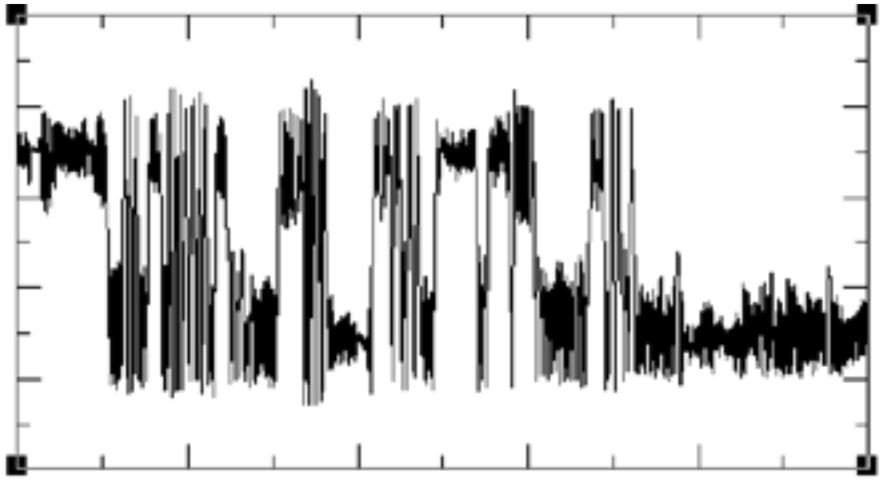
$$\boxed{S(\mathbf{k}) \equiv \frac{1}{N} \langle \hat{\rho}(\mathbf{k}) \hat{\rho}^*(\mathbf{k}) \rangle \, .}$$

Chapter 2: Time dependent properties of liquids

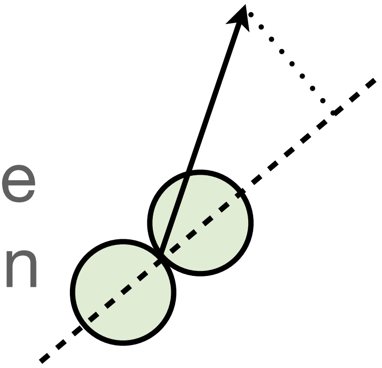
Dynamic properties of liquids

- even when a liquid appears to be at rest macroscopically, microscopically the molecules are continually changing their positions and velocities

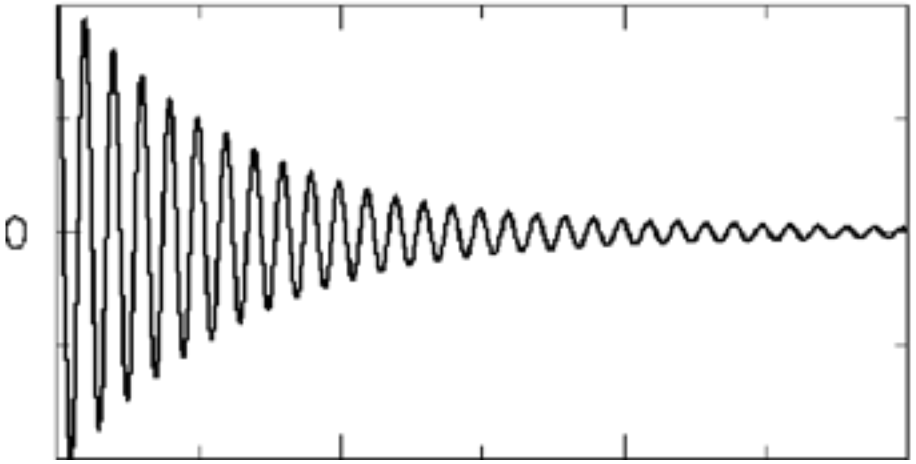
- therefore most observable quantities fluctuate in time



e.g. velocity of a diatomic particle (in a fluid) along its bond direction



- characterise the dynamics of fluctuations by time correlation functions



$$\langle A(t)A(0)\rangle = \lim_{T\to\infty}\frac{1}{T}\int_0^T \mathrm{d}\tau A(\tau+t)A(\tau).$$

$$\langle A(t)B(0)\rangle = \lim_{T\to\infty}\frac{1}{T}\int_0^T \mathrm{d}\tau A(\tau+t)B(\tau).$$

Properties of time-correlation functions

- it is easy to see that $\langle A(t)A(0)\rangle$ decays from $\langle A^2\rangle$ at t=0 to $\langle A\rangle^2$ for large times

- in equilibrium, the origin of time is irrelevant, so

  $$\frac{\mathrm{d}}{\mathrm{d}s}\langle A(t+s)B(s)\rangle = \left\langle \dot{A}(t+s)B(s)\right\rangle + \left\langle A(t+s)\dot{B}(s)\right\rangle = 0$$

  which gives the important property

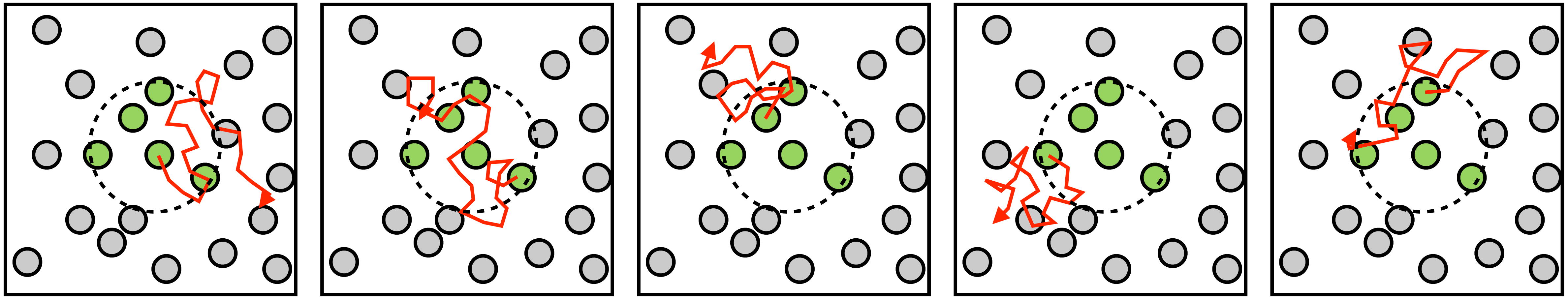
$$\boxed{\left\langle \dot{A}(t+s)B(s)\right\rangle = -\left\langle A(t+s)\dot{B}(s)\right\rangle} \tag{2.4}$$

- with this we can also derive

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle A(t)A(0)\rangle\bigg|_{t=0} = 0, \tag{2.5}$$

$$\frac{\mathrm{d}^2}{\mathrm{d}t^2}\langle A(t+s)B(s)\rangle = -\left\langle \dot{A}(t+s)\dot{B}(s)\right\rangle . \tag{2.6}$$

Example: self-diffusion



- at t=0 we label some particles in a dot of fluid; each particle will diffuse away via a different path

- define conditional probability P(**r**,t) that a labeled particle is at **r** at time t, given it was at **r**(0) at time t=0 $\longrightarrow$ $P(\mathbf{r},0) = \delta(\mathbf{r}-\mathbf{r}(0))$

- Fick's law states that $$\frac{\partial P(\mathbf{r},t)}{\partial t} = D\nabla^2 P(\mathbf{r},t)$$

D = self-diffusion coefficient $\left[\frac{m^2}{s}\right]$

Mean-square displacement and Einstein equation

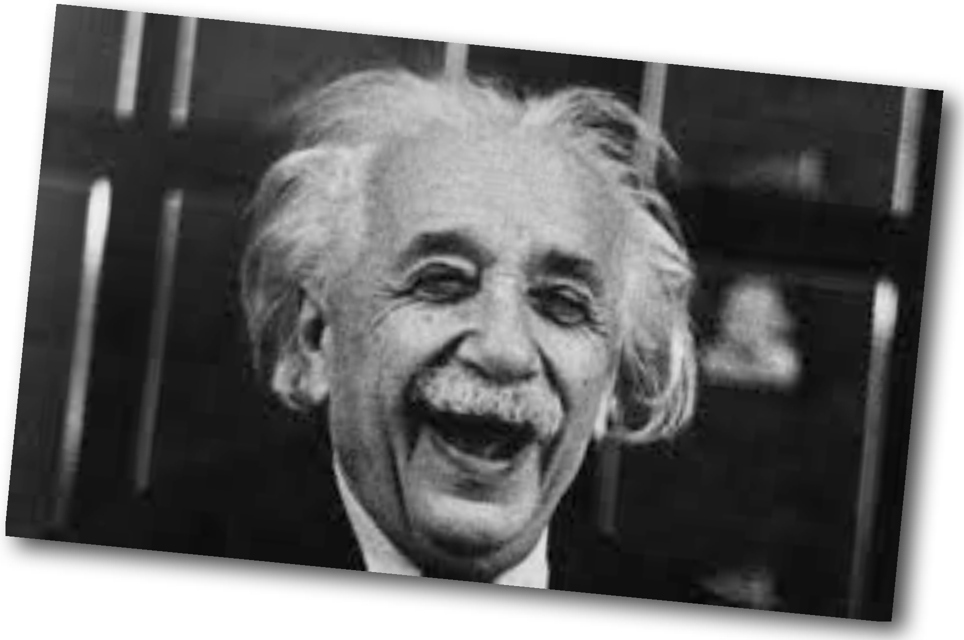
- averaging over all possible paths, we find:

$$\begin{aligned}
\frac{\mathrm{d}}{\mathrm{d}t}\left\langle |\mathbf{r}(t)-\mathbf{r}(0)|^2 \right\rangle &= \int \mathrm{d}^3r\, |\mathbf{r}(t)-\mathbf{r}(0)|^2 \,\frac{\partial P(\mathbf{r},t)}{\partial t} \\
&= D\int \mathrm{d}^3r\, |\mathbf{r}(t)-\mathbf{r}(0)|^2 \,\nabla^2 P(\mathbf{r},t) \\
&= D\int \mathrm{d}^3r P(\mathbf{r},t)\nabla^2 r^2 \\
&= 6D,
\end{aligned}$$

- for a real fluid, Fick's law only holds at large times (after many collisions)

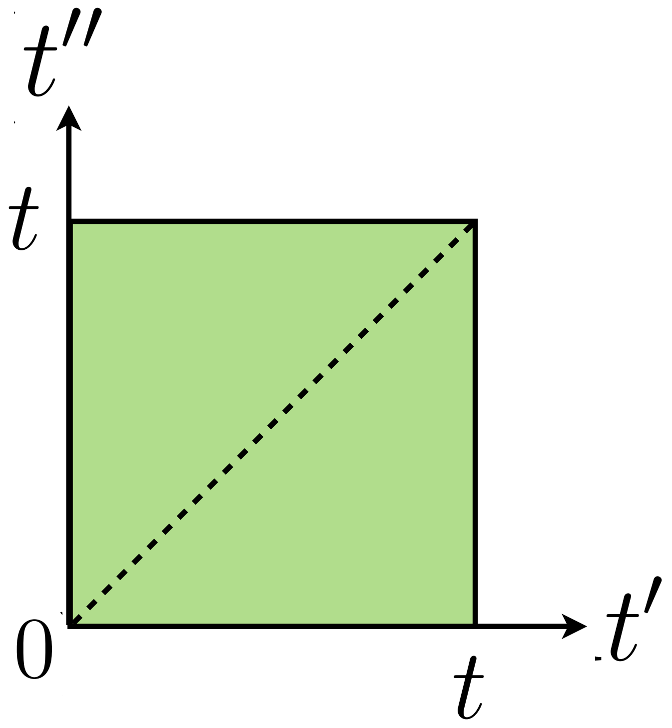
$$\boxed{D = \lim_{t\to\infty} \frac{1}{6t}\left\langle |\mathbf{r}(t)-\mathbf{r}(0)|^2 \right\rangle .}$$

Einstein equation



Connection with the velocity autocorrelation

$$
\begin{aligned}
\left\langle |\mathbf{r}(t)-\mathbf{r}(0)|^2 \right\rangle &= \int_0^t \mathrm{d}t' \int_0^t \mathrm{d}t'' \left\langle \mathbf{v}(t')\cdot\mathbf{v}(t'')\right\rangle \\
&= 2\int_0^t \mathrm{d}t' \int_0^{t'} \mathrm{d}t'' \left\langle \mathbf{v}(t')\cdot\mathbf{v}(t'')\right\rangle \\
&= 2\int_0^t \mathrm{d}t' \int_0^{t'} \mathrm{d}t'' \left\langle \mathbf{v}(t'-t'')\cdot\mathbf{v}(0)\right\rangle \\
&= 2\int_0^t \mathrm{d}t' \int_0^{t'} \mathrm{d}\tau \left\langle \mathbf{v}(\tau)\cdot\mathbf{v}(0)\right\rangle \\
&= 2\int_0^t \mathrm{d}\tau (t-\tau) \left\langle \mathbf{v}(\tau)\cdot\mathbf{v}(0)\right\rangle .
\end{aligned}
$$

