11th i-CoMSE Workshop: Mesoscale Particle-Based Modeling

Mississippi State University
July 21–25, 2025

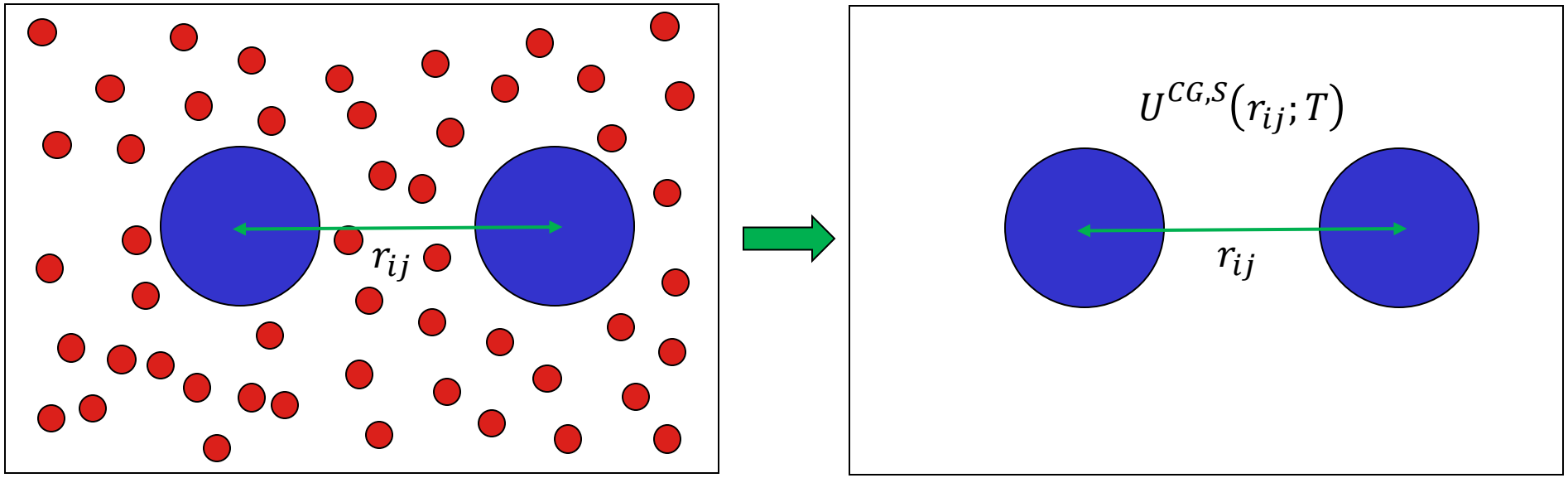
Session 6: Langevin dynamics

Implicit solvent simulations

- Recall that we can coarse-grain (CG) out the solvent by computing the potential of mean force between mesoparticles

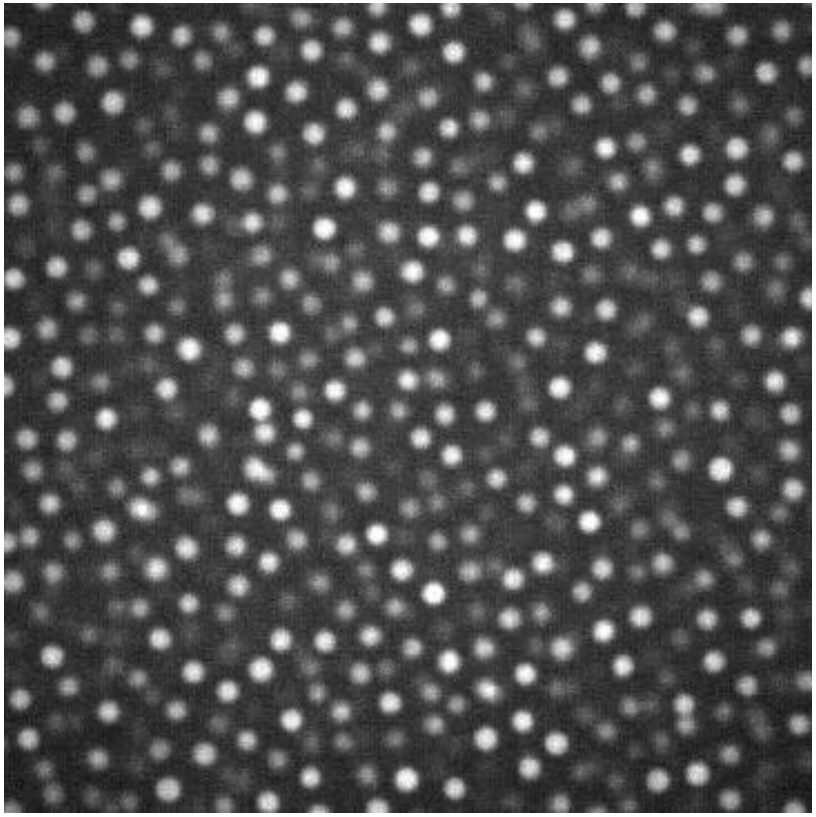
$$U^{CG,IS}(r_{ij};T) = U^{CG,V}(r_{ij};T) + \Delta u^{IS}(r_{ij};T)$$

