Coarse-Graining:

Representing a system with fewer degrees of freedom by eliminating "unimportant" details.

More generally: Omitting details from a model that is too expensive to compute by extracting the crucial physics or mathematical structure

In this course, we focus on classical models of materials:

gases, liquids, solids, granular matter

fluids

Molecular dynamics is the [MICROSCOPIC] or most detailed level of description. The position of every atom is represented explicitly, $\vec{r}_i(t)$, $i = 1, \dots, N$

[NEWTON'S 2ND LAW] $$m_i \ddot{\underline{r}}_i = m_i \frac{d^2 \vec{r}_i(t)}{dt^2} = F_i(\underline{r})$$

Notation: Vectors are denoted with bold in print but either underline or $\rightarrow$ in hand writing.

$$\underline{r} = \{\underline{r}_1, \underline{r}_2, \dots, \underline{r}_N\} \in \mathbb{R}^{3d}, \quad d = 2, 3 \ [\text{dimension}]$$

$$\underline{v}_i = \frac{d\vec{r}_i(t)}{dt} \quad [\text{velocity}]$$

Chemical bonding requires quantum mechanics

The problem with molecular dynamics [MD] is two-fold:

1. Too many DFs (degrees of freedom), $N \approx 10^{23}$,
2. Dynamics is too fast: characteristic timescale and thus timestep in simulations is on the order of fs-ps $[10^{-15} - 10^{-12}\ s]$

The two are closely related: The number of DFs depends on the characteristic lengthscale associated with the level of description. For MD, atomistic length scale is Å-nm [Note: $1\text{Å} = 10^{-10}\ m$]

Usually

$$\tau \sim \begin{cases} \ell / v \leftarrow \text{velocity} \\ \ell^2 / D \leftarrow \text{diffusion coefficient} \end{cases}$$

τ: timescale; ℓ: lengthscale

By coarse-graining the level of description we thus increase the length and time scale associated with the model.

MICRO → MESO → MACRO

Time scale: 10^{-15} fs | 10^{-12} ps | 10^{-9} ns | 10^{-6} μs | 10^{-3} ms | 10^{0} (s)

Length scale: 10^{-10} Å | 10^{-9} nm | 10^{-6} μm | 10^{-3} mm

Algorithms:	MD (Hamiltonian dynamics)	KMC DPD DSMC	Brownian D QC Langevin	Continuum mechanics or fluid dynamics
Mathematical Description:	ODEs	MCMC SODEs FPEs	Hybrids SODEs SPDEs	PDEs DEM

Coarse-graining notes

1. Coarser levels have a smaller number of effective (rather than formal) DFs
2. A coarse(r) level is valid for describing time scales (and length scales!) larger than some coarse-graining scale
3. Usually the most detailed (bottom of the hierarchy) level is called microscopic, and the top most level macroscopic. In-between there are many mesoscopic levels.

(4) Coarse-graining can be put on a formal mathematical foundation (Kirkwood, Green, Mori, Zwanzig), but this relies on taking some limit or expansion in a small parameter

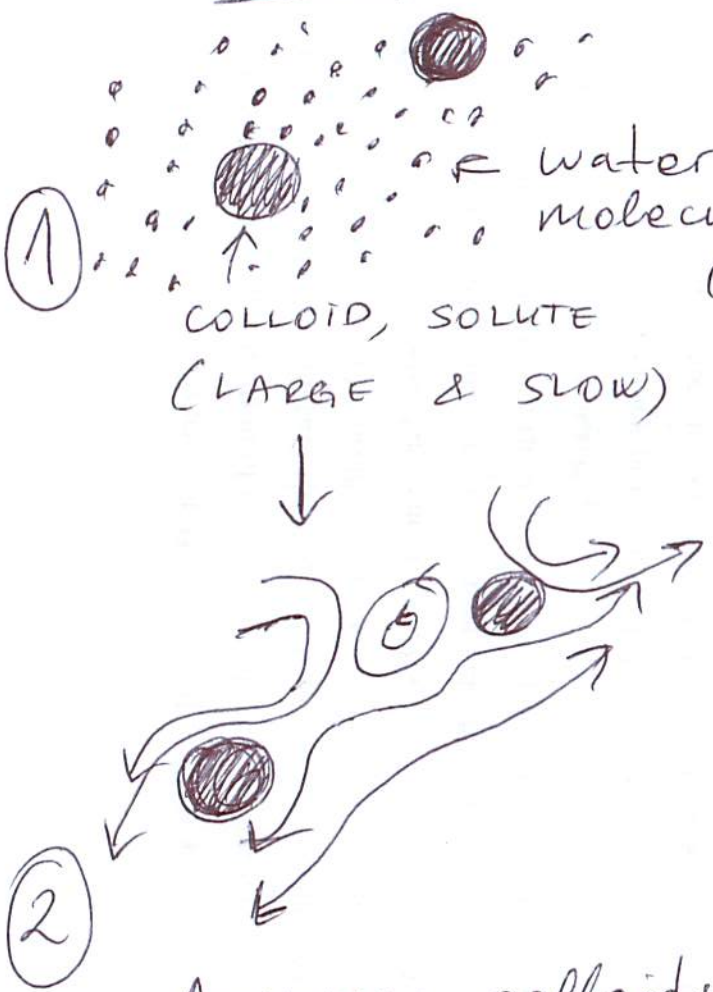
(5) Usually, it is assumed or demonstrated that there is a <u>separation of time scales</u> between the eliminated and the kept degrees of freedom (e.g. conservation of mass, momentum and energy makes those fields or moments slowly-evolving)