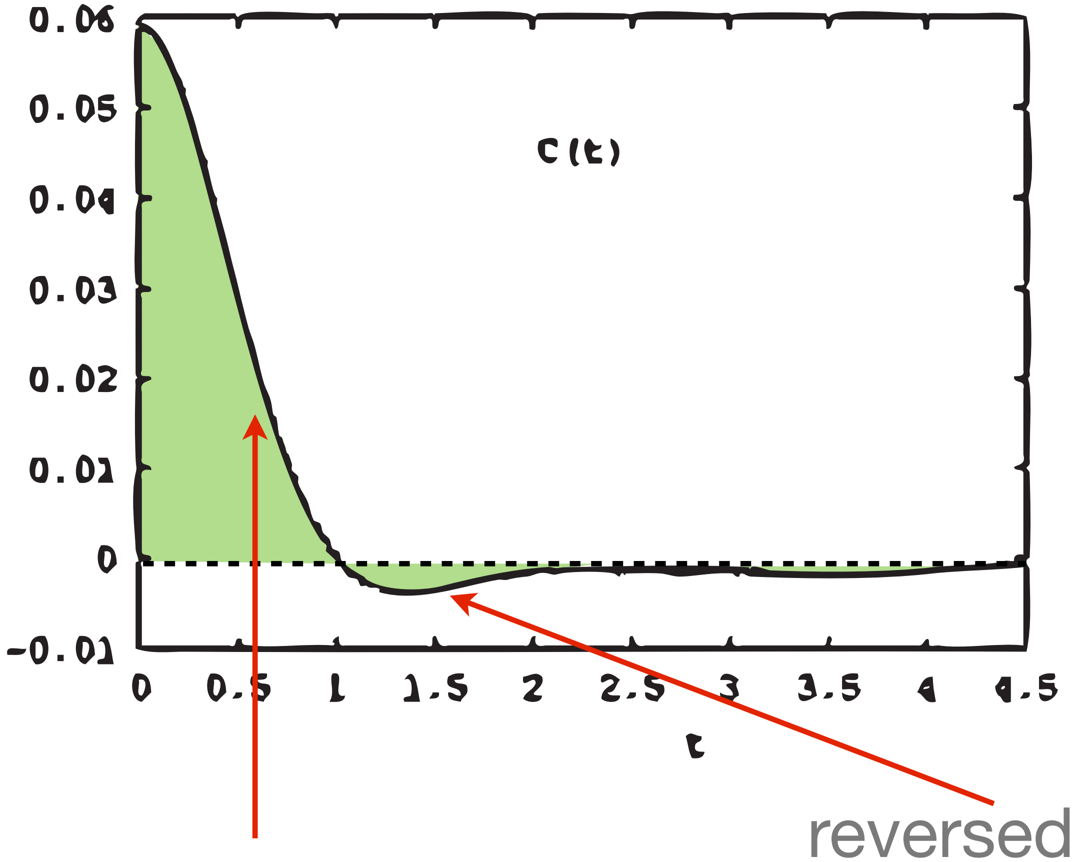


- comparing with the Einstein equation, we find

$$\boxed{D = \frac{1}{3}\int_0^\infty \mathrm{d}t \left\langle \mathbf{v}(t)\cdot\mathbf{v}(0)\right\rangle .} \tag{2.12}$$

this is the Green-Kubo relation for the self-diffusion coefficient

Velocity autocorrelation in a Lennard-Jones fluid



reversed velocity

particle collides with another
particle in front of it

$$\boxed{D = \frac{1}{3}\int_0^\infty \mathrm{d}t\,\langle \mathbf{v}(t)\cdot\mathbf{v}(0)\rangle}$$

Onsager's regression hypothesis

"the average decay of fluctuations is,
at large times and on macroscopic scales,
governed by the corresponding macroscopic laws"

$$\langle A(t) \rangle_{A(0)} = A(0)\alpha(t)$$

- macroscopic laws [the ones that determine α(*t*)] usually apply to non-equilibrium situations
- multiplying by *A*(0) and averaging over all initial conditions we get a useful equilibrium expression:

$$\boxed{\langle A(t)A(0) \rangle = \langle A^2 \rangle \, \alpha(t).} \qquad (2.14)$$

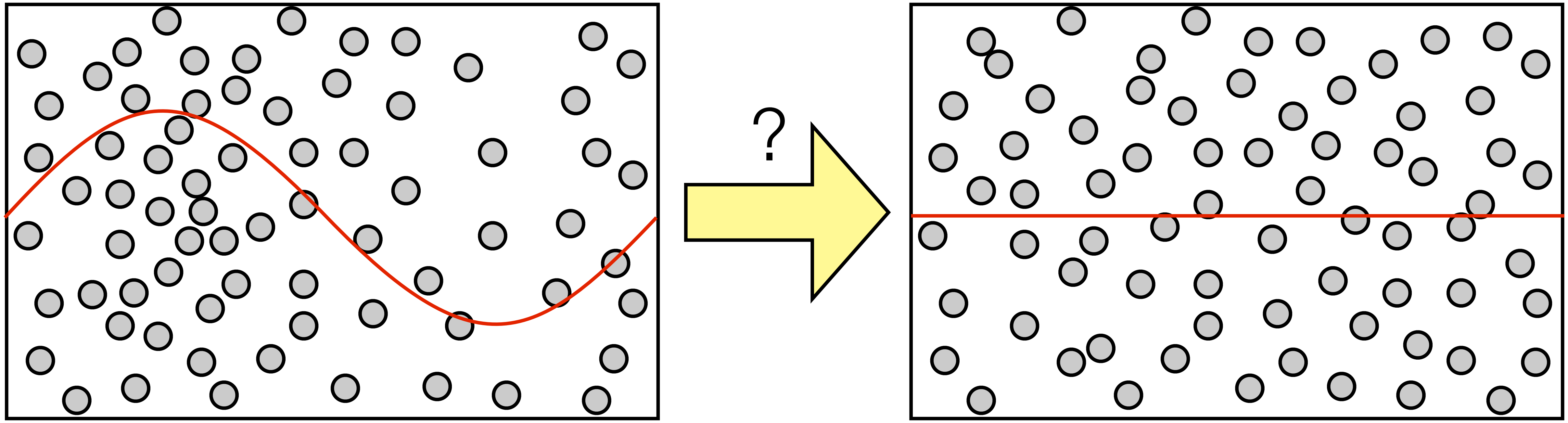
Application 1: collective diffusion

- we're interested in the time dependence of density fluctuations

$$\begin{aligned}\rho(\mathbf{r},t) &= \rho + \frac{1}{(2\pi)^3}\int \mathrm{d}^3k\ \hat{\rho}(\mathbf{k},t)\exp\{-\mathrm{i}\mathbf{k}\cdot\mathbf{r}\}\,,\\ \hat{\rho}(\mathbf{k},t) &= \int \mathrm{d}^3r\ \{\rho(\mathbf{r},t)-\rho\}\exp\{\mathrm{i}\mathbf{k}\cdot\mathbf{r}\}\,.\end{aligned}$$

- in order to apply Onsager, let's first study the decay of a macroscopic sinusoidal density fluctuation prepared at t=0

$$\rho(\mathbf{r},0) = \rho + \frac{1}{(2\pi)^3}\hat{\rho}(\mathbf{k},0)\exp\{-\mathrm{i}\mathbf{k}\cdot\mathbf{r}\}$$



Decay of macroscopic density fluctuations

- Fick's law applies here too, but now *D* is the collective diffusion coefficient

$$\begin{aligned}
\frac{\partial}{\partial t}\left[\frac{1}{(2\pi)^3}\hat{\rho}(\mathbf{k},t)\exp\{-\mathrm{i}\mathbf{k}\cdot\mathbf{r}\}\right] &= D\nabla^2\left[\frac{1}{(2\pi)^3}\hat{\rho}(\mathbf{k},t)\exp\{-\mathrm{i}\mathbf{k}\cdot\mathbf{r}\}\right], \\
\exp\{-\mathrm{i}\mathbf{k}\cdot\mathbf{r}\}\frac{\partial\hat{\rho}(\mathbf{k},t)}{\partial t} &= -D(k)k^2\hat{\rho}(\mathbf{k},t)\exp\{-\mathrm{i}\mathbf{k}\cdot\mathbf{r}\}, \\
\hat{\rho}(\mathbf{k},t) &= \hat{\rho}(\mathbf{k},0)\exp\left\{-D(k)k^2t\right\}. \qquad (2.18)
\end{aligned}$$

- a macroscopic density fluctuation decays exponentially (at large times) with a relaxation time given by

$$\tau(k) = \frac{1}{D(k)k^2}$$

short wavelength (large *k*) fluctuations decay rapidly
long wavelength (small *k*) fluctuations decay slowly

(relaxing a long wavelength inhomogeneity requires transport of fluid particles over large length scales, which is a slow process)

Microscopic equation for collective *D* [1/2]

- microscopic expression for density Fourier component:

$$\begin{aligned}\hat{\rho}(\mathbf{k},t) &= \int \mathrm{d}^3 r \left\{\sum_j \delta\left(\mathbf{r}-\mathbf{r}_j(t)\right) - \rho\right\} \exp\left\{\mathrm{i}\mathbf{k}\cdot\mathbf{r}\right\} \\ &= \sum_{j=1}^{N} \exp\left\{\mathrm{i}\mathbf{k}\cdot\mathbf{r}_j(t)\right\} - (2\pi)^3 \rho\delta(\mathbf{k}). \qquad (2.19)\end{aligned}$$

- Onsager: $\langle \hat{\rho}(\mathbf{k},t)\hat{\rho}^*(\mathbf{k},0)\rangle = \langle \hat{\rho}(\mathbf{k},0)\hat{\rho}^*(\mathbf{k},0)\rangle \exp\left\{-D(k)k^2 t\right\}$

then
$$\begin{aligned}-\frac{1}{k^2}\frac{\mathrm{d}}{\mathrm{d}t}\langle \hat{\rho}(\mathbf{k},t)\hat{\rho}^*(\mathbf{k},0)\rangle &= \langle \hat{\rho}(\mathbf{k},0)\hat{\rho}^*(\mathbf{k},0)\rangle D(k) \\ -\frac{1}{k^2}\int_0^t \mathrm{d}\tau \frac{\mathrm{d}^2}{\mathrm{d}t^2}\langle \hat{\rho}(\mathbf{k},\tau)\hat{\rho}^*(\mathbf{k},0)\rangle &= \langle \hat{\rho}(\mathbf{k},0)\hat{\rho}^*(\mathbf{k},0)\rangle D(k)\end{aligned}$$

using $\frac{\mathrm{d}^2}{\mathrm{d}t^2}\langle A(t+s)B(s)\rangle = -\left\langle \dot{A}(t+s)\dot{B}(s)\right\rangle$ we can write this as

$$\int_0^t \mathrm{d}\tau \frac{1}{k^2}\left\langle \dot{\hat{\rho}}(\mathbf{k},\tau)\dot{\hat{\rho}}^*(\mathbf{k},0)\right\rangle = \langle \hat{\rho}(\mathbf{k},0)\hat{\rho}^*(\mathbf{k},0)\rangle D(k)$$

Microscopic equation for collective *D* [2/2]

- choose specific orientation for wavevector, say $\mathbf{k} = k\hat{\mathbf{e}}_z$:

$$\int_0^t \mathrm{d}\tau \left\langle \sum_i \sum_j v_{iz}(\tau) v_{jz}(0) \exp\left\{\mathrm{i}k\left(z_i(\tau) - z_j(0)\right)\right\} \right\rangle = \langle \hat{\rho}(\mathbf{k},0)\hat{\rho}^*(\mathbf{k},0)\rangle\, D(k).$$

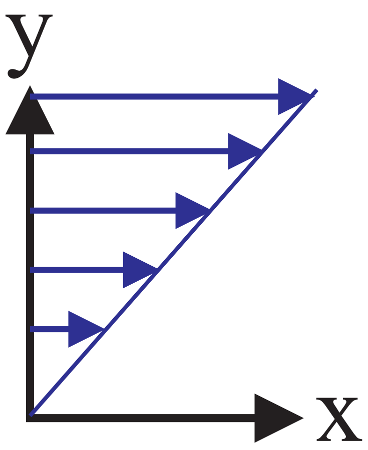
- we find the Green-Kubo relation for the collective diffusion coefficient:

$$\boxed{D(k) = \frac{1}{S(k)} \int_0^\infty \mathrm{d}t \frac{1}{N} \left\langle \sum_i \sum_j v_{iz}(t) v_{jz}(0) \exp\left\{\mathrm{i}k\left(z_i(t) - z_j(0)\right)\right\} \right\rangle}$$

compare this with the Green-Kubo relation for the self-diffusion coefficient:

$$D^{self} = \int_0^\infty \frac{1}{N} \left\langle \sum_i v_{iz}(t) v_{iz}(0) \right\rangle$$

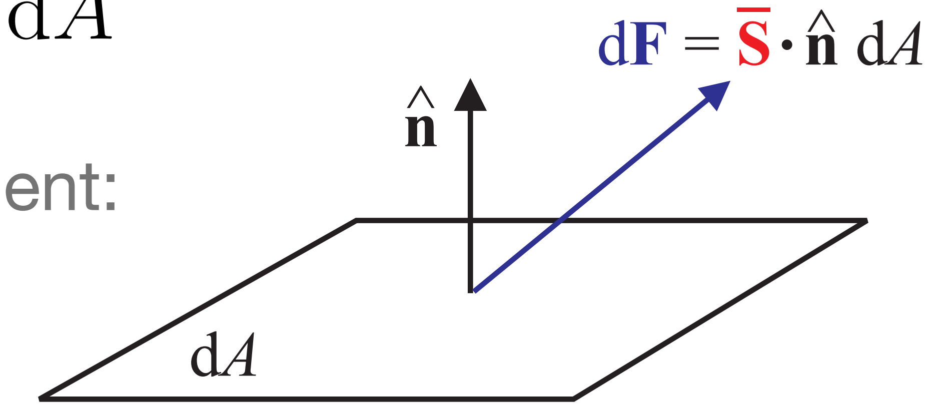
Application 2: shear viscosity



- suppose the fluid has a macroscopic velocity (flow) field $\mathbf{v}\left(\mathbf{r}\right)$
- neighbouring fluid elements exert forces on each other
  - friction due to velocity differences
  - momentum exchange due to migration of particles
  - momentum exchange due to interactions between particles
- all these forces can conveniently be summarized in the stress tensor $\bar{\mathbf{S}}$

