Simulation of samples

Samuel Hanot, Airidas Korolkovas

9/6/15

Why would you want to simulate your sample when you have the best neutron source ?

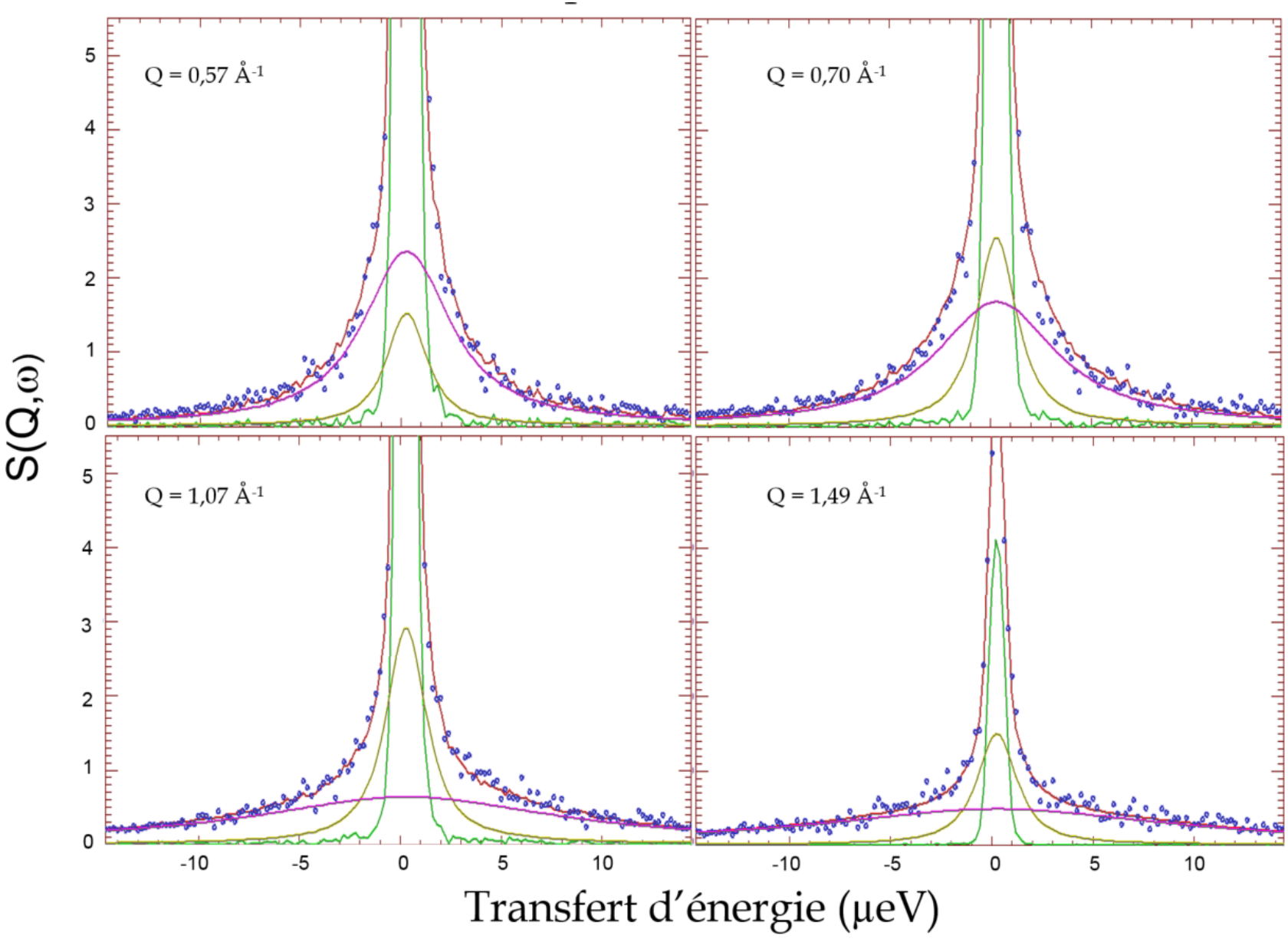
"Neutrons tell us where atoms are and what they do"

Bertram N. Brockhouse and Clifford G. Shull, 1994

i.e. Neutrons sample the Van Hove distribution

$$G(\vec{r},t) = \langle \frac{1}{N} \int \sum_{i=1}^{N} \sum_{j=1}^{N} \delta[\vec{r}' + \vec{r} - \vec{r}_j(t)] \delta[\vec{r}' - \vec{r}_i(0)] d\vec{r}' \rangle$$

Example: What is this ?



The interpretation of the data depends on the proper modeling of structural and dynamic properties of the system

It would be nice if we could use a computer to sample the Van Hove distribution...

This is exactly what a simulation is about

Correlations in the Motion of Atoms in Liquid Argon*

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molecular dynamics in solids, liquids, and gases.[1] The following is a description of a computer experiment on liquid argon (using the CDC 3600) to study the space and time dependence of two-body correlations which determine the manner in which slow neutrons are inelastically scattered from the liquid. If neutron scattering data of unlimited accuracy and completeness was available, then the kind of work presented here would serve the useful though unexciting purpose of confirming the results already obtained with neutrons. At present, however, the situation is that theorists are trying to build models for these two-body dynamical correlations to account for the observed neutron spectra; the current interest in the work presented here is thus to throw some light on the validity of these models, and to suggest the manner in which some improvements can be made.

We need some $\vec{r_i}(t)$ to feed our equations

Example: molecular dynamics

Idea:

1. construct your system in a simulation cell, chose P,T...
2. define interactions between parts of your system
3. solve equations of motion and save $\vec{r}(t)$ at various times
4. compute observable

Integrating Newton's equations of motion

Discretisation of time:
look for $\{\vec{r^n}\} = \{\vec{r}(t_n)\}$, $t^n = n\,\Delta t$, $n = 0, \ldots, N$
now $\frac{d\vec{r}}{dt}(t) = \lim_{dt\to 0} \frac{r(t+dt)-r(t)}{dt} = \vec{v}(t)$ becomes:

$$\vec{v}^n = \frac{r^{n+1} - r^n}{\Delta t}$$

Same for $\vec{v}$, find:

$$\vec{f}^n = m\frac{\vec{v}^{n+1} - \vec{v}^n}{\Delta t}$$

Integrating Newton's equations of motion 2

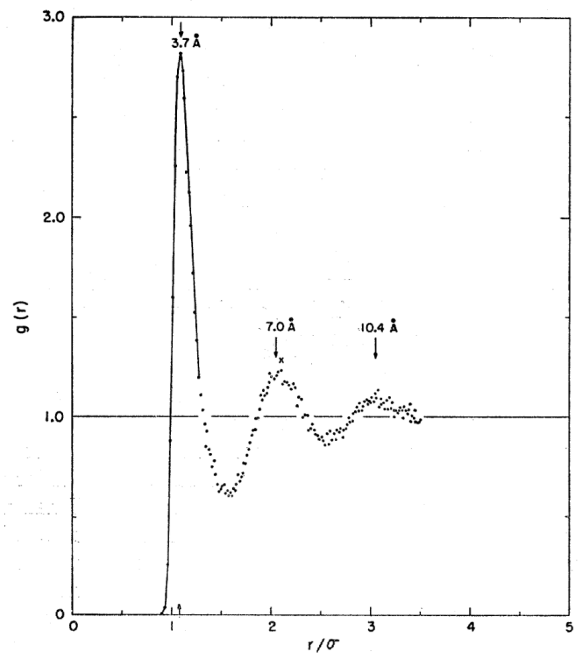
Solve for time $n+1$ and find:

