Complex Disordered Systems

Static and dynamic correlations

Francesco Turci

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Today

- **Characterisation of colloids**
    - Static (pair) corrleations
    - Diffusive dynamics

Pairwise interactions

True colloidal systems can be complex:

- charges
- shape deformability/swelling
- instabilities of the components

Their theoretical description focuses on **essential ingredients**.

A simplifying assumption is that the potential energy of a collection of colloids is purely **pairwise**

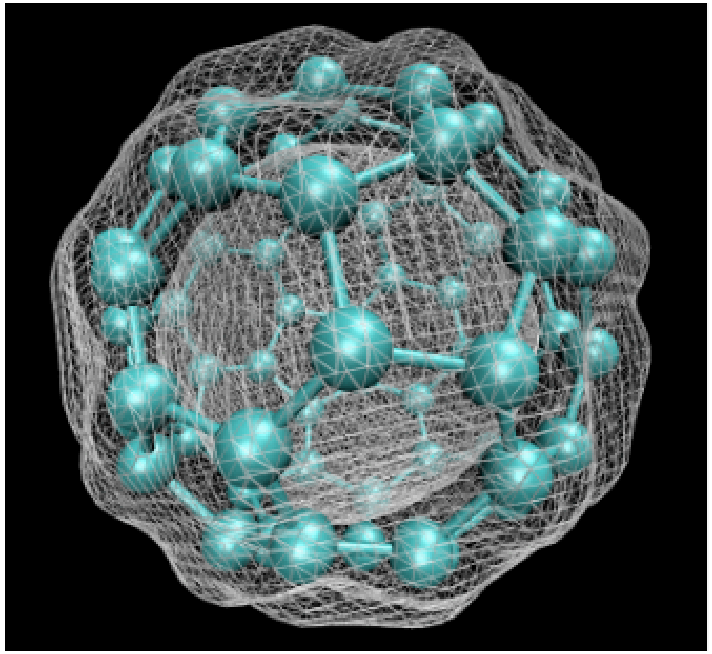
$$U_N\left(\mathbf{r}^N\right) = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} V\left(r_ij\right) = \frac{1}{2} \sum_{i \neq j} V\left(r_{ij}\right)$$

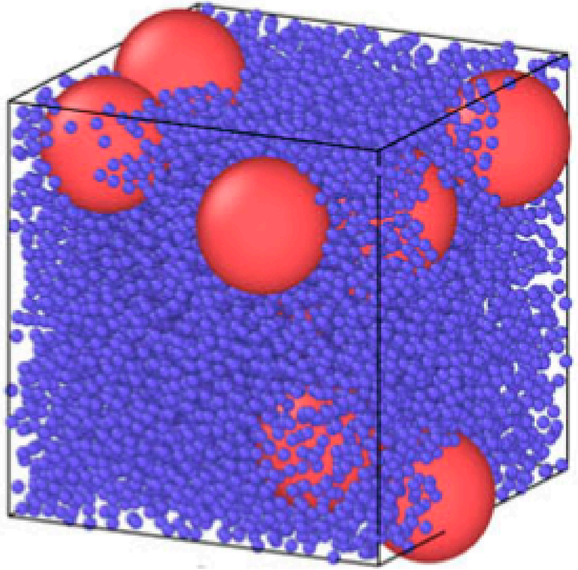
where $V(r_{ij})$ is the pairwise, radial interaction potential that only depends on the distance between particle centres $r_{ij} = \mathbf{r}_i - \mathbf{r}_j$.

Aside: Not pairwise?

Some examples of non-pariwise situations:

- **Atomistic models**: Electronic densities that fluctuate due to quantum effects are intrinsically many-body
- **True colloid-cpolymer mixtures**: if the polymers are not ideal, their spatial distribution and their forces depend on the positions of more than two colloids





C_{60} isosurface via density functional theory (Wikipedia) and configuration of non-deal colloid-polymer mixture, Rohrbach et al JCP (2022)

Pairwise interactions and pair correlations

- For **pairwise** systems, all the thermodynamic properties are solely encoded in the **pairwise correlations**.