(6) Coarse-grained models are statistical in nature: They describe certain averages of the finer levels and their dynamics or evolution equations must be probabilistic or stochastic rather than deterministic.

The eliminated DFs enter the description as random terms/variables and lead to dissipation and irreversibility even if the microscopic level is Hamiltonian and reversible.

(7) Statistical mechanics (equilibrium or non-equilibrium) is the foundation of coarse-graining.

Example: COLLOIDAL SUSPENSION



10^{-12} s

$\Gamma_1, \ldots, \Gamma_{N_c}$
$q_1, \ldots, q_N$ } MD

$N >> N_c >> 1$

Assumes colloids are large and move slowly compared to water molecules

$10^{-9} - 10^{-6}$ seconds

$\Gamma_1, \ldots, \Gamma_{N_c}$
$v_1, \ldots, v_{N_c}$ } MD

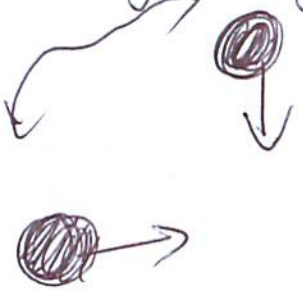
$u(r, t)$ — velocity field

fluctuating hydrodynamics (vortices, waves, collective modes)

Assumed to be SMOOTH on scales of interest

Hydrodynamic interactions (velocity-dependent)

(3)



implicit solvent

$\left\{ \begin{array}{l} r_1, \ldots, r_{N_c} \\ v_1, \ldots, v_{N_c} \end{array} \right.$ Langevin

Fluid assumed to evolve much faster than colloidal DFs

This level is INCONSISTENT! Except for very dense colloids.

Velocities of colloidal particles are also "fast" DFs and not separated

(4)

implicit solvent

$\{ r_1, \ldots, r_{N_c}$ Brownian dynamics

No velocities

(Smoluchowski dynamics)

(5) Concentration of colloids $c(r,t)$

$$\partial_t c = -\nabla\cdot\left[-D\nabla c + \tilde{J}\right]$$

$$= D\nabla^2 c - \nabla\cdot\tilde{J}$$ ← stochastic (random) flux

↑ Fick's law, diffusion equation (DILUTE suspensions)

Maybe also velocity field ?

(6) In the macroscopic limit or level the evolution law becomes deterministic (classical PDEs):

$$\partial_t c = D\nabla^2 c$$ ← non-equilibrium for

Or thermodynamics (only rigorously established for true equilibrium)

There are many time scales associated with the dynamics of the colloidal particles:

(1) Molecular or <u>collisional</u> time scale τ_{coll}

(2) Sonic or <u>sound</u> scale $\tau_s \approx \frac{a}{c}$ ← colloid size; ↖ speed of sound

(3) <u>Viscous</u> time scale

$$\tau_v \approx \frac{a^2}{\nu}$$

← viscosity (momentum diffusion coefficient)

(4) <u>Diffusive</u> or Brownian time scale

$$\tau_B \simeq \frac{a^2}{D} \approx \frac{\rho \nu a^3}{k_B T}$$

(5) Advective, diffusive and other <u>macroscopic</u> scales