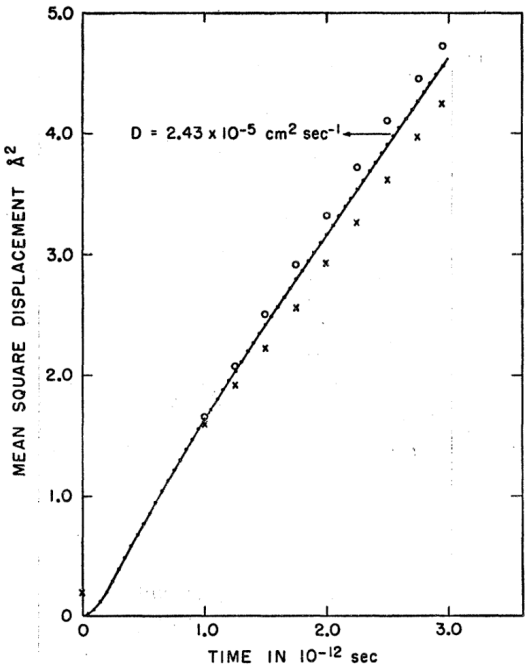
$$r^{n+1} = \vec{r}^n + \vec{v}^n \Delta t$$

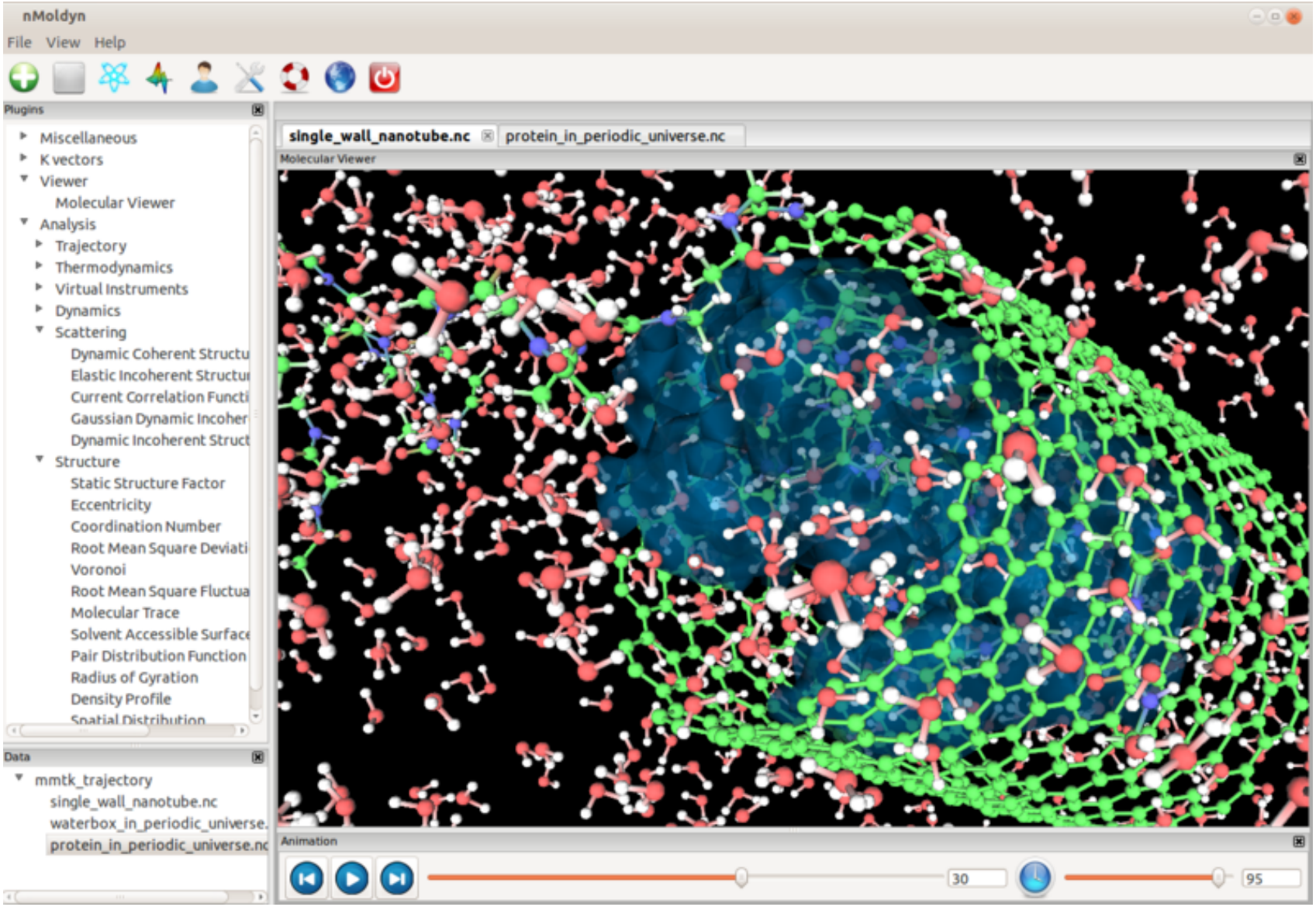
$$v^{n+1} = \vec{v}^n + \vec{f}^n \Delta t / m$$

Computing observables

We can now use the r_i^n, v_i^n to compute observables. What we can usually obtain is a discretized version, ie integrals of δ functions become histograms.