You have already seen such correlations in other contexts (Ising model, lattice gas).

The key pair correlation is the real space **radial distribution function**:

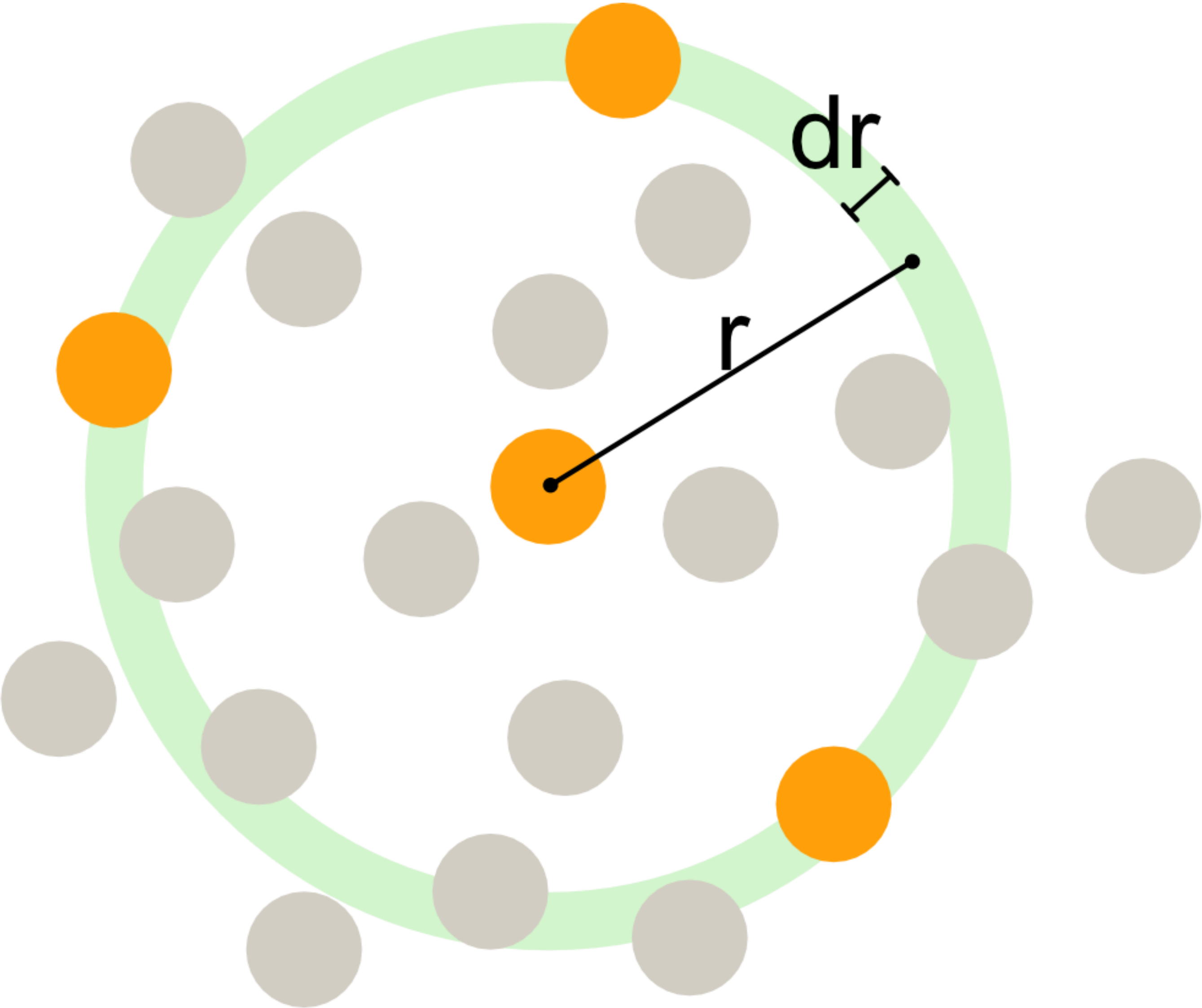
$$g(r) = \frac{1}{\rho N} \left\langle \sum_{i=1}^{N} \sum_{j \neq i} \delta\left(|\mathbf{r}_i - \mathbf{r}_j| - r\right) \right\rangle$$