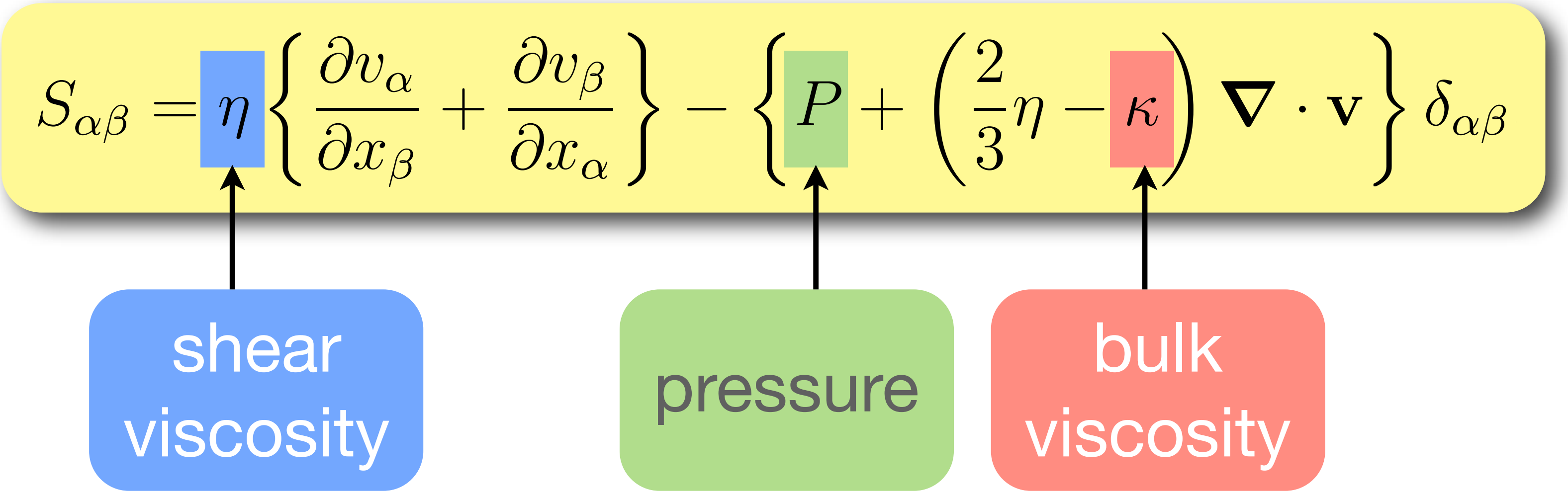
$\bar{\mathbf{S}}$ transforms the normal $\hat{\mathbf{n}}$ of a surface element $\mathrm{d}A$ to the force $\mathrm{d}\mathbf{F}$ exerted by the fluid below the surface element on the fluid above the fluid element:

$$\mathrm{d}F_\alpha = -\sum_\beta S_{\alpha\beta}\hat{n}_\beta \mathrm{d}A = -\left(\bar{\mathbf{S}}\cdot\hat{\mathbf{n}}\right)_\alpha \mathrm{d}A$$



Stress tensor for simple fluids

- simple fluids can be described by assuming that stress tensor consists of a
  - part which is independent of the flow velocity, and a
  - part which depends linearly on the instantaneous derivatives $\partial v_\alpha / \partial x_\beta$



$$S_{\alpha\beta} = \eta \left\{ \frac{\partial v_\alpha}{\partial x_\beta} + \frac{\partial v_\beta}{\partial x_\alpha} \right\} - \left\{ P + \left(\frac{2}{3}\eta - \kappa \right) \boldsymbol{\nabla} \cdot \mathbf{v} \right\} \delta_{\alpha\beta}$$

shear viscosity

pressure

bulk viscosity

- N.B. for complex fluids such as polymers, the stress tensor may actually depend on the history of fluid flow

Navier-Stokes and Stokes equations

- law of conservation of momentum + law of conservation of mass:

$$m\rho\left(\cancel{\mathbf{v}\cdot\nabla}+\frac{\partial}{\partial t}\right)\mathbf{v}=\nabla\cdot\bar{\mathbf{S}}$$

Navier-Stokes equation

- we focus on incompressible flow of simple fluids at small velocities:

$$S_{\alpha\beta}=\eta\left\{\frac{\partial v_\alpha}{\partial x_\beta}+\frac{\partial v_\beta}{\partial x_\alpha}\right\}-\left\{P+\cancel{\left(\frac{2}{3}\eta-\kappa\right)\boldsymbol{\nabla}\cdot\mathbf{v}}\right\}\delta_{\alpha\beta}$$

$$\begin{aligned}m\rho\frac{\partial\mathbf{v}}{\partial t}&=\eta\nabla^2\mathbf{v}-\nabla P\\ \boldsymbol{\nabla}\cdot\mathbf{v}&=0.\end{aligned}$$

Stokes equations

Decay of a macroscopic wavelike velocity field [1/2]

- consider a wavelike velocity field

$$\rho \mathbf{v}(\mathbf{r},t) = \frac{1}{(2\pi)^3}\mathbf{g}(\mathbf{k},t)\exp\{-i\mathbf{k}\cdot\mathbf{r}\}$$

- for an incompressible fluid the only possible wavelike velocity field is a transversal one:

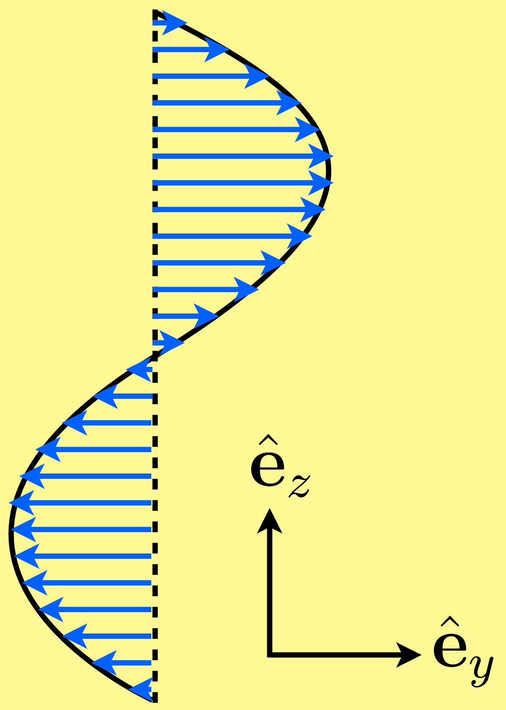
$$\mathbf{g}(\mathbf{k},t)\cdot\mathbf{k} = 0.$$

- e.g. choose **k** along *z* and flow along *y*

Stokes equation then gives $\partial P/\partial x = \partial P/\partial z = 0$ and taking the divergence of Stokes equation $\nabla^2 P = 0$ so we get $\partial P/\partial y = 0$ too.

$$\mathbf{k} = k\hat{\mathbf{e}}_z$$

$$\mathbf{g}(\mathbf{k},t) = g_y(\mathbf{k},t)\hat{\mathbf{e}}_y$$



Decay of a macroscopic wavelike velocity field [2/2]

- Stokes' equation is reduced to

$$m\rho\frac{\partial v_y}{\partial t} = \eta\frac{\partial^2 v_y}{\partial z^2}$$

which may be rewritten in terms of g_y

$$\begin{aligned} m\rho\frac{\partial g_y}{\partial t} &= -\eta k^2 g_y \\ g_y(\mathbf{k},t) &= g_y(\mathbf{k},0)\exp\left\{-\frac{\eta}{m\rho}k^2 t\right\} \end{aligned}$$

- a macroscopic wavelike velocity field decays exponentially (at large times) with a relaxation time determined by the shear viscosity and the density:

$$\tau(k) = \frac{m\rho}{\eta k^2}$$

Microscopic equation for shear viscosity [1/3]

- microscopic expression for velocity field Fourier component

$$
\begin{aligned}
\mathbf{g}(\mathbf{k},t) &= \int \mathrm{d}^3 r \sum_j \mathbf{v}_j(t)\delta\left(\mathbf{r}-\mathbf{r}_j(t)\right)\exp\left\{\mathrm{i}\mathbf{k}\cdot\mathbf{r}\right\} \\
&= \sum_j \mathbf{v}_j(t)\exp\left\{\mathrm{i}\mathbf{k}\cdot\mathbf{r}_j(t)\right\}.
\end{aligned}
$$

- Onsager: $\left\langle g_y(\mathbf{k},t)g_y^*(\mathbf{k},0)\right\rangle = \left\langle g_y(\mathbf{k},0)g_y^*(\mathbf{k},0)\right\rangle \exp\left\{-\frac{\eta}{m\rho}k^2 t\right\}$

same procedure...

$$\int_0^t \mathrm{d}\tau \frac{1}{k^2}\left\langle \dot{g}_y(\mathbf{k},t)\dot{g}_y^*(\mathbf{k},0)\right\rangle = \left\langle g_y(\mathbf{k},0)g_y^*(\mathbf{k},0)\right\rangle \frac{\eta}{m\rho}\exp\left\{-\frac{\eta}{m\rho}k^2 t\right\}$$

small *k*: $\left\langle g_y(\mathbf{k},0)g_y^*(\mathbf{k},0)\right\rangle \approx \left\langle g_y(\mathbf{0},0)g_y^*(\mathbf{0},0)\right\rangle = \left\langle \sum_j\sum_k v_{y,j}v_{y,k}\right\rangle = \frac{Nk_BT}{m}$

- so we find: $\eta = \frac{1}{Vk_BT}\lim_{k\to 0}\int_0^\infty \mathrm{d}t \frac{1}{k^2}\left\langle m\dot{g}_y(\mathbf{k},t)m\dot{g}_y^*(\mathbf{k},0)\right\rangle$

Microscopic equation for shear viscosity [2/3]

- write out the terms $m\dot{g}_y(\mathbf{k},t)$

$$m\dot{g}_y(\mathbf{k},t) = \sum_{j=1}^{N} \{m\dot{v}_{y,j}(t) + \mathrm{i}kmv_{z,j}(t)v_{y,j}(t)\} \exp\{\mathrm{i}kz_j(t)\}$$

$$\begin{aligned}
\sum_{j=1}^{N} m\dot{v}_{y,j} \exp\{\mathrm{i}kz_j\} &= \sum_{j=1}^{N}\sum_{i\neq j} F_{y,j}^{(i)} \exp\{\mathrm{i}kz_j\} \\
&= \frac{1}{2}\sum_{j=1}^{N}\sum_{i=1}^{N} F_{y,j}^{(i)} \left[\exp\{\mathrm{i}kz_j\} - \exp\{\mathrm{i}kz_i\}\right] \\
&= \frac{1}{2}\mathrm{i}k\sum_{j=1}^{N}\sum_{i=1}^{N} F_{y,j}^{(i)}(z_j - z_i). \qquad \text{(small } k\text{)}
\end{aligned}$$

Microscopic equation for shear viscosity [3/3]

- collecting everything, we get the Green-Kubo relation for the shear viscosity

$$\boxed{\eta = \frac{V}{k_B T}\int_0^\infty \mathrm{d}t\,\langle \sigma_{yz}(t)\sigma_{yz}(0)\rangle\,,}$$

where σ_{yz} is the microscopic stress tensor:

$$\sigma_{yz}(t) = \frac{1}{V}\left\{\sum_j m v_{y,j}(t) v_{z,j}(t) + \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N} F_{y,j}^{(i)}(t)(z_j(t) - z_i(t))\right\}$$

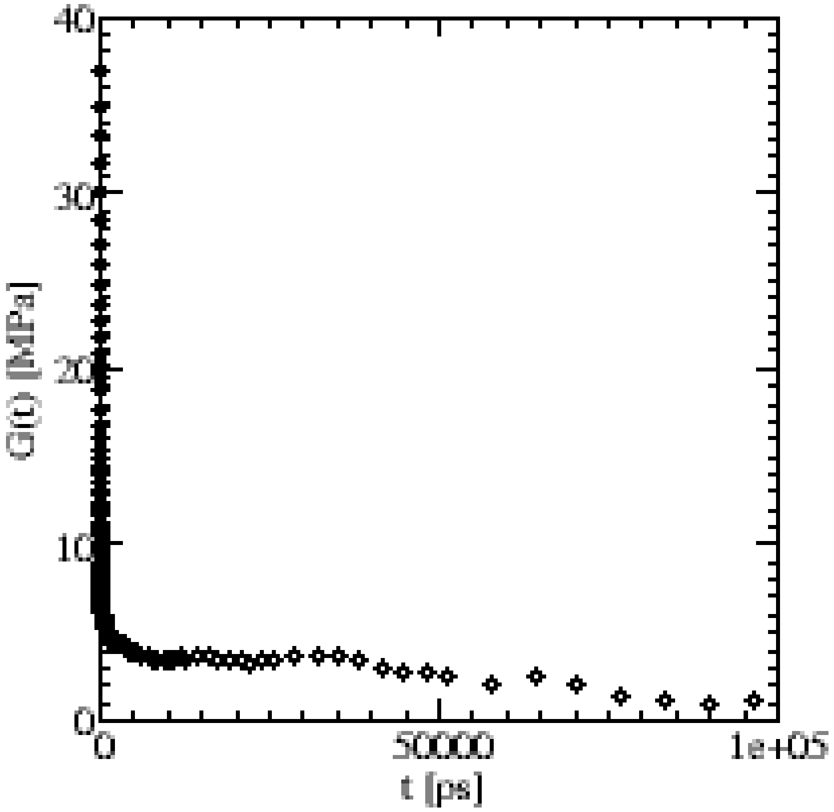
momentum transport through particle motion