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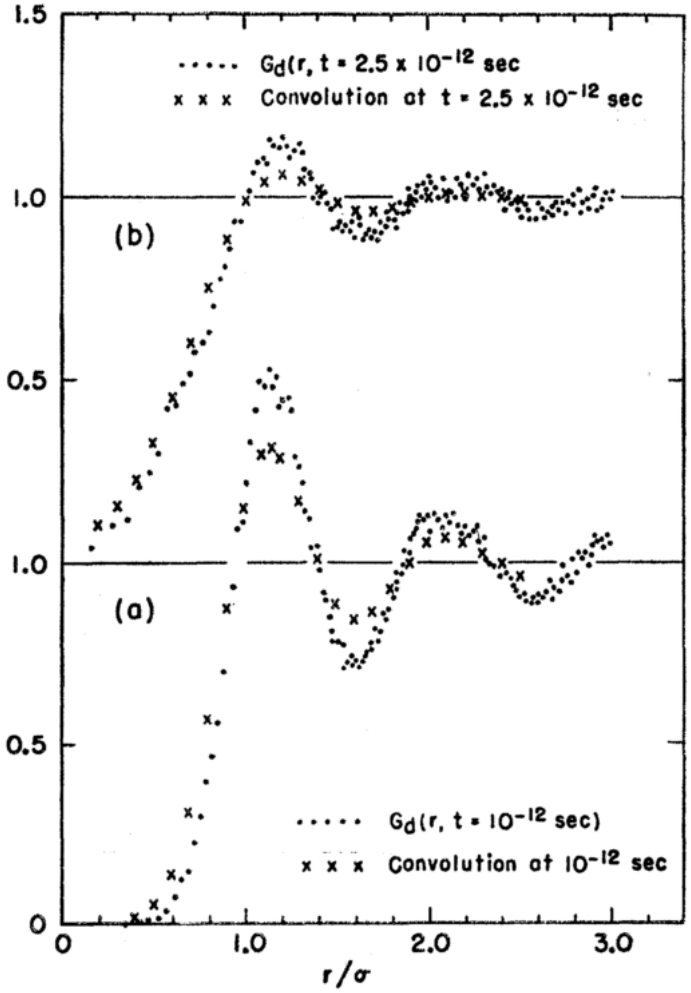
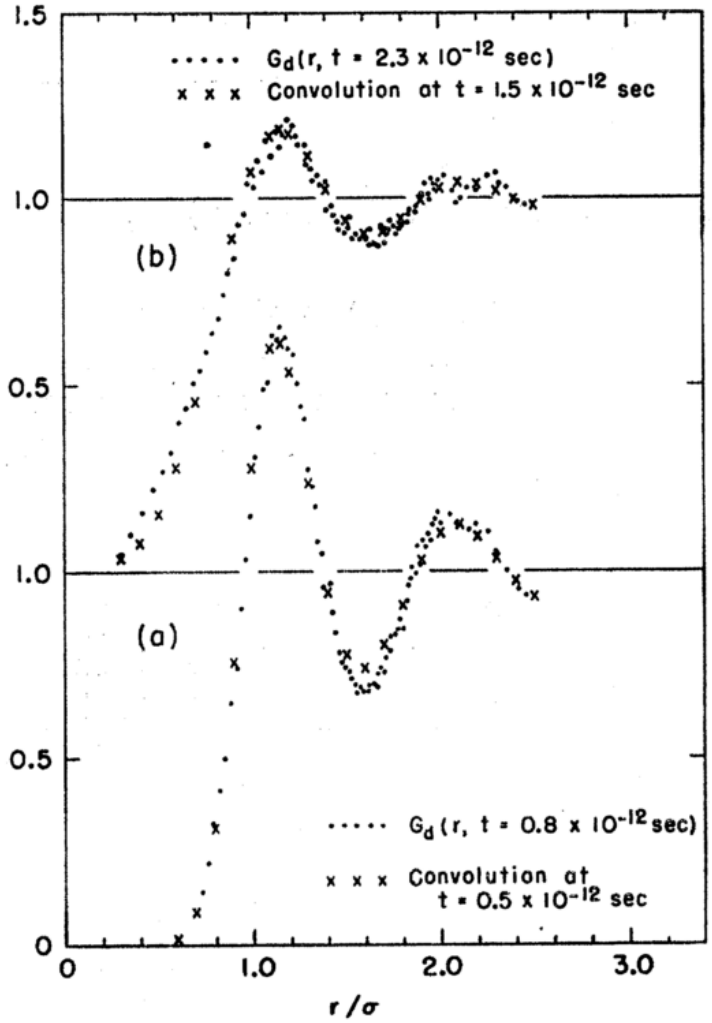
Molecular Viewer
Animation
30
95

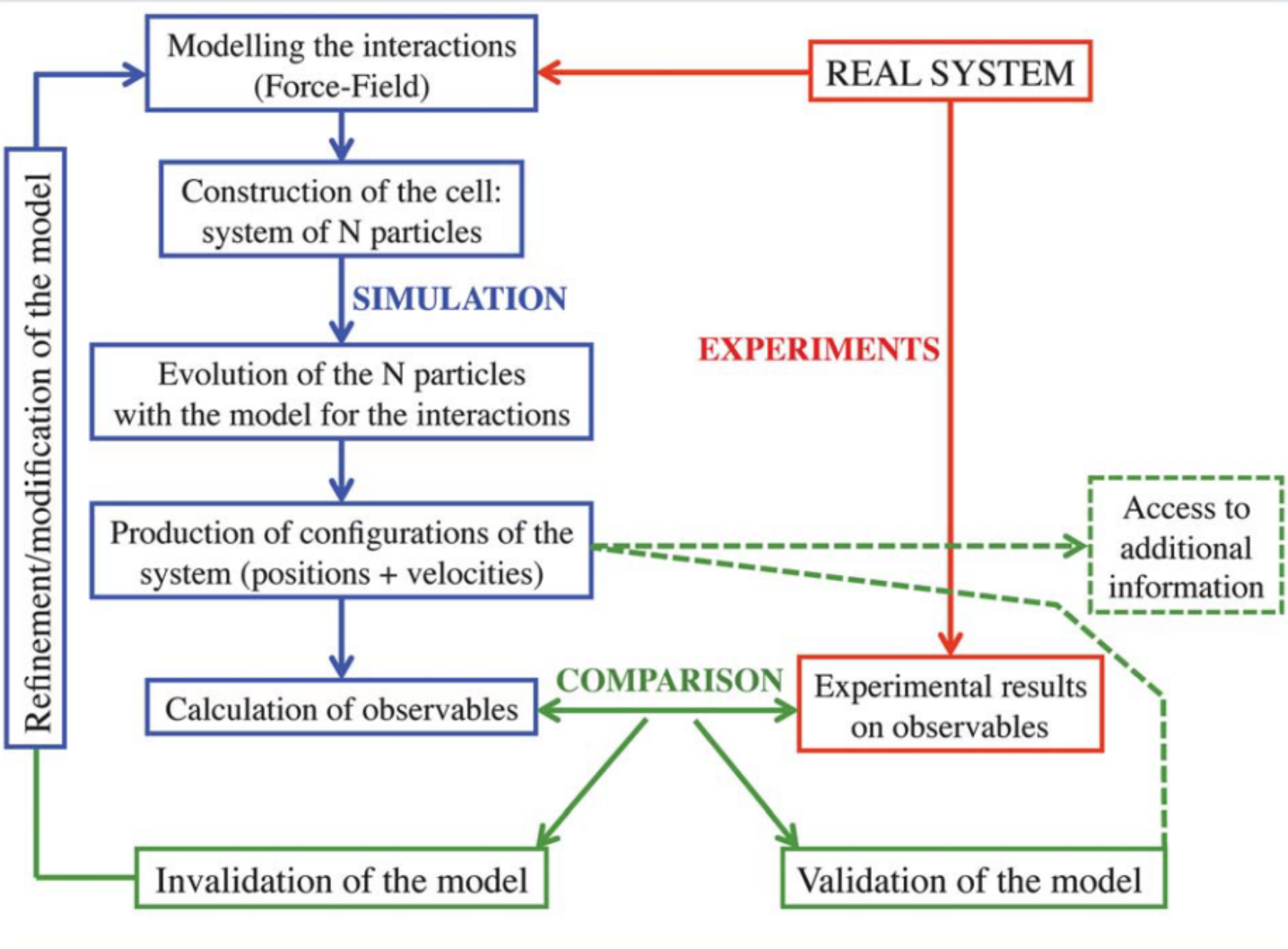
Improving the model of $G(\vec{r}, t)$ for liquids