The free energy can then be written as

$$\frac{F_{\mathrm{ex}}}{k_B T} = 2\pi\rho N \int_0^\infty [g(r)\ln g(r) - g(r) + 1] r^2 dr + \frac{\rho N}{2 k_B T} \int V(r) g(r) d^3 r$$

and you should be able to read out a part very reminiscent of an (information-theoretical) entropy and one reminiscent of an internal energy.

Radial distribution function



The radial distribution function, algorithmic interpretation: at a distance r, we count the number of particle centres within a slice of width dr and then normalise.

Radial distribution function

Radial distribution function

- For an **ideal gas**, $g(r) = 1$ everywhere (no correlations).
- For **hard spheres**, $g(r) = 0$ for $r < \sigma$ (no overlap), and $g(r)$ shows oscillations at higher r due to packing effects.

> ⓘ **Note**
>
> Hard spheres in 3D are not exactly solvable! We only have perturbative solutons to hard spheres

- The $g(r)$ is the central object of (equilibrium) liquid state theory
- Correlations between two particles 1 and 2 in a fluid to have two possible origins
  - a **direct** correlation between the two particles, mediated by direct interactions (e.g. collisions) between 1 and 2.
  - an **indirect correlation**, mediated by other particles in the fluid

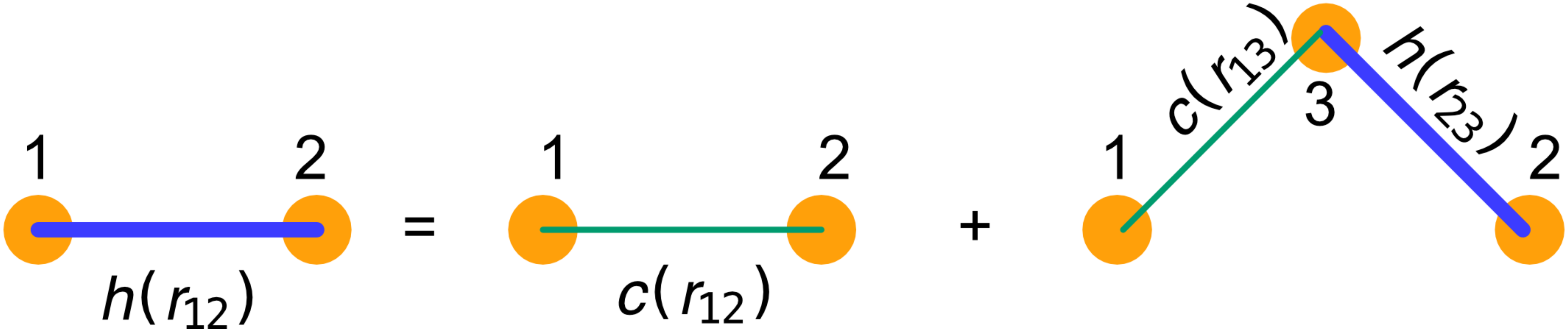
Direct and indirect correlations

- The $g(r)$ contains **both**.
- We can assume the existence of a correlation function that instead only incl;udes the **direct** part and call it $c(r)$. Then a hierarchy exists

$$h\left(r_{12}\right)=c\left(r_{12}\right)+\rho\int c\left(r_{13}\right)h\left(r_{32}\right)d\mathbf{r}_3$$

where $h(r)=g(r)-1$. This is the **Ornstein-Zernicke integral equation** between particles 1,2 and 3.

Both $h(r)$ and $c(r)$ are unknwon in principle. One needs an additional condition to fix box: these are **physical closures** leading to approximations.