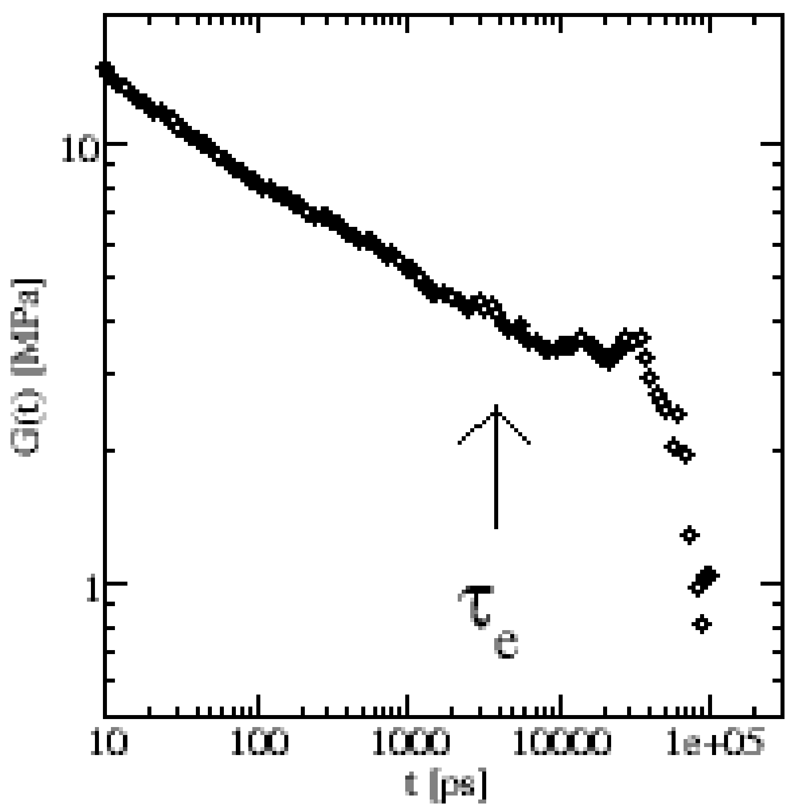
momentum transport through particle interactions

Example: shear relaxation modulus of polymer melt

- shear relaxation modulus *G*(*t*) is the (macroscopic, linear) stress relaxation following a sudden step strain
- we can determine *G*(t) and shear viscosity from equilibrium simulations without actually shearing!

$$G(t) = \frac{V}{k_B T} \langle \sigma_{yz}(t)\sigma_{yz}(0) \rangle \qquad \eta = \int_0^\infty G(t)\mathrm{d}t$$





melt of C400
polyethylene chains
with a shear viscosity of
0.2 Pa s (200 x water)

Summary of chapter 2

- most microscopic quantities fluctuate in time (due to thermal fluctuations); time correlation functions reveal their dynamics
- Onsager: the *average* decay of fluctuations obey macroscopic laws

$$\boxed{\langle A(t)A(0)\rangle = \left\langle A^2\right\rangle \alpha(t).}$$

- using Onsager we derived Green-Kubo relations for transport properties

self-diffusion $$D^{self} = \int_0^\infty \frac{1}{N}\left\langle \sum_i v_{iz}(t)v_{iz}(0)\right\rangle$$

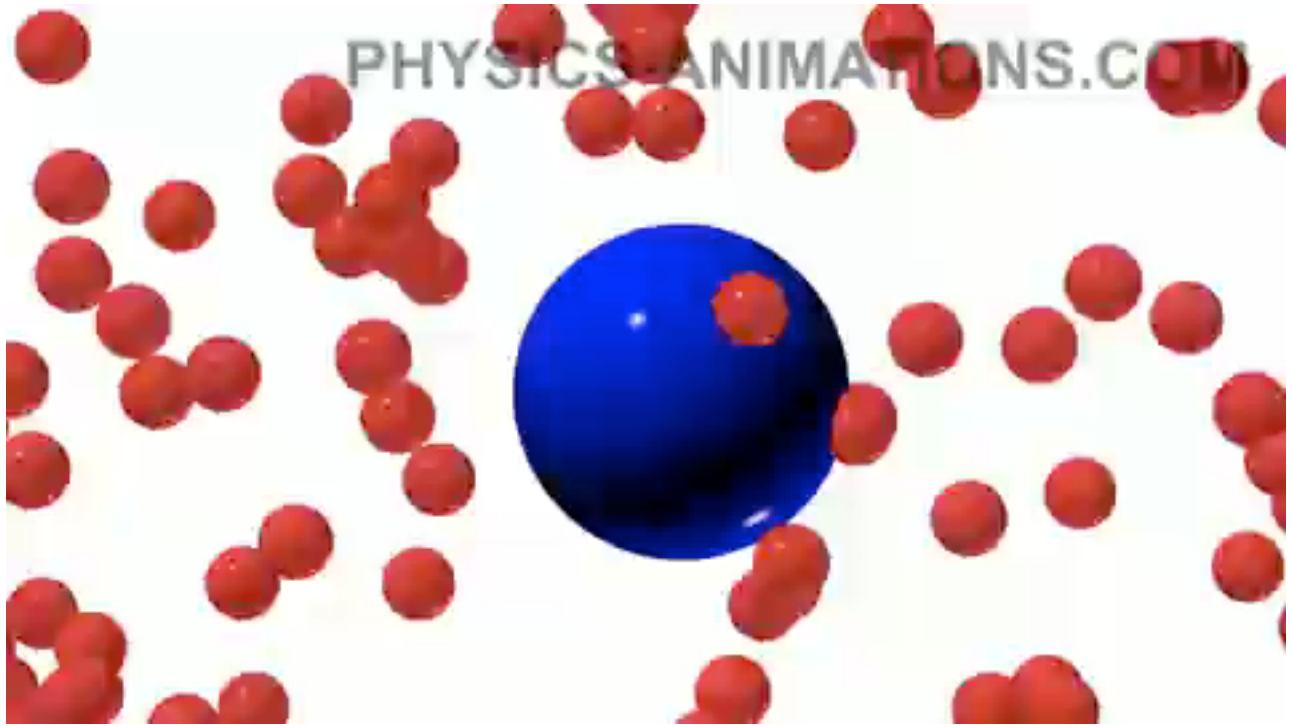
collective diffusion $$D(k) = \frac{1}{S(k)}\int_0^\infty \mathrm{d}t \frac{1}{N}\left\langle \sum_i \sum_j v_{iz}(t)v_{jz}(0)\exp\left\{\mathrm{i}k\left(z_i(t)-z_j(0)\right)\right\}\right\rangle$$

shear viscosity $$\eta = \frac{V}{k_B T}\int_0^\infty \mathrm{d}t\,\langle \sigma_{yz}(t)\sigma_{yz}(0)\rangle$$

Chapter 3: Brownian motion

Colloidal liquids

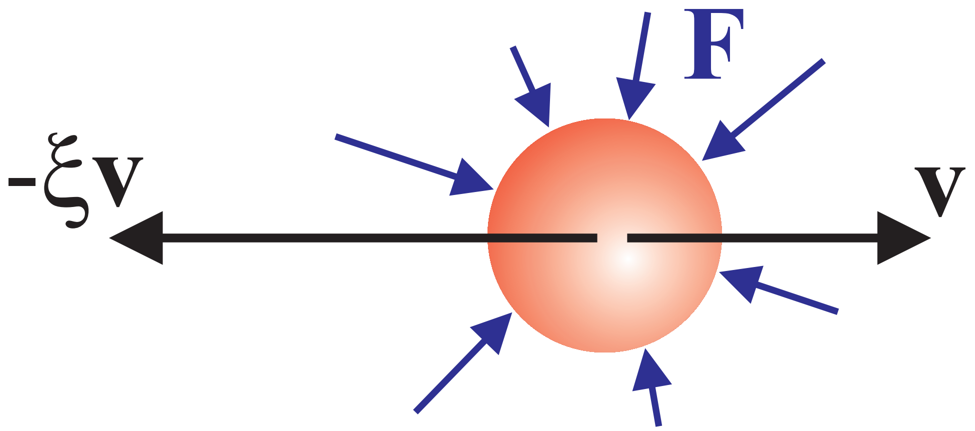
- colloidal liquids contain particles much larger than the solvent molecules (typically 1 nanometer to 1 micrometer)



- Brownian motion is caused by random collisions with solvent molecules

Friction and random forces on a colloidal particle

- suppose a colloidal particle (radius *a*, mass *M*) moves along a path **R**(*t*)
- colloid will collide on average more often on the front than on the back: systematic force proportional and opposite to its velocity = friction



$$\frac{\mathrm{d}\mathbf{R}}{\mathrm{d}t} = \mathbf{V}$$
$$\frac{\mathrm{d}\mathbf{V}}{\mathrm{d}t} = -\xi\mathbf{V} + \mathbf{F}.$$

- we can find an expression for the friction by solving Stokes' equations for a sphere moving through a hydrodynamic solvent:

$$\xi = \zeta/M = 6\pi\eta_s a/M$$

solvent viscosity η_s

Fluctuation-dissipation theorem [1/2]

$$\mathbf{V}(t) = \mathbf{V}_0 \mathrm{e}^{-\xi t} + \int_0^t \mathrm{d}\tau \ \mathrm{e}^{-\xi(t-\tau)} \mathbf{F}(t)$$

- average evolution of velocity **V** depends on characteristics of random force **F**(*t*). Suppose the random force has no memory

$$\begin{aligned} \langle \mathbf{F}(t) \rangle &= \mathbf{0} \\ \langle \mathbf{F}(t) \cdot \mathbf{F}(t') \rangle_{\mathbf{V}_0} &= C_{\mathbf{V}_0} \delta(t - t') \end{aligned}$$

- what is the magnitude of the random forces, i.e. $C_{\mathbf{V}_0}$?

$$\begin{aligned} \langle \mathbf{V}(t) \rangle_{\mathbf{V}_0} &= \mathbf{V}_0 \mathrm{e}^{-\xi t} + \int_0^t \mathrm{d}\tau \ \mathrm{e}^{-\xi(t-\tau)} \langle \mathbf{F}(\tau) \rangle_{\mathbf{V}_0} \\ &= \mathbf{V}_0 \mathrm{e}^{-\xi t} \\ \langle \mathbf{V}(t) \cdot \mathbf{V}(t) \rangle_{\mathbf{V}_0} &= V_0^2 \mathrm{e}^{-2\xi t} + 2 \int_0^t \mathrm{d}\tau \ \mathrm{e}^{-\xi(2t-\tau)} \mathbf{V}_0 \cdot \langle \mathbf{F}(\tau) \rangle_{\mathbf{V}_0} \\ &\quad + \int_0^t \mathrm{d}\tau' \int_0^t \mathrm{d}\tau \ \mathrm{e}^{-\xi(2t-\tau-\tau')} \langle \mathbf{F}(\tau) \cdot \mathbf{F}(\tau') \rangle_{\mathbf{V}_0} \\ &= V_0^2 \mathrm{e}^{-2\xi t} + \frac{C_{\mathbf{V}_0}}{2\xi} \left(1 - \mathrm{e}^{-2\xi t}\right) . \end{aligned}$$

Fluctuation-dissipation theorem [2/2]

$$\langle \mathbf{V}(t)\cdot\mathbf{V}(t)\rangle_{\mathbf{V}_0} = V_0^2 \mathrm{e}^{-2\xi t} + \frac{C_{\mathbf{V}_0}}{2\xi}\left(1-\mathrm{e}^{-2\xi t}\right)$$

- colloid is in thermal equilibrium with the solvent, so $\langle V^2\rangle = \dfrac{3k_BT}{M}$
- from this follows the fluctuation-dissipation theorem

$$\boxed{\langle \mathbf{F}(t)\cdot\mathbf{F}(t')\rangle = 6\frac{k_BT\xi}{M}\delta(t-t')}$$

fluctuations are coupled to dissipation

Einstein relation for the self-diffusion coefficient

- from the mean-square displacement...

$$\mathbf{R}(t) = \mathbf{R}_0 + \frac{\mathbf{V}_0}{\xi}\left(1 - \mathrm{e}^{-\xi t}\right) + \int_0^t \mathrm{d}\tau \int_0^\tau \mathrm{d}\tau' \, \mathrm{e}^{-\xi(\tau-\tau')}\mathbf{F}(\tau')$$

$$\left\langle (\mathbf{R}(t) - \mathbf{R}_0)^2 \right\rangle_{\mathbf{V}_0} = \frac{V_0^2}{\xi^2}\left(1 - \mathrm{e}^{-\xi t}\right)^2 + \frac{3k_BT}{M\xi^2}\left(2\xi t - 3 + 4\mathrm{e}^{-\xi t} - \mathrm{e}^{-2\xi t}\right)$$

$$\lim_{t\to\infty} \left\langle (\mathbf{R}(t) - \mathbf{R}_0)^2 \right\rangle = \frac{6k_BT}{M\xi} t \equiv 6Dt$$

... we find the Einstein relation for the self-diffusion coefficient

$$\boxed{D = \frac{k_BT}{\zeta},}$$

$$\zeta = M\xi = 6\pi\eta_s a$$

D is independent of the mass of the colloid!

Overdamped motion?