- $U^{CG,IS}(r_{ij};T)$ is an effective pair potential computed from equilibrium simulations → independent of dynamics
- *Solvent also affects the dynamics of the mesoparticles → "hydrodynamic effects"*



Hydrodynamic effects

- Solvent also affects the dynamics of the mesoparticles
  1. Solvent particles randomly collide with the mesoparticles
  2. Mesoparticles experience viscous drag as they move through the solvent



(Courtesy Jacinta Conrad at the University of Houston)

Hydrodynamic effects

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- At equilibrium, hydrodynamic effects average out and have no impact on equilibrium structural or thermodynamic quantities (e.g., $U^{CG,IS}(r_{ij};T)$)

- They affect equilibrium transport properties (e.g., diffusivities) and become very important when trying to describe nonequilibrium processes (e.g., flow-driven transport)

Random collisions and viscous drag

- Newton's Law $m_i \frac{d^2 \boldsymbol{r}_i}{dt^2} = \mathbf{F}_i^t$

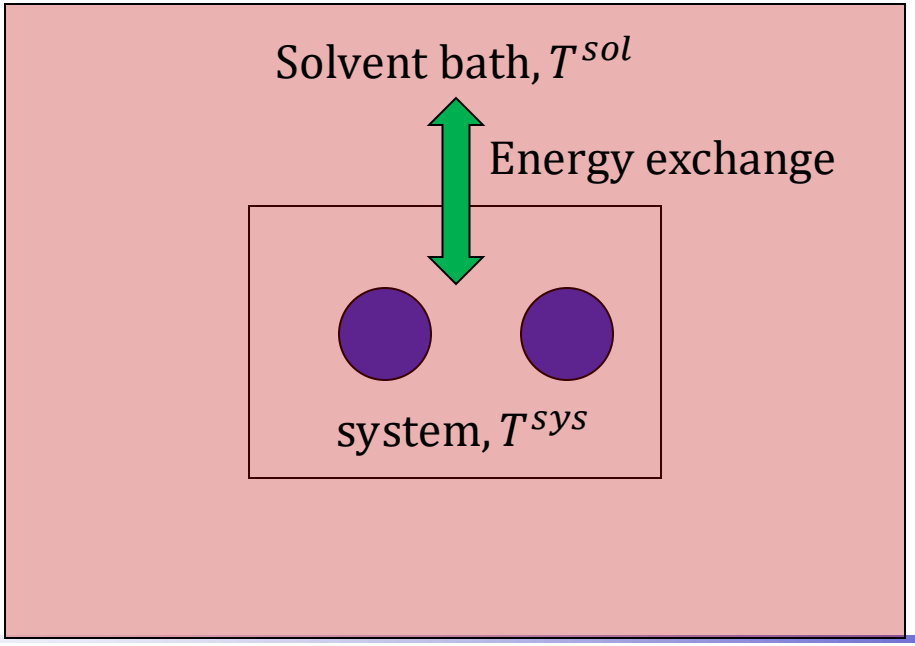
- Force contributions $\mathbf{F}_i^t$:
  - $\mathbf{F}_i^{CG,S}$: force from effective potential → derivative of $U^{CG,S}$
  - $\mathbf{F}_i^R$: force from random collisions with the solvent particles; we assume they are Gaussian with zero mean (average to zero over time $\langle \mathbf{F}_i^R \rangle = 0$)
  - $\mathbf{F}_i^D = -\gamma_i \boldsymbol{v}_i = - -\gamma_i \frac{d\boldsymbol{r}_i}{dt}$: force from viscous drag is assumed to be proportional to the mesoparticle's velocity; γ_i is the drag coefficient

Langevin equation

- Including all the force terms on the right-hand side, we obtain the Langevin equation

$$m_i \frac{d^2 \boldsymbol{r}_i}{dt^2} = \mathbf{F}_i^{CG,S} - \gamma_i \frac{d\boldsymbol{r}_i}{dt} + \mathbf{F}_i^R$$

- Random force adds energy to the mesoparticle system, whereas the drag force dissipates energy. If the solvent bath is very large, the energy exchange with the mesoparticles will not affect T^{sol}.