Meaning of teh Ornstein-Zernicke relation, adapted from Santos, Springer(2016)

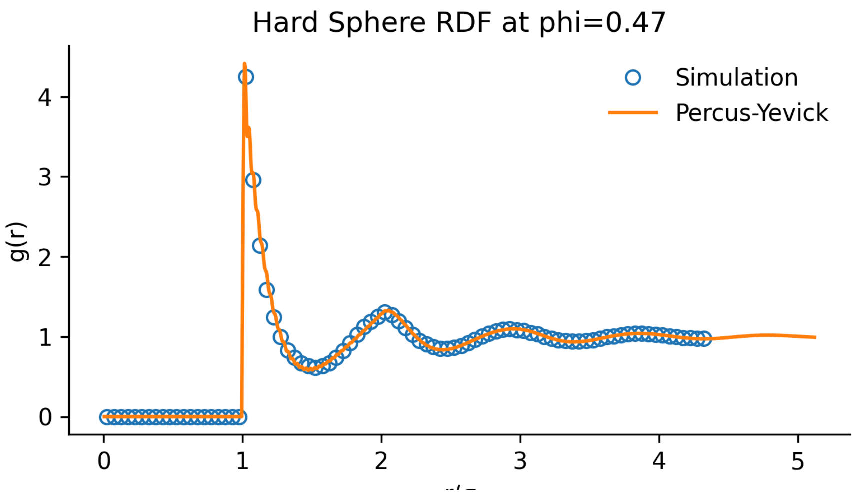
Percus-Yevick approximation

A common closure is the **Percus-Yevick approximation**.

$$c(r) = [1 + h(r)]\left[1 - e^{\beta U(r)}\right]$$

This closure interpolates between the hard-core exclusion (for $U(r) \to \infty$, $c(r) \to 0$ inside the core) and the ideal gas limit (for $U(r) = 0$, $c(r) = 0$).

The result (semi) analytical. For hard spheres, it allows to calculate the g(r) accurately in a wide range of packing fractions


Hard Sphere RDF at phi=0.47

PY approximation vs simulated data for hard spheres.

Equation of states from $g(r)$

The knowledge of the pair correlations also allows one to extract equation of states and significantly improve on the virial expansion, as the $g(r)$ contains packing effects!

$$P = \rho k_B T - \frac{2\pi\rho^2}{3}\int_0^\infty r^3 \frac{du(r)}{dr} g(r) dr$$

Note

For hard spheres, The derivative $\frac{du(r)}{dr}$ is zero everywhere except at the contact point $r = \sigma$, where it becomes a delta function:

$$\frac{dV(r)}{dr} = -\infty\delta(r-\sigma)$$

Substituting into the pressure equation:

$$P = \rho k_B T + \frac{2\pi\rho^2}{3}\sigma^3 g(\sigma)$$

Therefore, for hard spheres, the equation of state only requires knowledge of the contact value $g(\sigma)$.

We will see this in a problem class.

Structure factor

The real-space correlations and relations have their reciprocal (*Fourier* space) counterparts.

The structure factor is defined as

$$S(k) = 1 + \rho \int [g(r) - 1] e^{-i\mathbf{k}\cdot\mathbf{r}} d\mathbf{r}$$

Isotropicity in 3D simplifies the expression to

$$S(k) = 1 + 4\pi\rho \int_0^\infty r^2 [g(r) - 1] \frac{\sin(kr)}{kr} dr$$

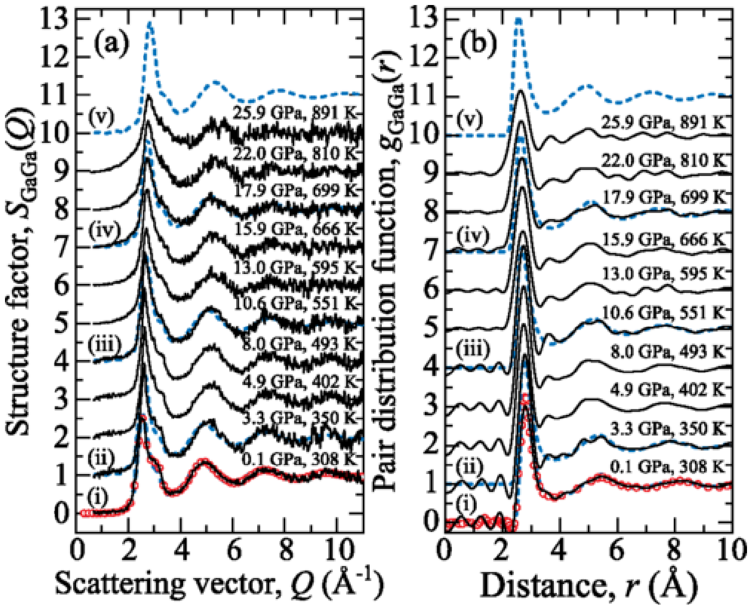
- Radial distribution functions → easily accessed in **confocal experiments** (large colloids)
- Structure factors → immediately accessed via **scattering experiments**

