Molecular Dynamics : Equilibrium and Non-Equilibrium

Subir K. Das

Theoeritical Sciences Unit
Jawaharlal Nehru Centre for Advanced Scientific Research
Bangalore-560064, India

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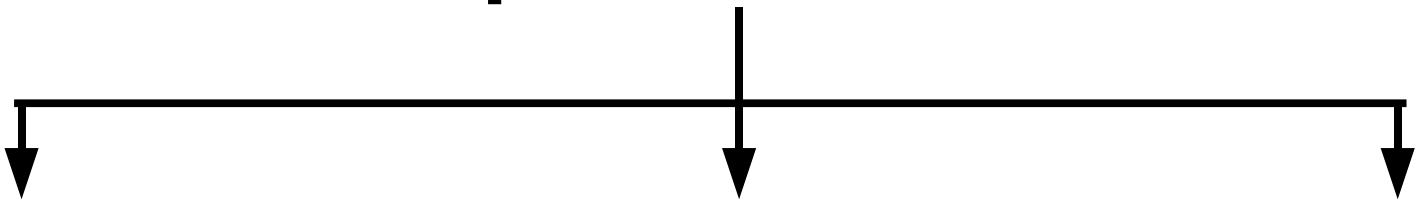
Computer Simulations



Monte Carlo Simulation

Molecular Dynamics Simulation

Solutions of Continuum Dynamical Equations, etc

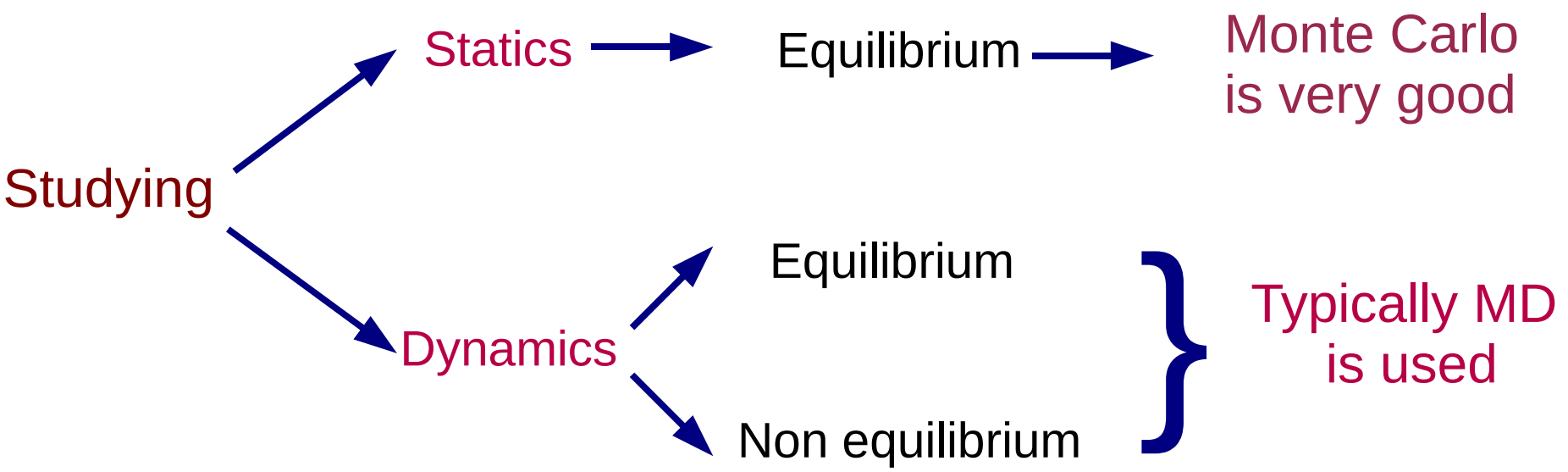
Bulk Systems →

- No walls are present.
- Simulations are done inside a finite box with periodic boundary conditions (PBC)

PBC →

Gets rid of surface or wall effects but does not necessarily take care of finite-size effects

Monte Carlo Simulation	Molecular Dynamics
1.Stochastic 2. Trial moves of various types are made and accepted or rejected according to standard Metropolis criterion where one uses the Boltzmann factor: $e^{-\Delta E/k_B T}$ → Important sampling	1. One solves Newton's equations of motion to get trajectories in phase space 2. A good algorithm, e.g., Verlet velocity, should preserve time reversibility, since Newton's equations are time reversible



Dynamics

- In dynamics both length and time scales are important as opposed to statics where one considers only length scales