before



after





10.1039/c2sm26061a

Good, but how do I get the forces ?

Simulation of Samples

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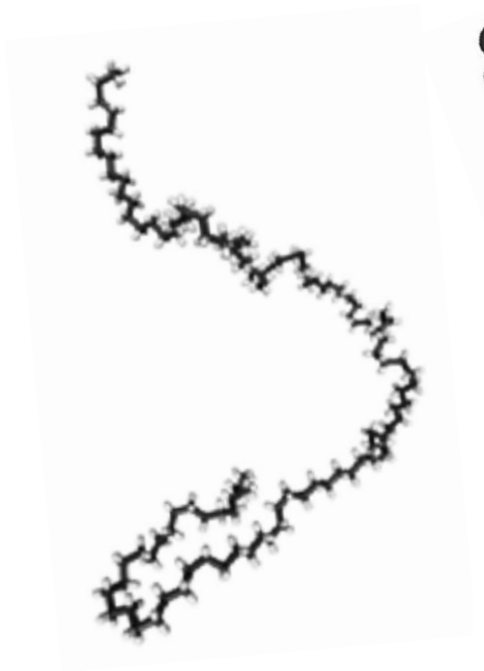
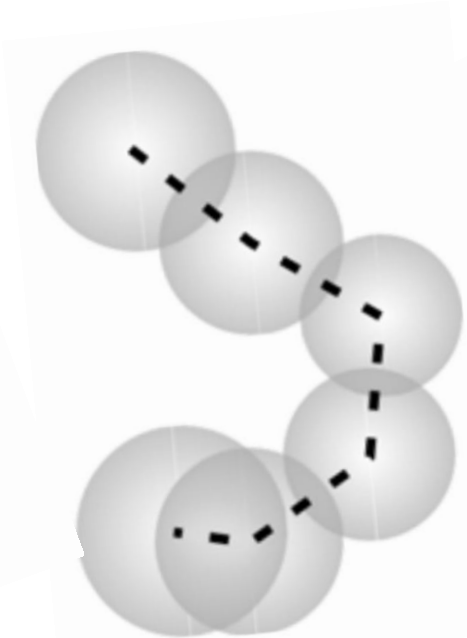
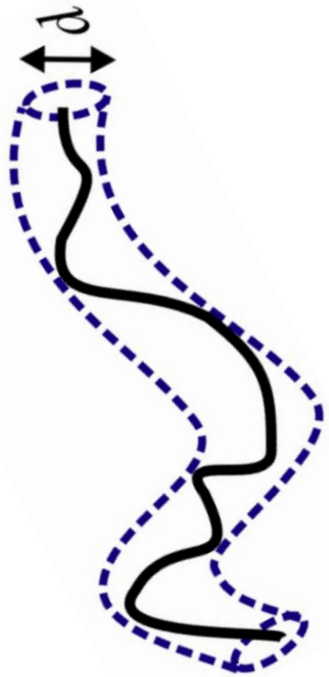
Roadmap

Atomistic	Hard spheres	Soft spheres	Topological	Single particle
0.1 nm	1 nm	10 nm	10 nm	100 nm







Molecular Dynamics	Langevin Dynamics	Brownian Dynamics	Slip-links	Smoothed particle hydrodynamics

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Langevin Dynamics

$$m\frac{d\mathbf{v}}{dt} = \mathbf{F} - \frac{m\mathbf{v}}{\tau_m} + \sqrt{\frac{2k_BTm}{\tau_m\Delta t}}\mathcal{N}^3(0,1)$$

Newton | Friction | Thermal Noise

Momentum Relaxation Time: $\tau_m = \frac{m}{6\pi\eta_s R} \approx 0.1\,\mathrm{ns}$

Average speed: $\langle \mathbf{v}^2 \rangle = \frac{3k_BT}{2m}$

Langevin dynamics

☺ Simple and straightforward to implement, but because friction and thermal forces are coupled directly to « background »,

Momentum conservation violated locally,

Hydrodynamic interaction lost,

Impossible to observe complex flow patterns such as shear-bands.

➢Upgrade: Dissipative Particle Dynamics

Dissipative Particle Dynamics

$$m\frac{d\mathbf{v}}{dt} = \mathbf{F} - \frac{mw(r_{ij})}{\tau_m}(\hat{\mathbf{r}}_{ij}\cdot\mathbf{v}_{ij})\hat{\mathbf{r}}_{ij} + \sqrt{\frac{2k_BTmw(r_{ij})}{\tau_m\Delta t}}\mathcal{N}_{ij}^3(0,1)$$

Newton | Friction | Thermal Noise

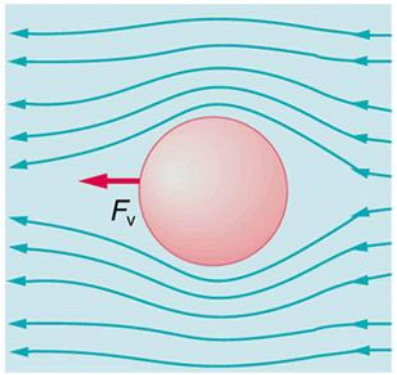
Friction and Thermal forces act between neighbouring particle pairs, no fictious « background » needed.

Local momentum conservation & hydrodynamics recovered.