Structure factor

Interestingly, reciprocal space simplifies integral equations such as Ornstein-Zernicke

$$\tilde{h}(k) = \frac{\tilde{c}(k)}{1 - \rho\tilde{c}(k)}$$

allowing one to read the direct correlation function directly from scattering data, as $\tilde{h}(k) =$ can be identified with the structure factor.

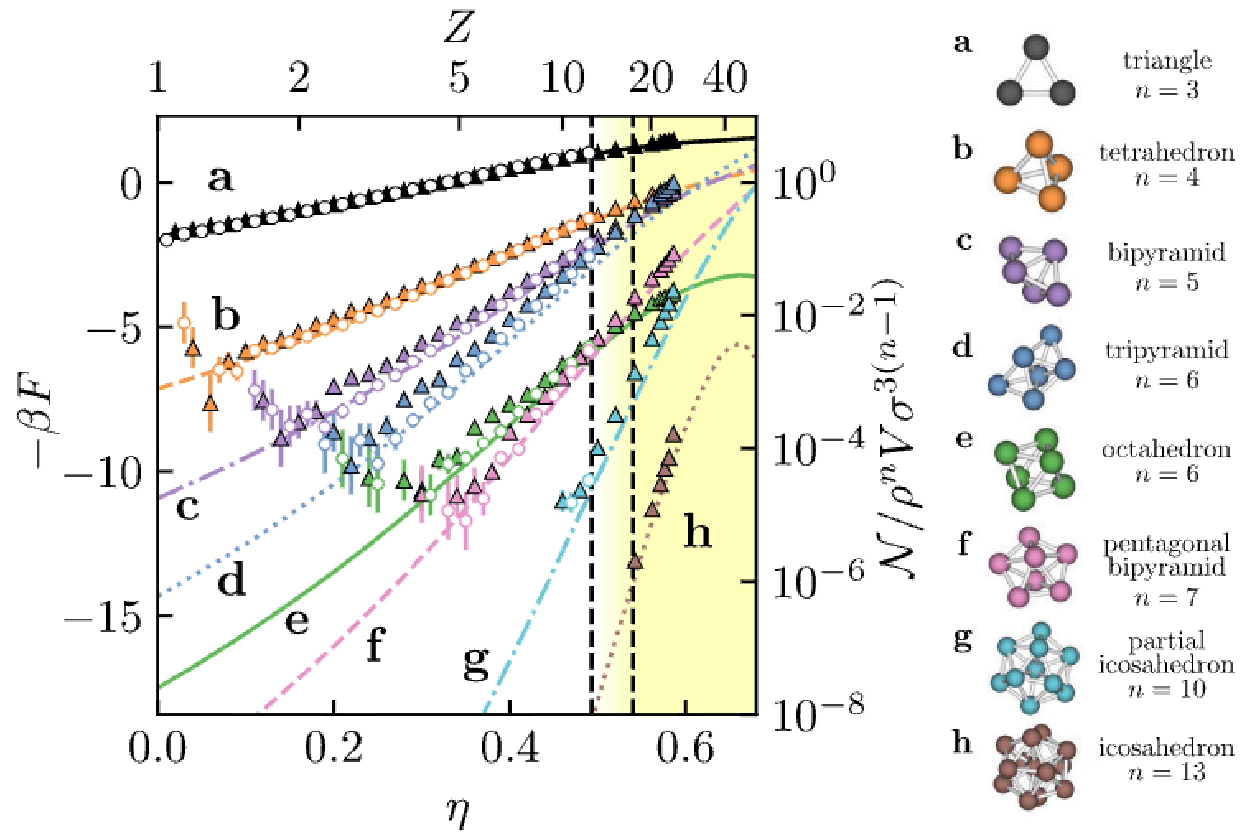


Structure factors (left) and radial distribution functions (right) for Gallium at extreme conditions, Drewitt et al PRL (2020)