- reconsider the evolution of the colloidal velocity

$$\langle \mathbf{V}(t)\rangle_{\mathbf{V}_0} = \mathbf{V}_0 \mathrm{e}^{-\xi t}$$

  - colloid loses memory of $V_0 \approx \sqrt{\frac{3k_BT}{M}}$ after $\tau = \frac{1}{\xi}$
  - traveled distance / radius $\approx 10^{-4} - 10^{-2}$

- on time scales on which particle configurations change, we may restrict our attention to the positions only, and average over the velocities

Smoluchowski equation [1/2]

- Question: how does a distribution of colloidal particles evolve in time when they are also subjected to an external potential $\Phi(\mathbf{R})$?

$\Psi(\mathbf{R}, \mathbf{R}_0; t)$ is probability density to find a particle at position $\mathbf{R}$ at time t, given it was at $\mathbf{R}_0$ at $t = 0$

- in the overdamped limit a flux **J** will exist, given by

$$\mathbf{J}(\mathbf{R}, \mathbf{R}_0, t) = -D\boldsymbol{\nabla}\Psi(\mathbf{R}, \mathbf{R}_0; t) - \frac{1}{\zeta}\Psi(\mathbf{R}, \mathbf{R}_0; t)\boldsymbol{\nabla}\Phi(\mathbf{R})$$

flux due to diffusion of the particles

flux in downhill gradient of external potential

- note that at equilibrium this re-confirms the Einstein relation:

$$\Psi_{eq}(\mathbf{R}) = C \exp\left[-\frac{\Phi(\mathbf{R})}{k_B T}\right] \quad \xrightarrow{\mathbf{J} = \mathbf{0}} \quad D = \frac{k_B T}{\zeta}$$

Smoluchowski equation [2/2]

- inserting the flux equation in an equation for particle number conservation,

$$\frac{\partial}{\partial t}\Psi(\mathbf{R},\mathbf{R}_0;t) = -\boldsymbol{\nabla}\cdot\mathbf{J}(\mathbf{R},\mathbf{R}_0,t)$$

... we arrive at the important Smoluchowski equation:

$$\frac{\partial}{\partial t}\Psi(\mathbf{R},\mathbf{R}_0;t) \quad = \quad \boldsymbol{\nabla}\cdot\left[\frac{1}{\zeta}\Psi(\mathbf{R},\mathbf{R}_0;t)\boldsymbol{\nabla}\Phi(\mathbf{R})\right] + \boldsymbol{\nabla}\cdot\left[D\boldsymbol{\nabla}\Psi(\mathbf{R},\mathbf{R}_0;t)\right] \tag{3.18}$$

$$\lim_{t\to 0}\Psi(\mathbf{R},\mathbf{R}_0;t) \quad = \quad \delta(\mathbf{R}-\mathbf{R}_0). \tag{3.19}$$

- this may be viewed as a generalization of Fick's law

$$\frac{\partial P(\mathbf{r},t)}{\partial t} = D\nabla^2 P(\mathbf{r},t)$$

$$P(\mathbf{r},0) = \delta(\mathbf{r}-\mathbf{r}(0))$$

Langevin equations

- Smoluchowski equation describes how particle distribution functions change
- the corresponding explicit stochastic equations of motion for the particles are called the Langevin equations

$$\begin{aligned} \frac{\mathrm{d}\mathbf{R}}{\mathrm{d}t} &= -\frac{1}{\zeta}\boldsymbol{\nabla}\Phi + \boldsymbol{\nabla}D + \mathbf{f} \\ \langle \mathbf{f}(t) \rangle &= \mathbf{0} \\ \langle \mathbf{f}(t)\mathbf{f}(t') \rangle &= 2D\bar{\mathbf{I}}\delta(t-t'). \end{aligned}$$

- the Langevin equations are used as a starting point for many soft matter simulations and theories; in the next chapter we will use them to build a theory of polymer dynamics

Summary of chapter 3

- Brownian motion of colloids is caused by collisions with solvent molecules

- the random forces are related to the friction experienced by a colloid

$$\langle \mathbf{F}(t) \cdot \mathbf{F}(t') \rangle = 6 \frac{k_B T \xi}{M} \delta(t - t')$$ (fluctuation-dissipation theorem)

- or equivalently the diffusion is related to the friction

$$\boxed{D = \frac{k_B T}{\zeta},}$$ (Einstein relation)

- motion of colloidal particles in an external potential

$$\begin{aligned} \frac{\mathrm{d}\mathbf{R}}{\mathrm{d}t} &= -\frac{1}{\zeta} \boldsymbol{\nabla} \Phi + \boldsymbol{\nabla} D + \mathbf{f} \\ \langle \mathbf{f}(t) \rangle &= \mathbf{0} \\ \langle \mathbf{f}(t) \mathbf{f}(t') \rangle &= 2D\bar{\mathbf{I}}\delta(t - t'). \end{aligned}$$

(Langevin equations)

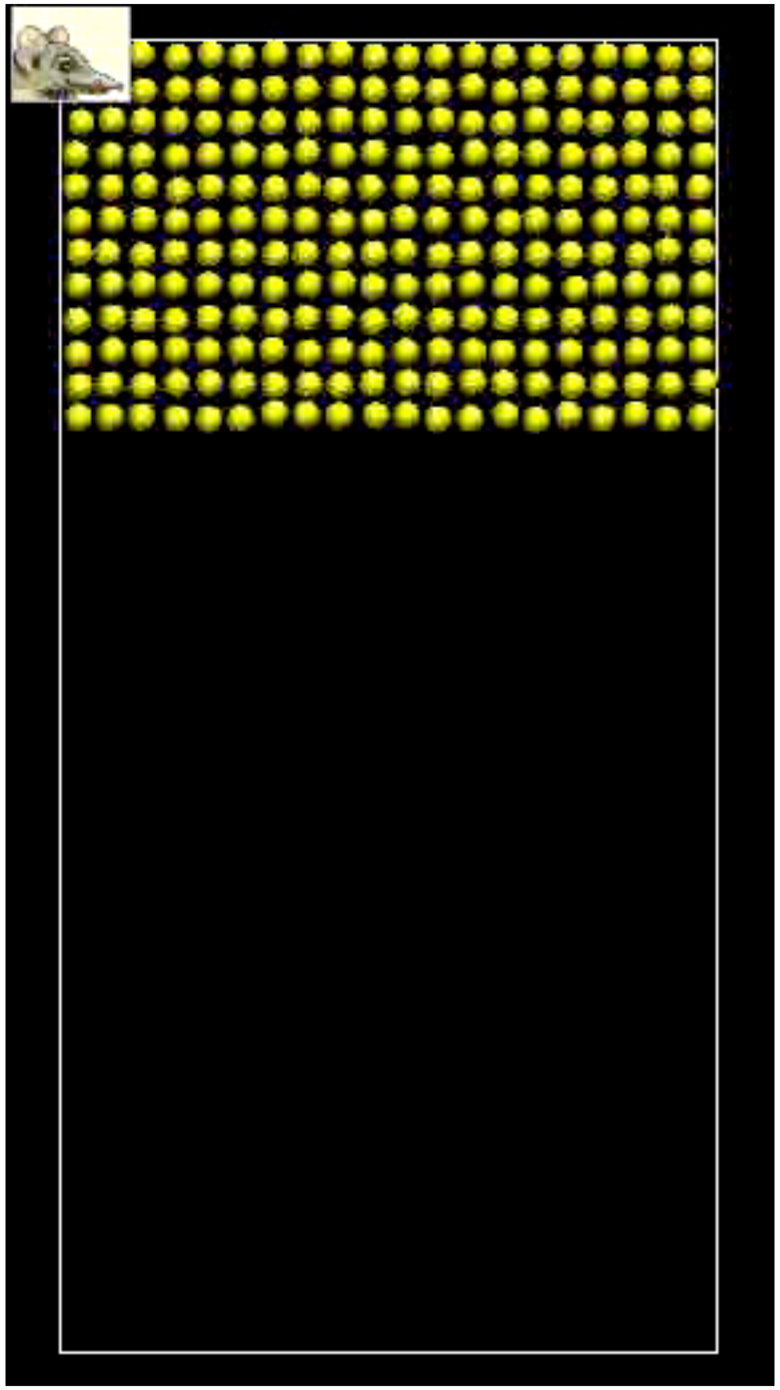
Langevin and Einstein in 1911

Intermezzo: hydrodynamic interactions

- note that Langevin equations neglect hydrodynamic interactions:
  when a colloid moves, it induces a solvent flow which affects the motion of other colloids too

- example: sedimentation of micron-sized colloids in a closed vessel under the influence of gravity

- hydrodynamic interactions may be neglected
  - at very low colloid concentration, or
  - when other interparticle interactions dominate



Chapter 4:
The dynamics of unentangled polymer liquids

Polymer liquids

- long molecules consisting of
  N = 100 - 100.000 identical monomers

- characteristics of polymeric liquids:
  - high shear viscosity η
  - often highly elastic
    (memory in shear relaxation modulus $G(t)$)
  - slow dynamics
    (low diffusion coefficient)

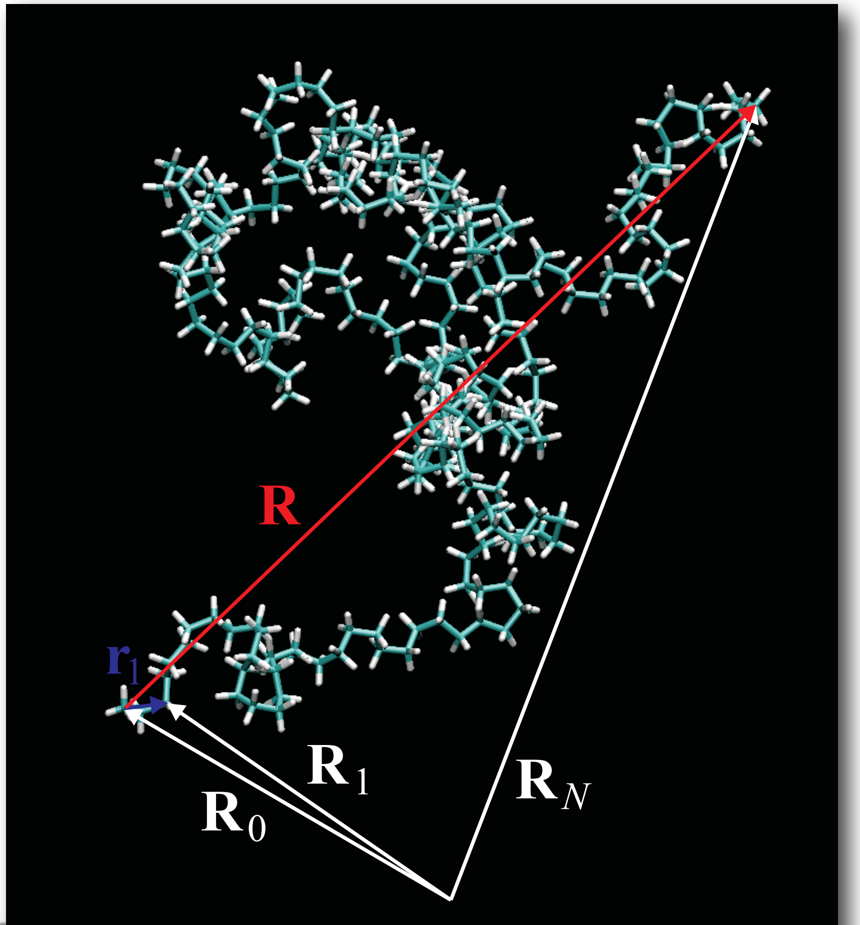
Conformations of a polymer

- specified by *N*+1 backbone atom positions

$$\mathbf{R}_0, \mathbf{R}_1, \dots, \mathbf{R}_N$$

or by *N* bond vectors

$$\mathbf{r}_1 = \mathbf{R}_1 - \mathbf{R}_0, \dots, \mathbf{r}_N = \mathbf{R}_N - \mathbf{R}_{N-1}$$