Weight function: $w(r_{ij}) = e^{-r_{ij}^2/R^2}$

P. ESPAÑOL AND P. WARREN 1995 EUROPHYS. LETT. 30 191

Momentum relaxation time

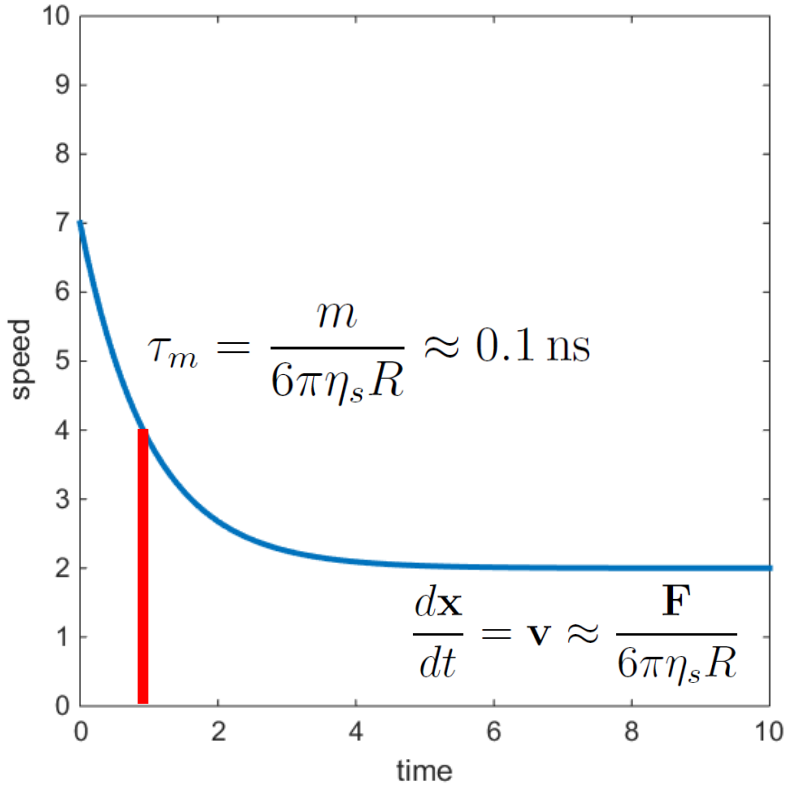


Viscous drag:

$$m\frac{d\mathbf{v}}{dt} = \mathbf{F} - 6\pi\eta_s R\mathbf{v}$$

Solution:

$$\mathbf{v}(t+\Delta t) = \left(\mathbf{v}(t) - \frac{\mathbf{F}}{6\pi\eta_s R}\right) e^{-6\pi\eta_s R\Delta t/m} + \frac{\mathbf{F}}{6\pi\eta_s R}$$



Brownian dynamics

$$(6\pi\eta_s R)\frac{d\mathbf{x}}{dt} = \mathbf{F} + \sqrt{\frac{2(6\pi\eta_s R)k_B T}{\Delta t}}\,\mathcal{N}^3(0,1)$$

Overdamped Newton

Thermal Noise

$$\tau_d = \frac{6\pi\eta_s R^3}{k_B T} \approx 10\,\mu\text{s}$$

$$\frac{\tau_d}{\tau_m} \approx \frac{\eta_s^2 R}{\rho k_B T} \approx 10^5$$

☺ Very big time step
☹ Unresolved momentum
☹ No hydrodynamics

Hydrodynamic Interaction

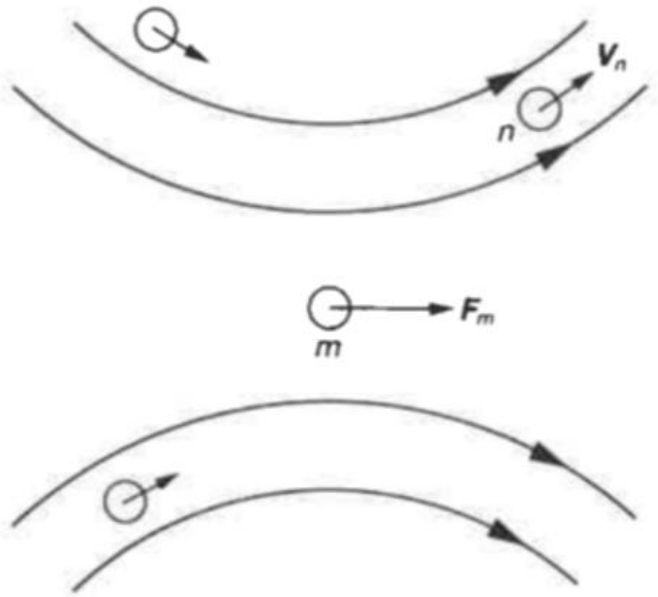


Fig. 3.6. The hydrodynamic interaction. The force acting on the particle m creates a velocity field and causes the motion of other particles.

Incompressible Navier-Stokes

$$\frac{\partial \mathbf{v}}{\partial t} = \nu \nabla^2 \mathbf{v} - \nabla P + \mathbf{F}(\mathbf{r}, t)$$

In Fourier domain

$$\tilde{\mathbf{v}}(\mathbf{k}, t) = \int \mathbf{v}(\mathbf{r}, t) e^{-i\mathbf{r}\cdot\mathbf{k}}\, d\mathbf{r}$$

$$\tilde{\mathbf{F}}(\mathbf{k}, t) = \int \mathbf{F}(\mathbf{r}, t) e^{-i\mathbf{r}\cdot\mathbf{k}}\, d\mathbf{r}$$

Solution

$$\tilde{\mathbf{v}}(t + \Delta t) = \tilde{\mathbf{v}} e^{-\nu |\mathbf{k}|^2 \Delta t} + \left(\tilde{\mathbf{F}} - (\tilde{\mathbf{F}} \cdot \hat{\mathbf{k}}) \hat{\mathbf{k}} \right) \left(\frac{1 - e^{-\nu |\mathbf{k}|^2 \Delta t}}{m \nu |\mathbf{k}|^2} \right)$$

Momentum relaxation

Incompressibility

Transport properties (ex. viscosity)