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- At equilibrium, $T = T^{sys} = T^{sol}$ → **the Langevin equation yields constant temperature equilibrium dynamics!**

- The equilibrium condition implies the fluctuation-dissipation relation

$$\langle |\mathbf{F}_i^R|^2 \rangle = 2dk_B T\gamma_i/\delta t,\ d = 3 \text{ for 3D system}$$

Langevin and Brownian equations

- The Langevin equation for constant temperature dynamics

$$m_i \frac{d^2 \boldsymbol{r}_i}{dt^2} = \mathbf{F}_i^{CG,S} - \gamma_i \frac{d\boldsymbol{r}_i}{dt} + \sqrt{2k_B T \gamma_i / \delta t}\boldsymbol{R}_i(t)$$

- $\boldsymbol{R}_i(t)$: each component is random number drawn from a Gaussian distribution with mean of 0 and variance of 1

- In the limit of large γ_i, the inertial term ($m_i \frac{d^2 \boldsymbol{r}_i}{dt^2}$) can be neglected, yielding the Brownian dynamics or "overdamped" Langevin dynamics equation

$$\gamma_i \frac{d\boldsymbol{r}_i}{dt} = \mathbf{F}_i^{CG,S} + \sqrt{2k_B T \gamma_i / \delta t}\boldsymbol{R}_i(t)$$

Drag coefficient

- In addition to the temperature of the solvent bath T, we also need to specify the drag coefficient γ_i

- Einstein relation for the diffusion coefficient (D_i) of a sphere:

$$\gamma_i = k_B T / D_i$$

- Stoke's law for viscous drag on a sphere of radius a in a solvent with viscosity η:

$$\gamma_i = 6\pi a \eta$$

→ D_i can be estimated from atomistic simulations of the mesoparticles in the solvent, whereas η can be estimated from simulations of the pure solvent

Thermostatted MD

- The Langevin or Brownian dynamics equations can also be used to perform simulations of atomistic systems
- In this context, they are viewed as “thermostats” that act on the system to simulate constant T rather than constant E conditions (canonical vs. microcanonical ensembles)
- Since we are no longer dealing with mesoparticles in an implicit solvent, the physical interpretation of γ_i is less clear; it is simply a parameter that controls the rate of energy exchange with a fictitious thermal reservoir
- The choice of γ_i will not influence structural or thermodynamic equilibrium properties

Other hydrodynamic effects

- Many-body hydrodynamic interactions (HI): As mesoparticles move in the solvent, they exchange momentum with nearby solvent particles, which in turn exchange momentum with other solvent particles. This momentum propagation results in flow of the solvent around the meosparticles, which affects their motions and those of other mesopartices – even those at relatively far away!
- Implicit solvent approaches
  - Replace γ with a more compilated "resistance matrix" that depends on the positions of all of the mesoparticles
  - Brownian dynamics with HI & Stokesian dynamics
- Explicit (coarse-grained) solvent approaches
  - Include a CG solvent to capture these HI
  - **Multiparticle collision dynamics**, dissipative particle dynamics, lattice Boltzmann methods

Exercise

- Langevin dynamics simulations of a 30-mer FENE polymer chain

$$u_{FENE}(r_{ij}) = -\frac{1}{2}kr_0^2\left[1-\left(\frac{r_{ij}}{r_0}\right)^2\right]$$

$$u_{WCA}(r_{ij}) = 4\varepsilon\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12}-\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]+\varepsilon \text{ for } r < 2^{1/6}\sigma_{ij};\ 0 \text{ otherwise}$$

- Examine the effect of the friction coefficient γ_i on properties such as the kinetic temperature and potential energy

$$\langle KE\rangle = \frac{1}{2}kTN_{dof};\quad N_{dof} = 3N-3$$

- Examine the momentum / velocity distribution and compare with the theoretical expectation

$$P(p_{i,x}) = \left(\frac{1}{2\pi m_i kT}\right)^{\frac{1}{2}}\exp\left(-\frac{p_{i,x}^2}{2m_i kT}\right)$$