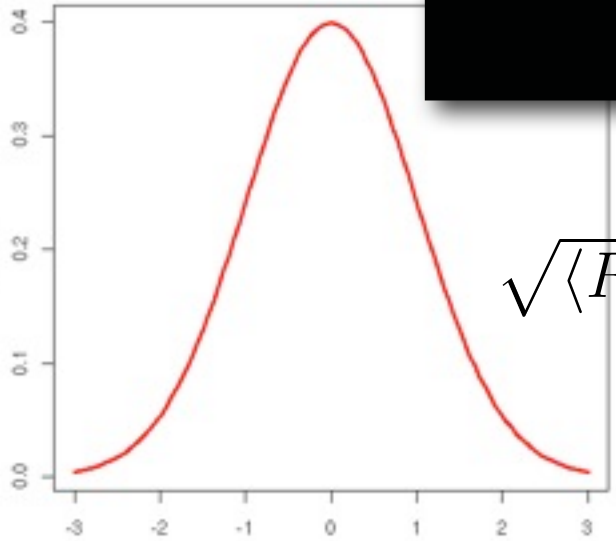


- large scale properties independent of chemistry:

e.g. end-to-end vector $\mathbf{R} = \mathbf{R}_N - \mathbf{R}_0 = \sum_{i=1}^{N} \mathbf{r}_i$

often has a Gaussian distribution

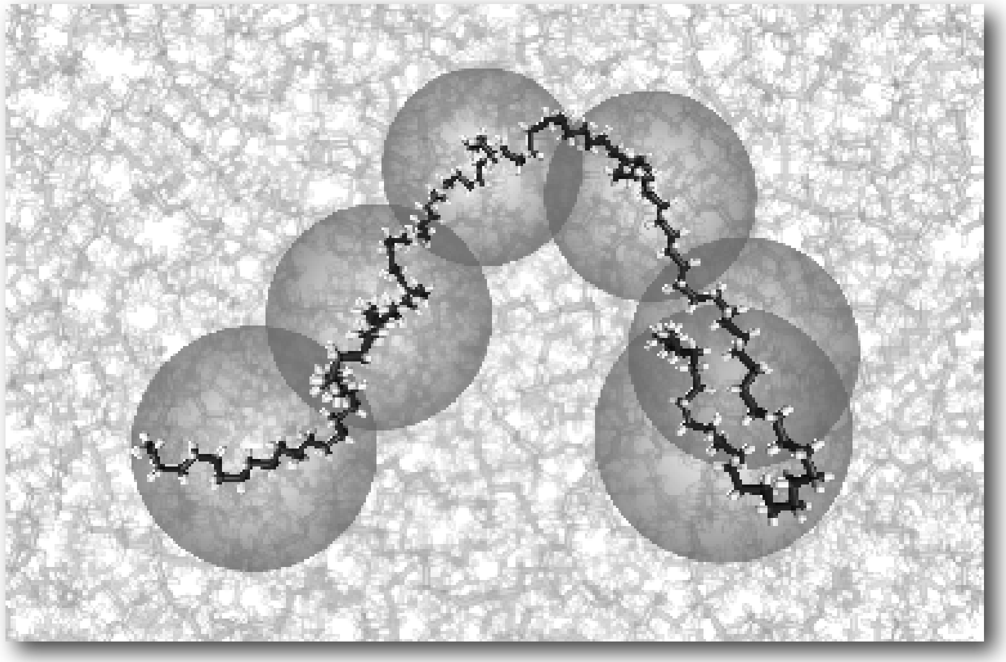
$$\Omega\left(\mathbf{R}; N\right) = \left\{\frac{3}{2\pi N b^2}\right\}^{3/2} \exp\left\{-\frac{3R^2}{2Nb^2}\right\}$$



$$\sqrt{\langle R^2 \rangle} \propto \sqrt{N}$$

WHY?

The central limit theorem



- if enough consecutive monomers are combined into one segment, vectors connecting the segments are independent (neglecting long-range excluded volume)

  i.e. the probability density for segment-to-segment bond vectors factorizes:

$$\Psi\left(\mathbf{r}^N\right) = \prod_{i=1}^{N} \psi\left(\mathbf{r}_i\right)$$

- now suppose $\psi\left(\mathbf{r}_i\right)$ depends only on length of bond vector; define the statistical segment (or Kuhn) length *b* as $\left\langle r^2 \right\rangle = \int \mathrm{d}^3 r \; r^2 \psi(r) \equiv b^2$

- the central limit theorem then states that for large *N*, irrespective of the precise form of $\psi\left(\mathbf{r}_i\right)$, the distribution of $\Psi\left(\mathbf{r}^N\right)$ will be Gaussian

Polymer elasticity

- end-to-end vector distribution

$$\boxed{\Omega\left(\mathbf{R};N\right)=\left\{\frac{3}{2\pi Nb^2}\right\}^{3/2}\exp\left\{-\frac{3R^2}{2Nb^2}\right\}.}$$

- entropy and free energy of a polymer chain in which **R** is kept constant:

$$S\left(\mathbf{R};N\right)=k_B\ln\Omega\left(\mathbf{R};N\right)=S_0-\frac{3kR^2}{2Nb^2}$$

$$A=U-TS=A_0+\frac{3k_BTR^2}{2Nb^2}$$

entropic spring with spring constant

$$k=\frac{3k_BT}{Nb^2}$$

$$\Phi(x)=\frac{1}{2}kx^2$$

Gaussian chain

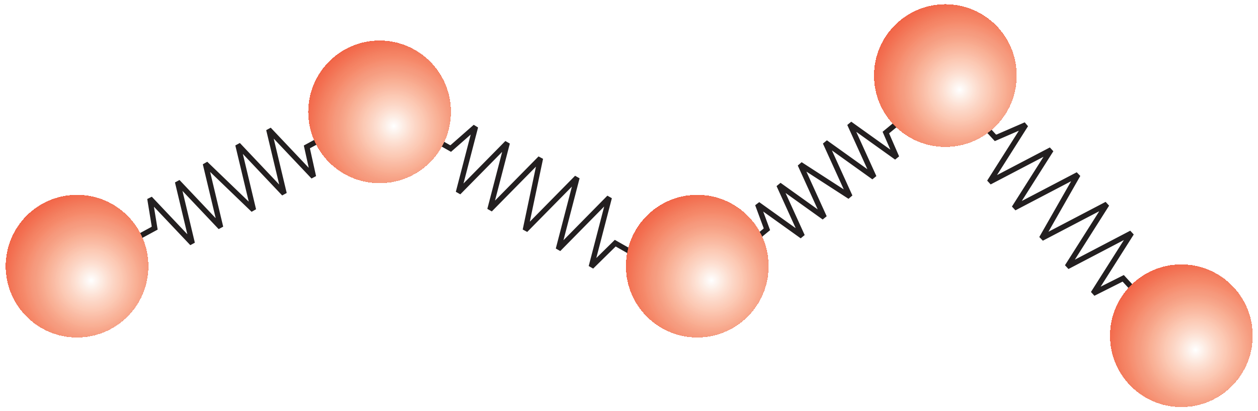
- simplest polymer model: every bond is Gaussianly distributed

$$\psi\left(\mathbf{r}\right) = \left\{\frac{3}{2\pi b^2}\right\}^{3/2} \exp\left\{-\frac{3}{2b^2}r^2\right\}$$

- mechanical equivalent: beads connected by springs

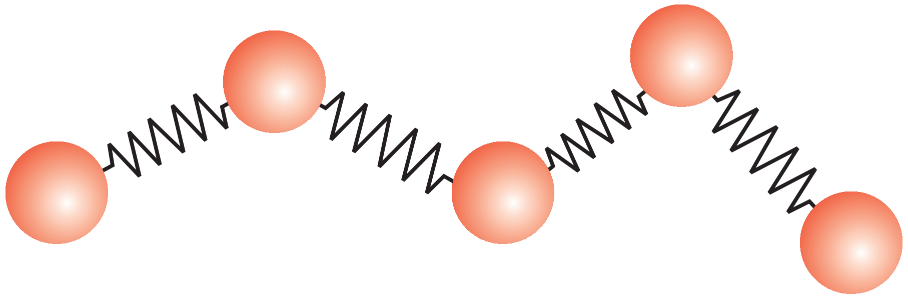
$$\Phi\left(\mathbf{r}_1, \ldots, \mathbf{r}_N\right) = \frac{1}{2}k\sum_{i=1}^{N} r_i^2$$

$$k = \frac{3k_BT}{b^2}$$

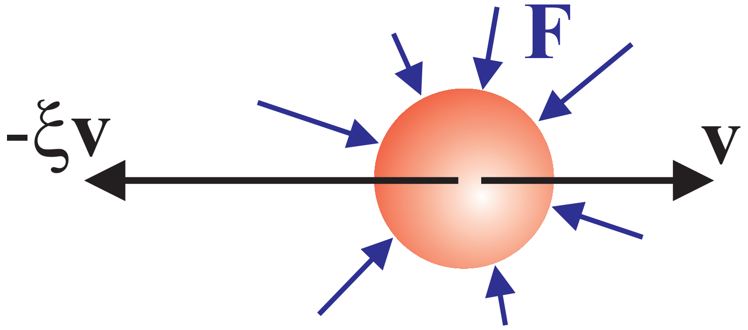


From statics to dynamics

- statics: Gaussian chain

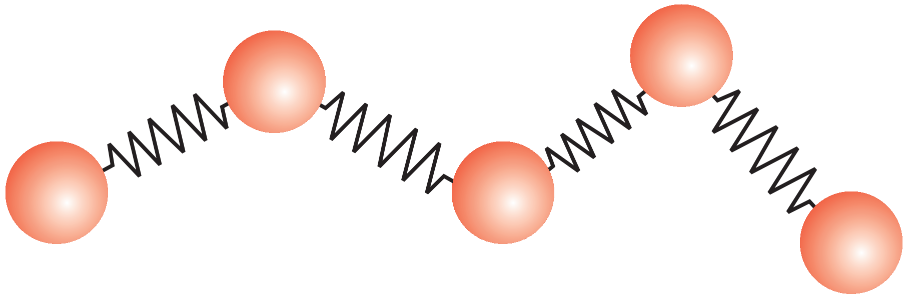


- dynamics: collisions with neighbouring particles cause
  - friction forces on each bead
  - random forces on each bead



- note that the resulting Rouse model
  - neglects hydrodynamic interactions (important in dilute polymer solutions)
  - neglects entanglements (important for very long polymers)
  - applies best to melts of relatively short polymer chains (100 monomers)

Langevin equations for the Rouse chain



- each bead feels the same friction ζ
- for each bead, the external potential is generated by bonds to predecessor and successor

$$
\begin{aligned}
\frac{\mathrm{d}\mathbf{R}_0}{\mathrm{d}t} &= -\frac{3k_BT}{\zeta b^2}\left(\mathbf{R}_0-\mathbf{R}_1\right)+\mathbf{f}_0\\
\frac{\mathrm{d}\mathbf{R}_n}{\mathrm{d}t} &= -\frac{3k_BT}{\zeta b^2}\left(2\mathbf{R}_n-\mathbf{R}_{n-1}-\mathbf{R}_{n+1}\right)+\mathbf{f}_n\\
\frac{\mathrm{d}\mathbf{R}_N}{\mathrm{d}t} &= -\frac{3k_BT}{\zeta b^2}\left(\mathbf{R}_N-\mathbf{R}_{N-1}\right)+\mathbf{f}_N\\
\left\langle \mathbf{f}_n\left(t\right)\right\rangle &= \mathbf{0}\\
\left\langle \mathbf{f}_n\left(t\right)\mathbf{f}_m\left(t'\right)\right\rangle &= 2D\bar{\mathbf{I}}\delta_{nm}\delta(t-t').
\end{aligned}
$$

($3N$+3) coupled stochastic differential equations

Normal modes [1/3]

- first ignore the random forces and try a specific solution of the form

$$\mathbf{R}_n(t) = \mathbf{X}(t)\cos(an+c)$$

this yields

$$\begin{aligned}\frac{d\mathbf{X}}{dt}\cos c &= -\frac{3k_BT}{\zeta b^2}\left\{\cos c - \cos(a+c)\right\}\mathbf{X} && (4.17)\\ \frac{d\mathbf{X}}{dt}\cos(na+c) &= -\frac{3k_BT}{\zeta b^2}4\sin^2(a/2)\cos(na+c)\mathbf{X} && (4.18)\\ \frac{d\mathbf{X}}{dt}\cos(Na+c) &= -\frac{3k_BT}{\zeta b^2}\left\{\cos(Na+c) - \cos\left((N-1)a+c\right)\right\}\mathbf{X}, && (4.19)\end{aligned}$$

[make use of $\cos(x+y) = \cos(x)\cos(y) - \sin(x)\sin(y)$
and $\sin(x+y) = \cos(x)\sin(y) + \sin(x)\cos(y)$]

Normal modes [2/3]

- consistent description of boundaries of chain if we choose

$$\begin{aligned} \cos c - \cos(a+c) &= 4\sin^2(a/2)\cos c \\ \cos(Na+c) - \cos\left((N-1)a+c\right) &= 4\sin^2(a/2)\cos(Na+c) \end{aligned}$$

$$\downarrow$$

$$\begin{aligned} \cos(a-c) &= \cos c \\ \cos\left((N+1)a+c\right) &= \cos(Na+c) \end{aligned}$$

- we find independent solutions from

$$\begin{aligned} a-c &= c \\ (N+1)a+c &= p2\pi - Na - c. \end{aligned}$$

where *p* is an integer

Normal modes [3/3]

- so set of differential equations is decoupled by

$$\mathbf{R}_n(t) = \mathbf{X}(t)\cos\left[\frac{p\pi}{N+1}(n+\frac{1}{2})\right]$$

- to find the general solution, we form a linear combination of all independent solutions by taking *p* in the range *p* = 0, ..., *N*

$$\mathbf{R}_n = \mathbf{X}_0 + 2\sum_{p=1}^{N}\mathbf{X}_p\cos\left[\frac{p\pi}{N+1}(n+\frac{1}{2})\right]$$

- this may be inverted to

$$\mathbf{X}_p = \frac{1}{N+1}\sum_{n=0}^{N}\mathbf{R}_n\cos\left[\frac{p\pi}{N+1}(n+\frac{1}{2})\right]$$