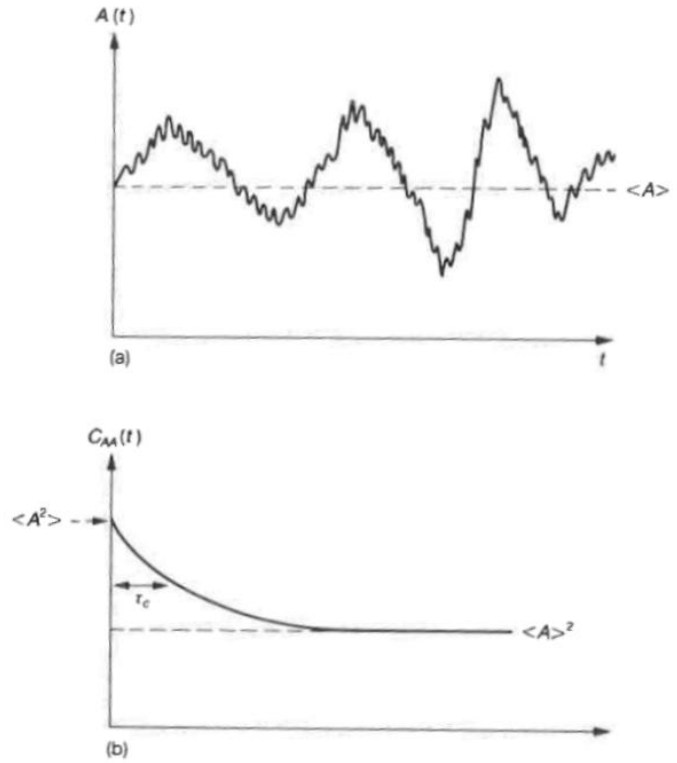
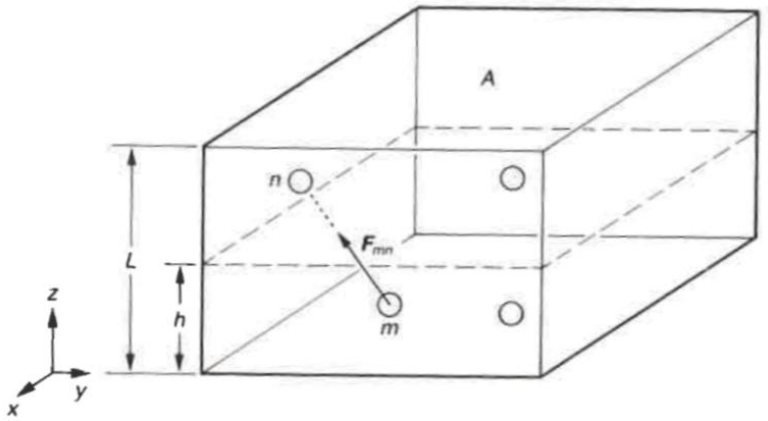


Fig. 3.3. (*a*) Example of measured values of a certain physical quantity A as a function of time. (*b*) A typical behaviour of the time correlation function $C_{AA}(t) = \langle A(t)A(0)\rangle$. The correlation time is denoted by τ_c.

Definition of stress



Microscopic shear stress

$$\sigma_{yz} = \frac{1}{V}\sum_{n,m}(\mathbf{F}_{nm}\cdot\hat{\mathbf{y}})(\mathbf{r}_{nm}\cdot\hat{\mathbf{z}})$$

Green-Kubo relation

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

M. DOI AND S.F. EDWARDS, THE THEORY OF POLYMER DYNAMICS, 1986

Externally applied shear

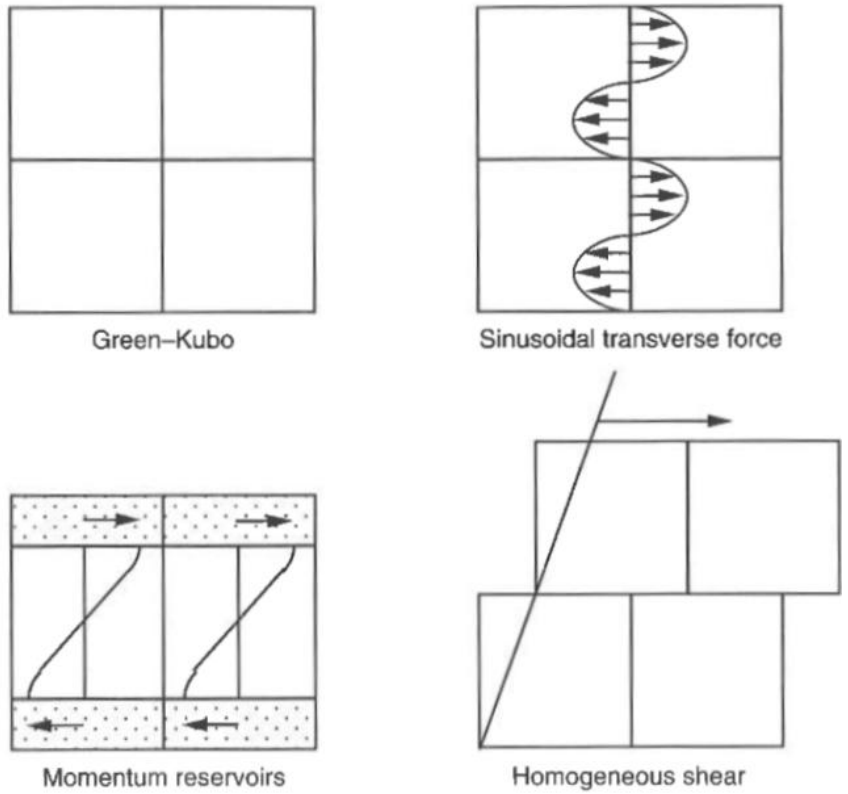


Figure 1.1 Methods of determining the shear viscosity

Lees-Edwards boundary conditions, 1972

Slip-links

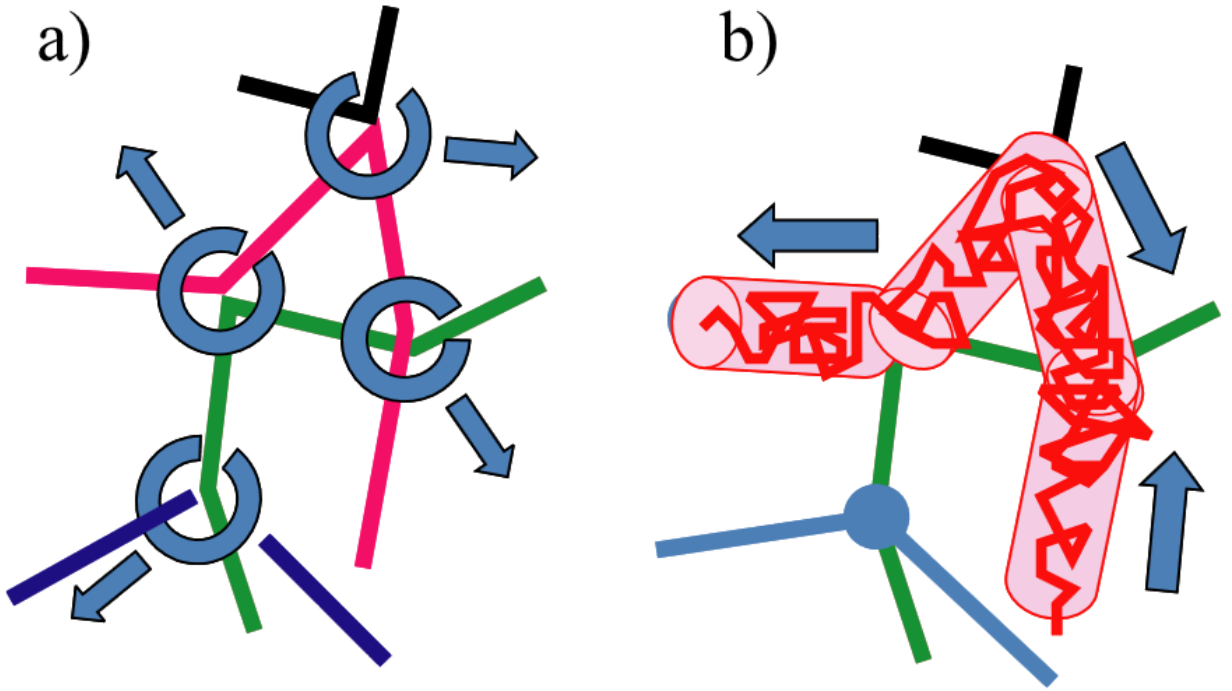


Figure 10. Schematic representation of a primitive chain network model. (a) The motion of slip-links (rings) is influenced by the tension in the chain segments (arrows) and an osmotic force. (b) The motion of the monomers through the slip-links (arrows) results in repetitive motion. (Picture kindly provided by Y Masubuchi.)