Aside: higher order correlations

Nothing prevents us to quantify higher order correlations. In general these are non-trivial are controlled by the indirect part of the correlations.

Standard ways to identify **n-particle*** correlations is to measure **structural motifs**.



Many body correlations in hard spheres, seminal work from Josh Robinson, PhD student in Bristol a few years ago, Robinson et al PRL (2019)

This is particularly important for dense systems (e.g. glasses, see future lecture).

Dynamics: single vs collective displacements

The thermal motion of individual colloids is often well modeled via the **Langevin equation**

$$m\frac{d\vec{v}}{dt} = -\gamma\vec{v} + \vec{\eta}(t)$$

Coarse-graining over small volumes (and short times) gives us access to the local density $\rho(\mathbf{r}, t)$ which obeys a **diffusion equation**

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

The diffusivity is linked to the microscopic Langevin parameters via **fluctuation-dissipation** (Einstein's relation)

$$D = \frac{k_B T}{\gamma}$$

(where the friction is the dissipation and the random force is the fluctuations).

Diffusion equation: macroscopic picture

It is possible to (re)-derive the diffusion equation solely from macroscopic requirements. We have a macroscopic density $\rho(r,t)$ and a macroscpic flux $\vec{J}(r,t)$

- **continuity**: there is no mass loss in the dynamics

$$\frac{\partial \rho(\mathbf{r},t)}{\partial t} + \nabla \cdot \mathbf{J}(\mathbf{r},t) = 0$$

where the divergence $\nabla \cdot \mathbf{J}(\mathbf{r},t)$ represents the net outflow of particles from a given region due to the flux $\mathbf{J}$.

- **Fick's law** : we assume the flow is a gradient field of the density, flowing from high to low density

$$\mathbf{J}(\mathbf{r},t) = -D\nabla\rho(\mathbf{r},t)$$

It is immediate to combine the two to obtain the diffusion equation

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

Measuring diffusion coefficients

The distribution $\rho(\mathbf{r}, t)$ encodes all the information about the motion of an ensemble.

Often, less is sufficient to characterise the diffusion. The second moment of the displacements (the mean squared displacement) provides this information. In d dimensions

$$\left\langle \left|\mathbf{r}(t) - \mathbf{r}(t_0)\right|^2 \right\rangle = 2dDt$$

Hence D can be extracted from linear fits to the MSD.

Stokes-Einstein relation: fluctuation dissipation for colloids

In dilute conditions, let's think of a particle slowly sedimenting in a viscous fluid.

The density distribution is Boltzmann

$$n(x) = n_0 \exp\left(-U(x)/k_B T\right) = n_0 \exp\left(-Fx/k_B T\right)$$

where $F = m_B g$ is the force from the buoyant mass.

A flux is produced $J_F = n(x)v = \frac{n(x)F}{\xi}$

where we used the fact that the velocity is set by the viscosity η as $v = F/\eta$.

Diffusion occurs at the same time, driven by the gradient (Fick's law)

$$J_D(x) = -D\frac{\partial n(x)}{\partial x}$$

Stokes-Einstein relation: fluctuation dissipation for colloids

Equating the two we have

$$\frac{n(x)F}{\xi} = -D\frac{\partial n(x)}{dx} = D\frac{F}{k_B T}n(x)$$

and differentiating the Boltzmann distribution gives

$$\frac{n(x)F}{\xi} = D\frac{F}{k_B T}n(x)$$

Hence a balance exists between thermal fluctuations and viscosities. For a sphere, **Stoke's law** $\xi = 6\pi\eta R$ yielding simply

$$D = \frac{k_B T}{\xi} = \frac{k_B T}{6\pi\eta R}$$

This is a re-statement of the Einstein relation, called the **Stokes-Einstein** relation.

$$\text{Fluctuations: } k_B T \quad \longrightarrow \quad \text{Observed motion: } D \quad \longrightarrow \quad \text{Dissipation: } 6\pi\eta R.$$

Which is generic under (moderate) driving.