Rouse modes

- in summary, the equations are decoupled by transforming to

$$\boxed{\mathbf{X}_p = \frac{1}{N+1}\sum_{n=0}^{N}\mathbf{R}_n \cos\left[\frac{p\pi}{N+1}(n+\frac{1}{2})\right].}$$

called the Rouse modes. The equations of motion for the Rouse modes are

$$\begin{aligned}
\frac{\mathrm{d}\mathbf{X}_p}{\mathrm{d}t} &= -\frac{3k_BT}{\zeta b^2}4\sin^2\left(\frac{p\pi}{2(N+1)}\right)\mathbf{X}_p + \mathbf{F}_p \\
\langle \mathbf{F}_p(t)\rangle &= \mathbf{0} \\
\langle \mathbf{F}_0(t)\mathbf{F}_0(t')\rangle &= \frac{2D}{N+1}\bar{\mathbf{I}}\delta(t-t') \\
\langle \mathbf{F}_p(t)\mathbf{F}_q(t')\rangle &= \frac{D}{N+1}\bar{\mathbf{I}}\delta_{pq}\delta(t-t') \qquad (p+q>0)
\end{aligned}$$

where p, q = 0, ..., N

Centre-of-mass motion

- *p* = 0: centre-of-mass motion of the polymer chain

$$\mathbf{X}_0 = \frac{1}{N+1}\sum_{n=0}^{N}\mathbf{R}_n$$

$$\mathbf{X}_0(t) = \mathbf{X}_0(0) + \int_0^t \mathrm{d}\tau\ \mathbf{F}_0(\tau) \tag{4.36}$$

$$\begin{aligned} g_{\mathrm{cm}}(t) &= \left\langle (\mathbf{X}_0(t) - \mathbf{X}_0(0))^2 \right\rangle = \left\langle \int_0^t \mathrm{d}\tau \int_0^t \mathrm{d}\tau'\ \mathbf{F}_0(\tau)\cdot\mathbf{F}_0(\tau') \right\rangle \\ &= \frac{6D}{N+1}t \equiv 6D_G t. \end{aligned} \tag{4.37}$$

the Rouse model predicts that the diffusion coefficient of a (unentangled) polymer in a melt scales inversely with its molecular weight!

this is confirmed in experiments and computer simulations

Internal motion of the polymer chain

- *p* = 1, ..., *N*: independent vibrations of the polymer chain, wavelength corresponding to a subchain of *N*/*p* segments

$$\mathbf{X}_p(t) = \mathbf{X}_p(0)\mathrm{e}^{-t/\tau_p} + \int_0^t \mathrm{d}\tau\ \mathrm{e}^{-(t-\tau)/\tau_p}\mathbf{F}_p(\tau)$$

if *p* << *N*

$$\boxed{\tau_p = \frac{\zeta b^2}{3k_BT}\left[4\sin^2\left(\frac{p\pi}{2(N+1)}\right)\right]^{-1} \approx \frac{\zeta b^2(N+1)^2}{3\pi^2 k_BT}\frac{1}{p^2}.}$$

τ_p is the characteristic relaxation time of mode *p*

τ_1 is the relaxation time of the slowest mode (Rouse time τ_R)

the time correlation functions of the Rouse modes are given by

$$\boxed{\langle \mathbf{X}_p(t)\cdot\mathbf{X}_p(0)\rangle = \left\langle X_p^2\right\rangle \exp\left(-t/\tau_p\right).}$$

Rouse mode amplitudes

- statistical weight (probability) of a configuration

$$P\left(\mathbf{R}_0,\ldots,\mathbf{R}_N\right)=\frac{1}{Z}\exp\left[-\frac{3}{2b^2}\sum_{n=1}^{N}\left(\mathbf{R}_n-\mathbf{R}_{n-1}\right)^2\right]$$

transformation to Rouse coordinates is a linear transformation, so Jacobian of transformation is a constant:

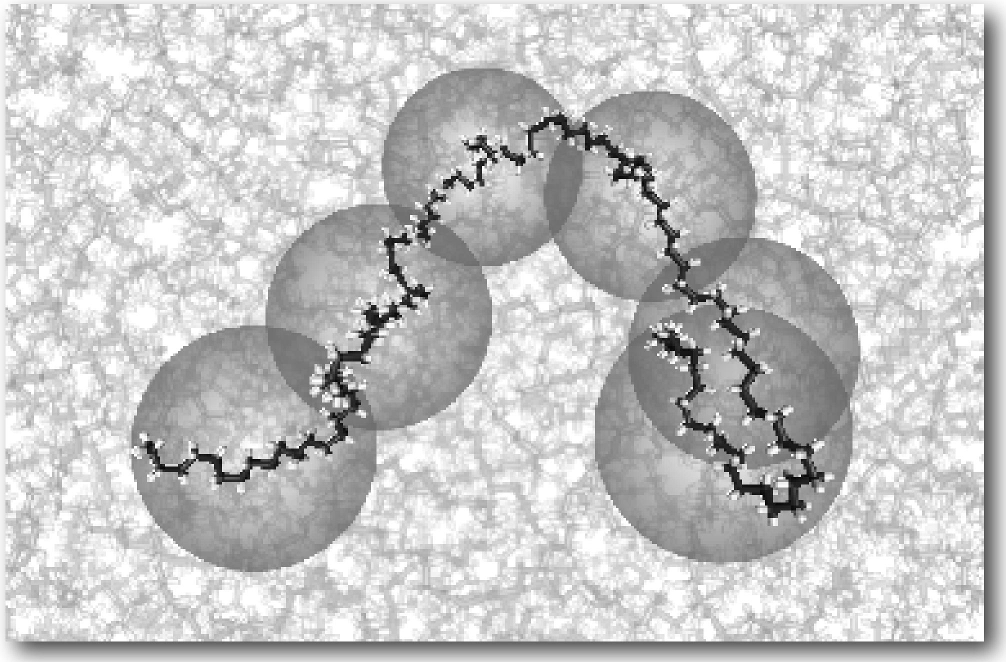
$$P\left(\mathbf{X}_0,\ldots,\mathbf{X}_N\right)=\frac{1}{Z}\exp\left[-\frac{12}{b^2}(N+1)\sum_{p=1}^{N}\mathbf{X}_p\cdot\mathbf{X}_p\sin^2\left(\frac{p\pi}{2(N+1)}\right)\right]$$

this is a product of independent Gaussians, therefore

$$\langle X_p^2\rangle=\frac{b^2}{8(N+1)\sin^2\left(\frac{p\pi}{2(N+1)}\right)}\approx\frac{(N+1)b^2}{2\pi^2}\frac{1}{p^2}$$

if *p* << *N*

Predictions of the Rouse model; comparison with atomistically detailed simulations of a C120 polyethylene melt

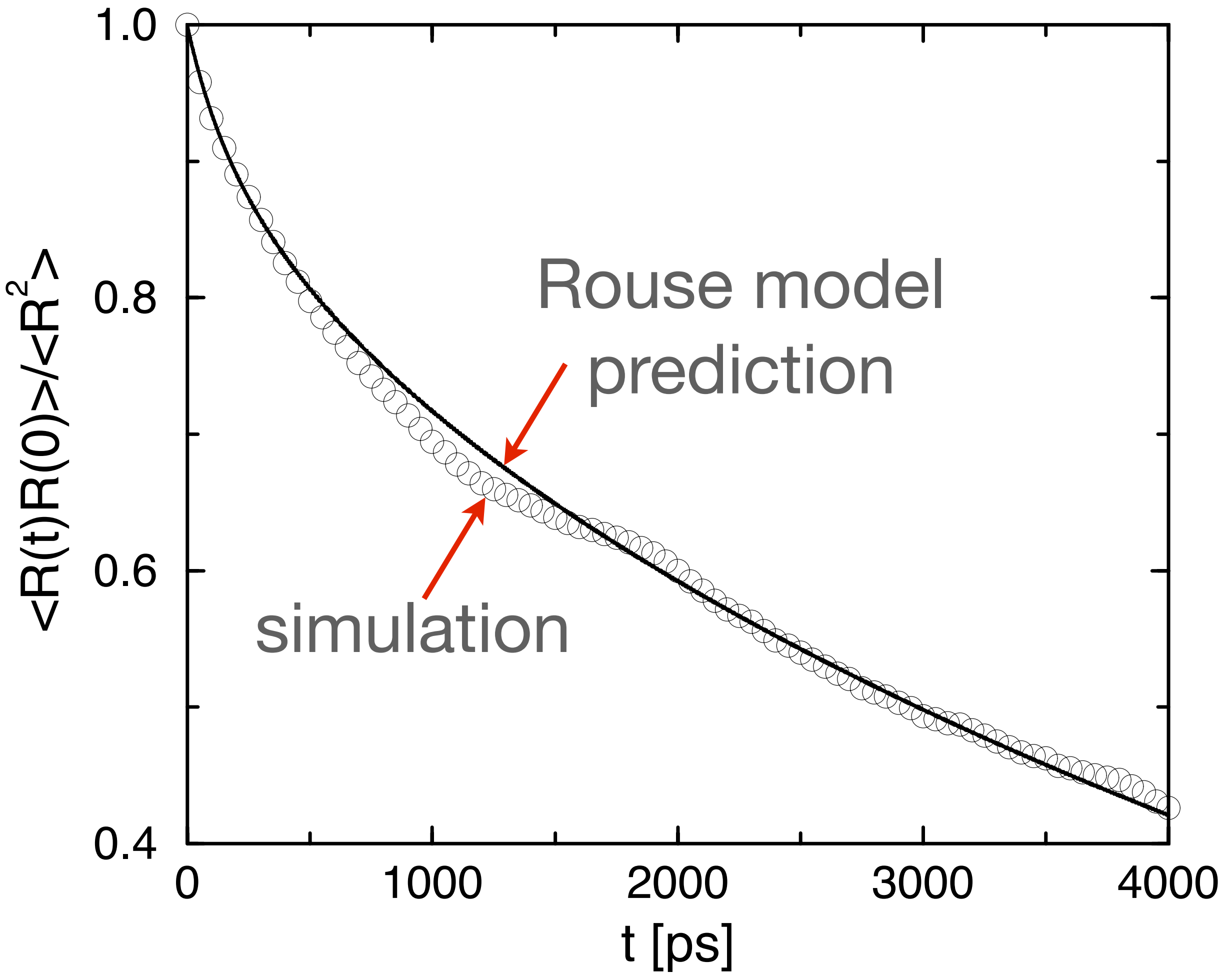


Time correlation of the end-to-end vector

$$\mathbf{R} = \mathbf{R}_N - \mathbf{R}_0 = 2\sum_{p=1}^{N} \mathbf{X}_p \left\{(-1)^p - 1\right\} \cos\left[\frac{p\pi}{2(N+1)}\right] = -4\sum_{p=1}^{N}{}' \, \mathbf{X}_p$$

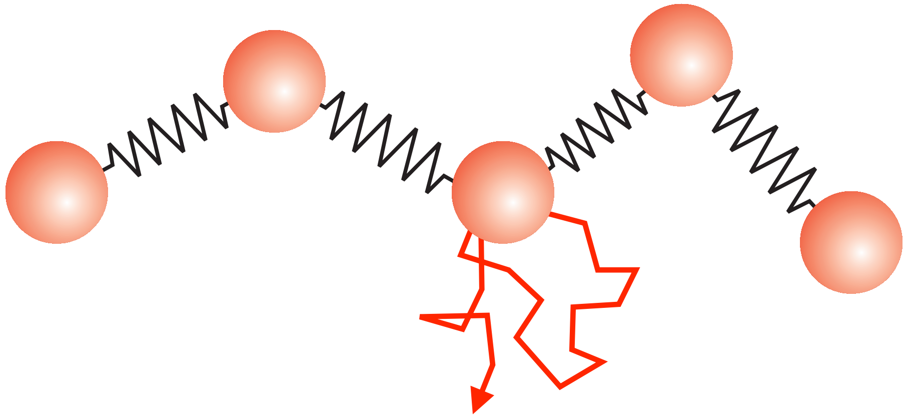
$$\langle \mathbf{R}(t)\cdot\mathbf{R}(0)\rangle = 16\sum_{p=1}^{N}{}' \langle \mathbf{X}_p(t)\cdot\mathbf{X}_p(0)\rangle$$

$$= \frac{8b^2}{\pi^2}(N+1)\sum_{p=1}^{N}{}' \frac{1}{p^2}\mathrm{e}^{-t/\tau_p}$$



Segmental motion [1/2]

$$\mathbf{R}_n = \mathbf{X}_0 + 2\sum_{p=1}^{N} \mathbf{X}_p \cos\left[\frac{p\pi}{N+1}(n+\frac{1}{2})\right]$$