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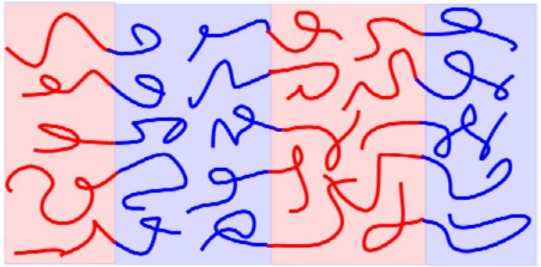
Diblock Copolymer Lamellar Phase



Self-Consistent Field Theory

Partition function for the first (0,s) segments of a polymer which start at $\mathbf{r}_0$ and end at $\mathbf{r}$:

$$\frac{\partial}{\partial s} q(\mathbf{r}, \mathbf{r}_0, s) = \left[\frac{a^2 N}{6} \nabla^2 - w(\mathbf{r}) \right] q(\mathbf{r}, \mathbf{r}_0, s) \qquad q(\mathbf{r}, s) = \frac{1}{(a^2 N)^{3/2}} \int d\mathbf{r}_0 \, q(\mathbf{r}, \mathbf{r}_0, s)$$

Partition function for the last (1,(1-s)) segments of a polymer which start at $\mathbf{r}_0$ and end at $\mathbf{r}$:

$$\frac{\partial}{\partial s} q^\dagger(\mathbf{r}, \mathbf{r}_0, s) = - \left[\frac{a^2 N}{6} \nabla^2 - w(\mathbf{r}) \right] q^\dagger(\mathbf{r}, \mathbf{r}_0, s) \qquad q^\dagger(\mathbf{r}, s) = \frac{1}{(a^2 N)^{3/2}} \int d\mathbf{r}_0 \, q^\dagger(\mathbf{r}, \mathbf{r}_0, s)$$

Full partition function

$$\mathcal{Q}[w] = \int d\mathbf{r} \, q(\mathbf{r}, s) q^\dagger(\mathbf{r}, s)$$

Segment density

$$\phi_\alpha = \frac{N}{\rho_0 \mathcal{Q}[w]} \int_0^1 ds \, q(\mathbf{r}, s) q^\dagger(\mathbf{r}, s)$$

ABC triblock copolymer melt study with Self-Consistent Field Theory

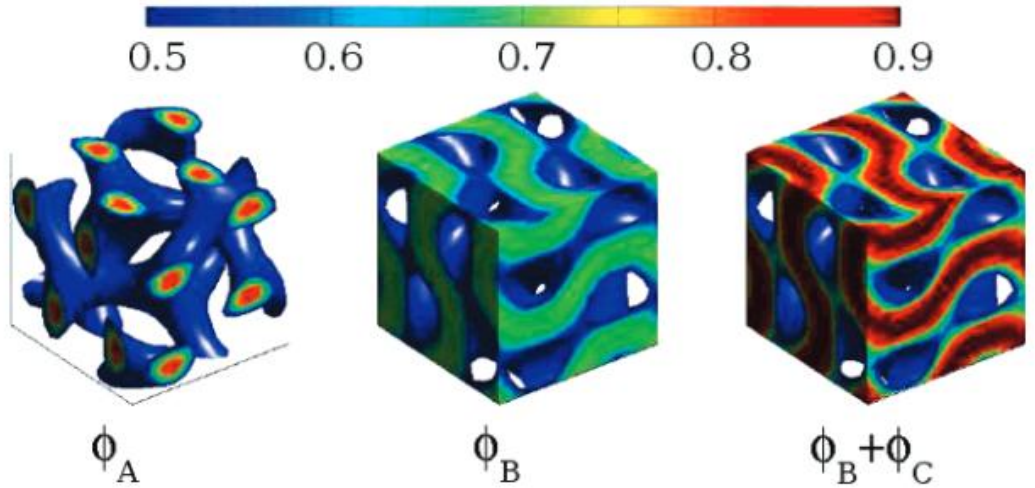
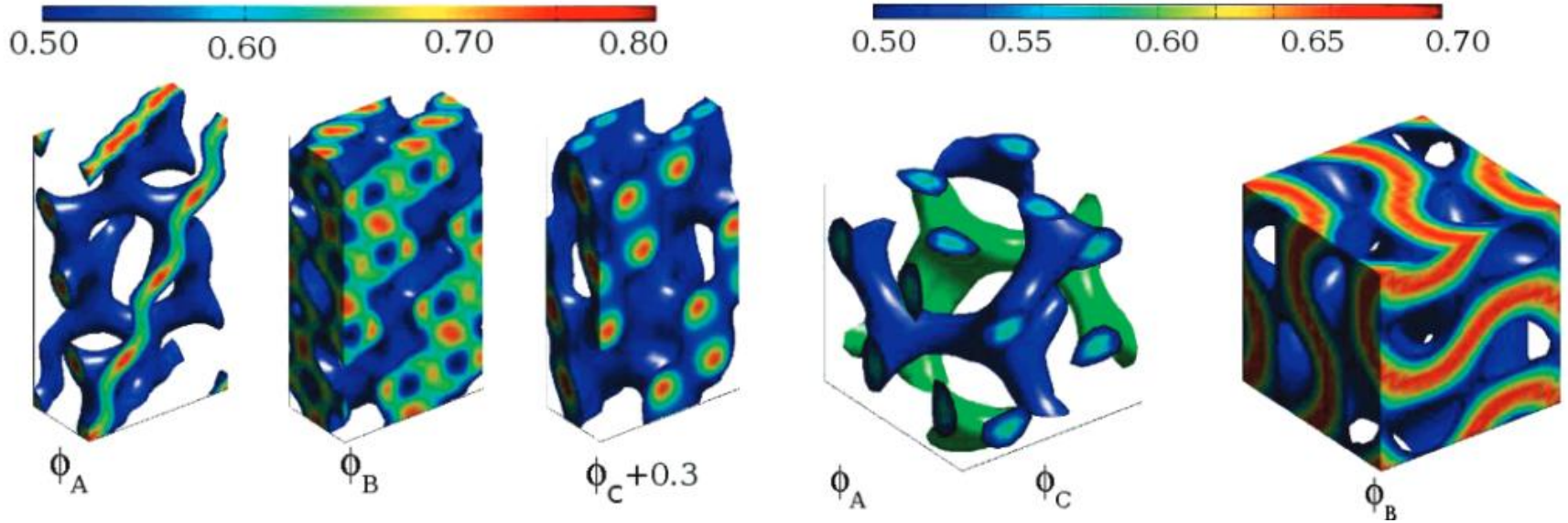


Figure 5. Isosurfaces for ϕ_A, ϕ_B, and $\phi_B + \phi_C$, from left to right, for an idealized triblock copolymer in the G phase with $f_A = 0.27$, $f_B = 0.55$, and $f_C = 0.18$. The isosurfaces are shown for a value of 0.50 for each of these volume fractions. The values of the volume fractions within the isosurfaces indicate that B and C monomers are completely mixed deep within the matrix and that the A/B interface is quite diffuse.