Random walkers in 2d, example

```python
n_steps, n_walkers, dim = 10000, 500, 2
steps = np.random.randint(-1, 2, size=(n_walkers, n_steps, dim))
positions = np.cumsum(steps, axis=1)  # cumulative sum along steps
msd = positions.var(axis=0).sum(axis=1)  # MSD at each timestep
plot_tj(positions,msd,walker=0,loglog=False)
```

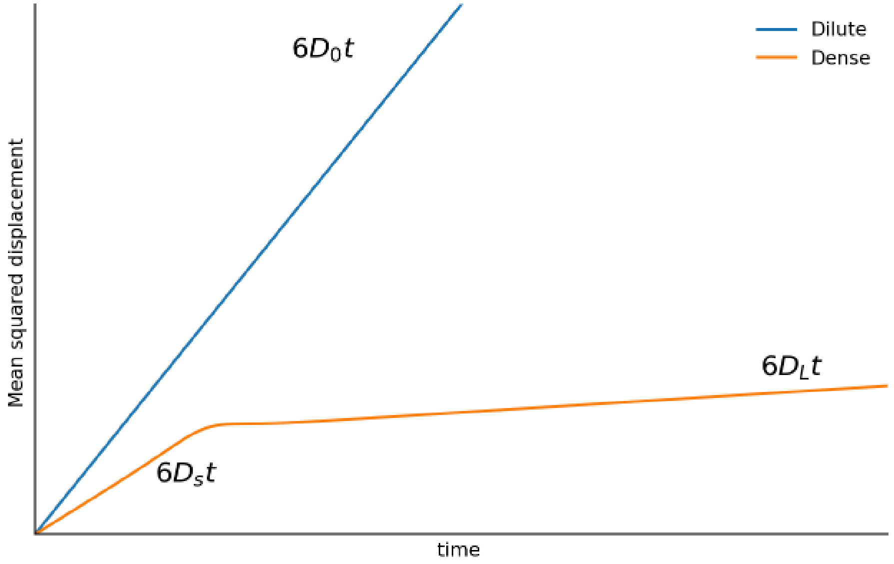
Hidden assumptions

Note

- We have been considering ensembles of particles microscopically governed by the Langevin equation
- We did not comment on the inter-particle interactions and assumed that the properties of the thermal bath determine the diffusivity D. In reality, interactions between particles can lead to deviations from simple diffusion, especially at higher concentrations, where collective effects and hydrodynamic interactions become important.

Dilute vs dense diffusion

- Consider hard spheres in a fluid.
- At low volume fractions ϕ they rarely collide and they perofrm under/over-damped (Langevin) dynamics. They will therefore diffuse as $\mathrm{MSD}(t) = 6D_0t$
- Things change when we increase the packing.
  - Short times: $D_s < D_0$, diffusion within **cages** formed by the neighbours. Mostly free, but with some collisions.
  - Long times: $D_L \ll D_0$ cage breaking. Interactions are both hard core and hydrodynamic



MSD of colloids

Dilute vs dense diffusion

- At **very high** volume fractions the cage mechanism becomes more complex: paricles are trapped for long times and only occasionaly break cages:
  - cage-jump dynamics $\to$ glassy dynamics (see future lectures)
  - rare events $\to$ Levy-flight statistics $\neq$ Gaussian/diffusive statistics
  - Breaking of fluctuation-dissipation condition encoded in the **Stokes-Einstein** relation
    - the viscosity increases much faster than the decrease in diffusion $D\xi/T \neq \mathrm{constant}$