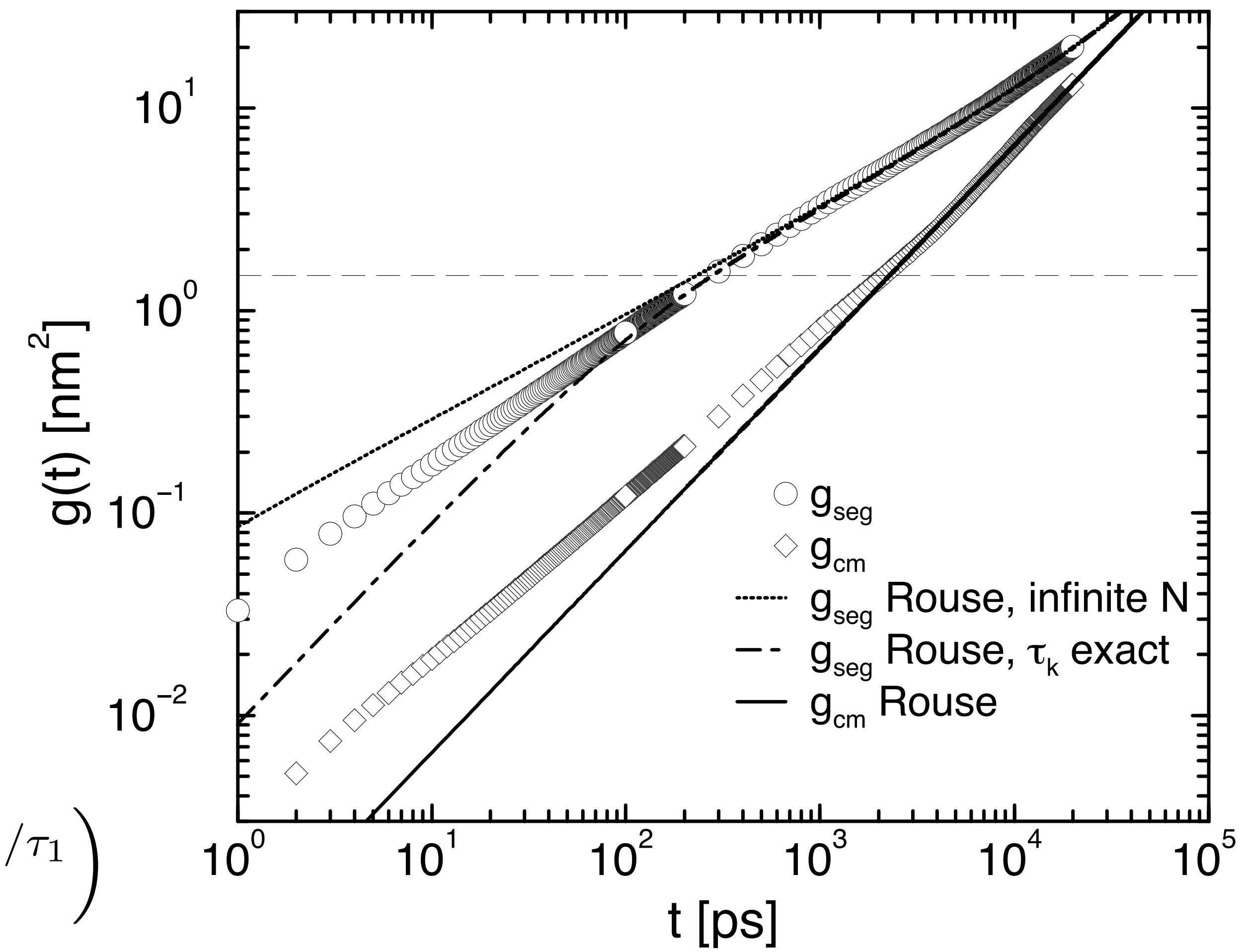
- mean-square displacement of segment *n*

$$\left\langle(\mathbf{R}_n(t)-\mathbf{R}_n(0))^2\right\rangle = \left\langle(\mathbf{X}_0(t)-\mathbf{X}_0(0))^2\right\rangle$$
$$+4\sum_{p=1}^{N}\left\langle(\mathbf{X}_p(t)-\mathbf{X}_p(0))^2\right\rangle \cos^2\left[\frac{p\pi}{N+1}(n+\frac{1}{2})\right]$$

- mean-square displacement of a typical segment (average over all *n*)

$$\begin{aligned} g_{\mathrm{seg}}(t) &= \frac{1}{N+1}\sum_{n=0}^{N}\left\langle(\mathbf{R}_n(t)-\mathbf{R}_n(0))^2\right\rangle \\ &= 6D_G t + 4\sum_{p=1}^{N}\left\langle X_p^2\right\rangle\left(1-\mathrm{e}^{-t/\tau_p}\right) \end{aligned}$$

Segmental motion [2/2]



- good agreement with simulations (for displacements > segment size)

- long time limit:

$$g_{\mathrm{seg}}(t) \approx 6 D_G t \qquad (t \gg \tau_1)$$

- intermediate times:

$$\begin{aligned}
g_{\mathrm{seg}}(t) &= \frac{2b^2}{\pi^2}(N+1)\int_0^\infty \mathrm{d}p\ \frac{1}{p^2}\left(1-\mathrm{e}^{-tp^2/\tau_1}\right) \\
&= \frac{2b^2}{\pi^2}(N+1)\int_0^\infty \mathrm{d}p\ \frac{1}{\tau_1}\int_0^t \mathrm{d}t'\ \mathrm{e}^{-t'p^2/\tau_1} \\
&= \frac{2b^2}{\pi^2}\frac{(N+1)}{\tau_1}\frac{1}{2}\sqrt{\pi\tau_1}\int_0^t \mathrm{d}t'\ \frac{1}{\sqrt{t'}} \\
&= \left(\frac{12 k_B T b^2}{\pi\zeta}\right)^{1/2} t^{1/2} \qquad (\tau_N \ll t \ll \tau_1,\ N \gg 1)
\end{aligned}$$

Stress and viscosity

- remember the Green-Kubo relations for viscosity & shear relaxation modulus

$$\eta = \int_0^\infty G(t) \mathrm{d}t$$

$$G(t) = \frac{V}{k_B T} \langle \sigma_{yz}(t) \sigma_{yz}(0) \rangle$$

$$\boldsymbol{\sigma} = -\frac{1}{V} \left(\sum_{i=1}^{N_{\mathrm{tot}}} M_i \mathbf{V}_i \mathbf{V}_i + \sum_{i=1}^{N_{\mathrm{tot}}-1} \sum_{j=i+1}^{N_{\mathrm{tot}}} (\mathbf{R}_i - \mathbf{R}_j) \mathbf{F}_{ij} \right)$$

- microscopic stress tensor is a collective property
  - sums run over all segments of all polymer chains in the system
  - Rouse model: dynamics of one chain uncorrelated with that of another
  - we can study stress relaxation of single chain and make ensemble average
  - overdamped: kinetic contribution to stress may be neglected

Microscopic stress tensor of a Rouse chain

- the forces are due to the entropic springs connecting the segments:

$$\sigma = -\frac{1}{V}\sum_{n=1}^{N}\left(\mathbf{R}_{n-1}-\mathbf{R}_{n}\right)\frac{3k_BT}{b^2}\left(\mathbf{R}_{n}-\mathbf{R}_{n-1}\right)$$

- rewrite in terms of Rouse modes

$$\begin{aligned}
\boldsymbol{\sigma} &= \frac{1}{V}\frac{3k_BT}{b^2}\sum_{n=1}^{N}\left(\mathbf{R}_{n-1}-\mathbf{R}_{n}\right)\left(\mathbf{R}_{n-1}-\mathbf{R}_{n}\right) \\
&= \frac{1}{V}\frac{48k_BT}{b^2}\sum_{n=1}^{N}\sum_{p=1}^{N}\sum_{q=1}^{N}\mathbf{X}_p\mathbf{X}_q\sin\left(\frac{p\pi n}{N+1}\right)\sin\left(\frac{p\pi}{2(N+1)}\right)\times \\
&\quad \sin\left(\frac{q\pi n}{N+1}\right)\sin\left(\frac{q\pi}{2(N+1)}\right) \\
&= \frac{1}{V}\frac{24k_BT}{b^2}N\sum_{p=1}^{N}\mathbf{X}_p\mathbf{X}_p\sin^2\left(\frac{p\pi}{2(N+1)}\right) = \frac{3k_BT}{V}\sum_{p=1}^{N}\frac{\mathbf{X}_p\mathbf{X}_p}{\left\langle X_p^2\right\rangle}.
\end{aligned}$$

Stress relaxation in a melt of Rouse chains

- we need averages of

$$\sigma_{xy}(t)\sigma_{xy}(0) = \left(\frac{3k_BT}{V}\right)^2 \sum_{p=1}^{N}\sum_{q=1}^{N} \frac{X_{px}(t)X_{py}(t)X_{qx}(0)X_{qy}(0)}{\left\langle X_p^2\right\rangle \left\langle X_q^2\right\rangle}$$

- Rouse modes are Gaussian variables:

$$\begin{aligned}\left\langle X_{px}(t)\,X_{py}(t)\,X_{qx}(0)\,X_{qy}(0)\right\rangle &= \cancel{\left\langle X_{px}(t)\,X_{py}(t)\right\rangle}\,\cancel{\left\langle X_{qx}(0)\,X_{qy}(0)\right\rangle}\\ &+ \cancel{\left\langle X_{px}(t)\,X_{qy}(0)\right\rangle}\,\cancel{\left\langle X_{py}(t)\,X_{qx}(0)\right\rangle}\\ &+ \left\langle X_{px}(t)\,X_{qx}(0)\right\rangle \left\langle X_{py}(t)\,X_{qy}(0)\right\rangle\end{aligned}$$

$$\left\langle X_{px}(t)X_{qx}(0)\right\rangle = \left\langle X_{px}(t)X_{px}(0)\right\rangle \delta_{pq} = \frac{1}{3}\left\langle \mathbf{X}_p(t)\cdot\mathbf{X}_p(0)\right\rangle \delta_{pq}$$

$$G(t) = \frac{k_BT}{V}\sum_{p=1}^{N}\left[\frac{\left\langle \mathbf{X}_p(t)\cdot\mathbf{X}_p(0)\right\rangle}{\left\langle X_p^2\right\rangle}\right]^2 = \frac{ck_BT}{N+1}\sum_{p=1}^{N}\exp\left(-2t/\tau_p\right)$$

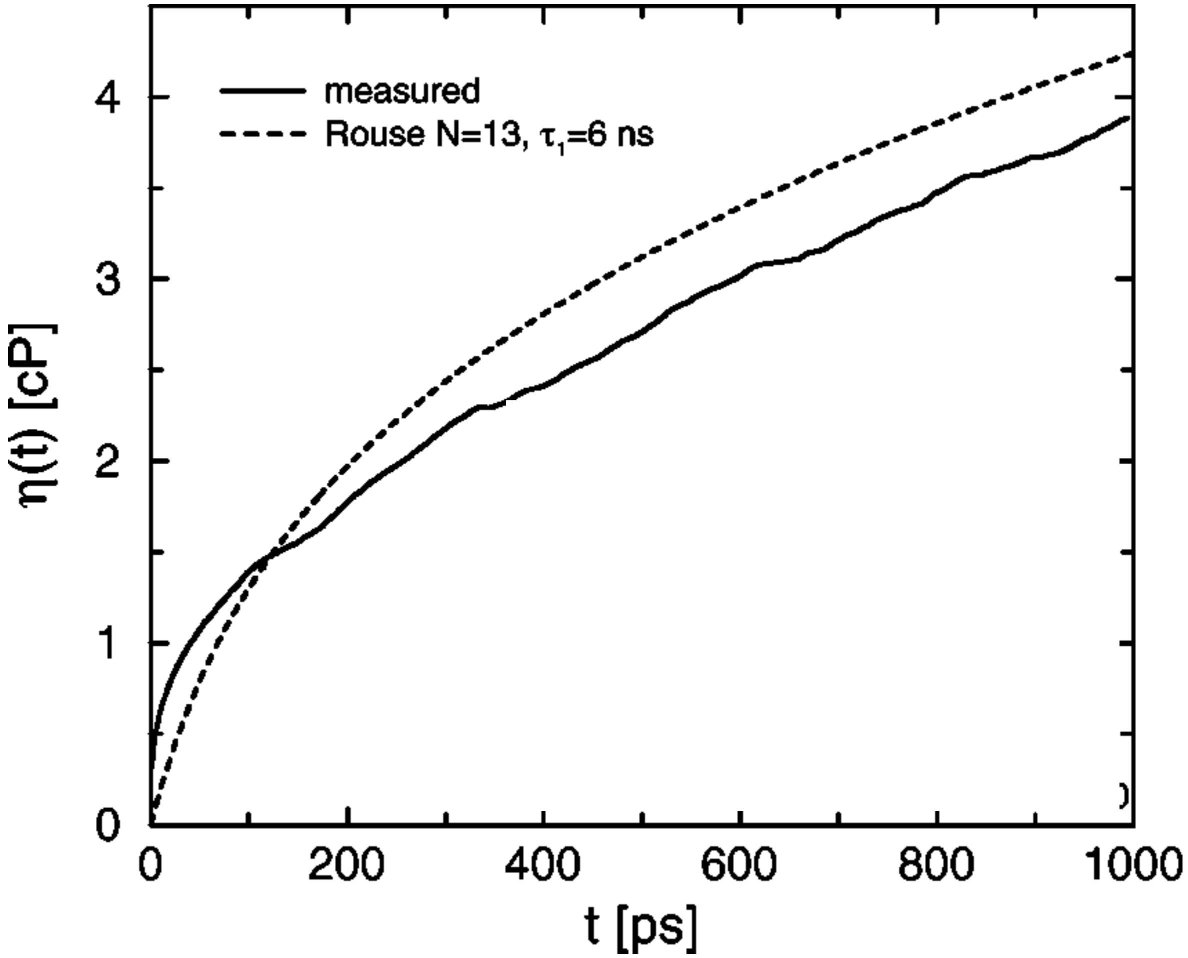
Viscosity of a melt of Rouse chains

$$\eta = \int_0^\infty \mathrm{d}t G(t) \approx \frac{ck_BT}{N+1}\frac{\tau_1}{2}\sum_{p=1}^{N}\frac{1}{p^2}$$

$$\approx \frac{ck_BT}{N+1}\frac{\tau_1}{2}\frac{\pi^2}{6} = \frac{c\zeta b^2}{36}(N+1)$$

- viscosity scales linearly with molecular weight of the polymer

- in good agreement with experiments and simulations of unentangled polymer melts



$$\eta(t) \equiv \int_0^t \mathrm{d}\tau G(\tau)$$

Summary of chapter 4

- large scale properties of polymers are independent of chemistry; end-to-end vector distribution is Gaussian

$$\boxed{\Omega\left(\mathbf{R}; N\right) = \left\{\frac{3}{2\pi N b^2}\right\}^{3/2} \exp\left\{-\frac{3R^2}{2Nb^2}\right\}.}$$

- Rouse model = Gaussian chain + Langevin equations for segments; normal mode analysis reveals characteristic scalings:

$\tau_1 \propto N^2$ longest relaxation time

$D_G \propto N^{-1}$ diffusion of the centre-of-mass

$\eta \propto N$ shear viscosity

in agreement with experiments & simulations of unentangled polymer melts

The end