Fluctuating Navier-Stokes

Fluctuating Navier-Stokes Equations

- We will consider a binary fluid mixture with mass **concentration** $c = \rho_1/\rho$ for two fluids that are dynamically **identical**, where $\rho = \rho_1 + \rho_2$ (e.g., **fluorescently-labeled** molecules).
- Ignoring density and temperature fluctuations, equations of **incompressible isothermal fluctuating hydrodynamics** are

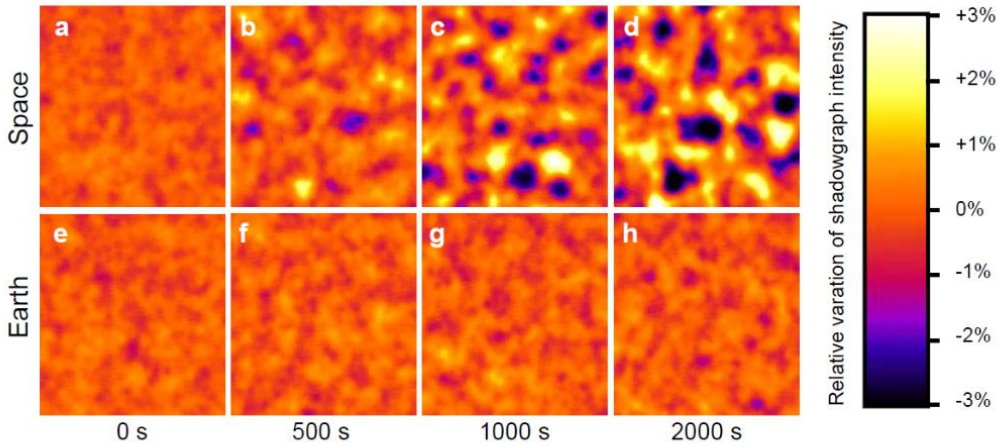
$$\partial_t \mathbf{v} + \mathbf{v}\cdot\nabla\mathbf{v} = -\nabla\pi + \nu\nabla^2\mathbf{v} + \nabla\cdot\left(\sqrt{2\nu\rho^{-1}k_B T}\,\mathcal{W}\right)$$

$$\partial_t c + \mathbf{v}\cdot\nabla c = \chi\nabla^2 c + \nabla\cdot\left(\sqrt{2m\chi\rho^{-1}\,c(1-c)}\,\mathcal{W}^{(c)}\right),$$

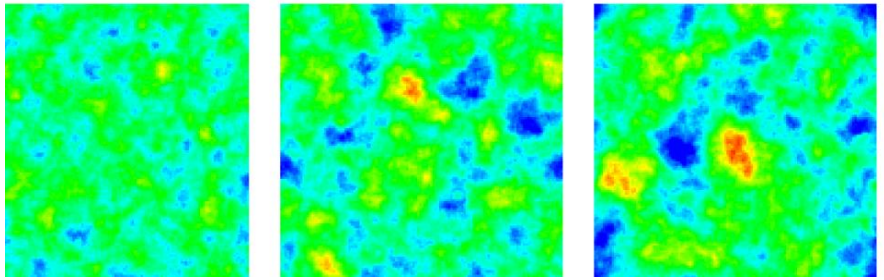
where the **kinematic viscosity** $\nu = \eta/\rho$, and π is determined from incompressibility, $\nabla\cdot\mathbf{v} = 0$.

- We assume that $\mathcal{W}$ can be modeled as spatio-temporal **white noise** (a delta-correlated Gaussian random field), e.g.,

$$\langle \mathcal{W}_{ij}(\mathbf{r},t)\mathcal{W}^{\star}_{kl}(\mathbf{r}',t')\rangle = (\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})\,\delta(t-t')\delta(\mathbf{r}-\mathbf{r}').$$



Experimental results by A. Vailati *et al.* from a microgravity environment [2] showing the enhancement of concentration fluctuations in space (box scale is **macroscopic**: 5mm on the side, 1mm thick).



Simulation

Conclusion

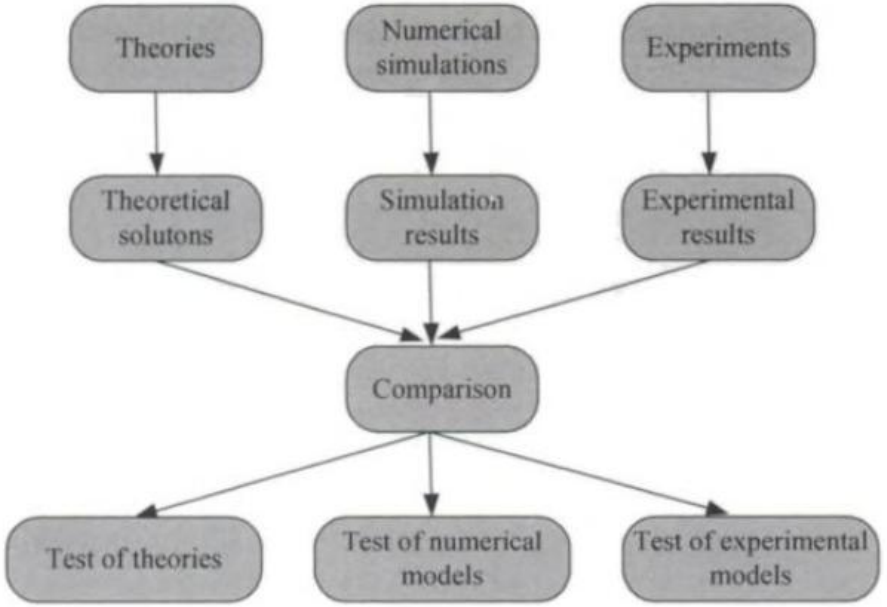


Figure 1.1 Connection between the numerical simulations, theories and experiments. The connection is very important in conducting scientific investigations. In the connection, the numerical simulation is playing an increasingly important role.