- At long wavelengths a fluid behaves as a continuum and hydrodynamic descriptions works in such length scales where length and time are much larger compared to the molecular level

For hydrodynamics, one needs conservation of

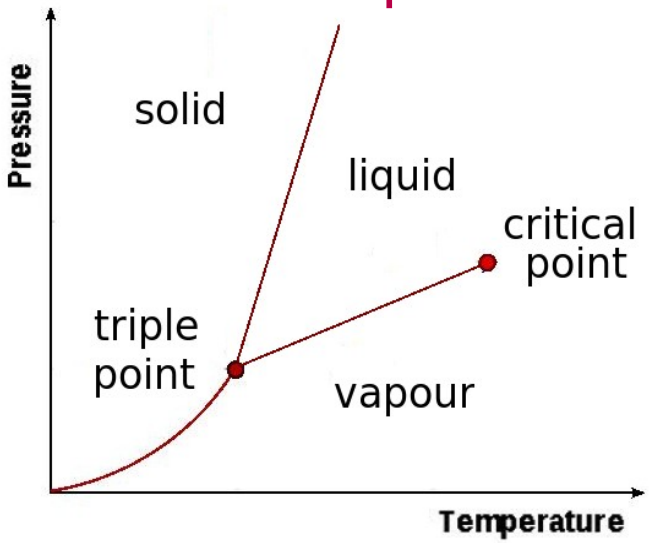
- Mass
- Energy
- Linear Momentum

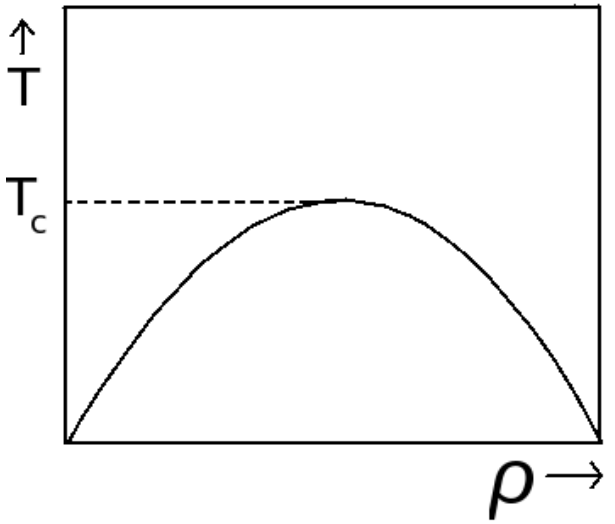
Consider Two Ensembles

- Microcanonical (N,V,E)
- Canonical (N,V,T)

Equilibrium Dynamics

An important example: Dynamic Critical Phenomena





Static critical exponent	Dynamic critical exponent
$C \sim t^{-\alpha}$	$D_T \sim t^{x_D}$
$\rho_L - \rho_G \sim t^{\beta}$	$\eta \sim t^{-x_\eta}$
$K_T \sim t^{-\gamma}$	$\zeta \sim t^{-x_\zeta}$
etc	etc

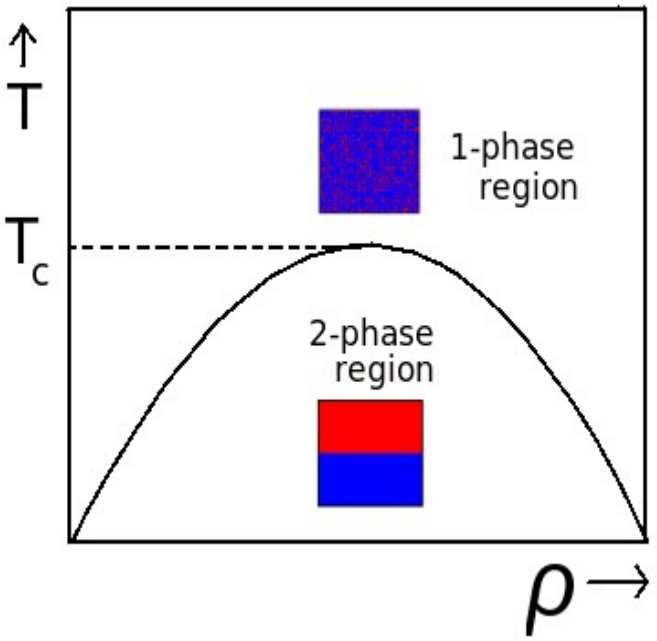
One can study using Microcanonical (NVE) ensemble

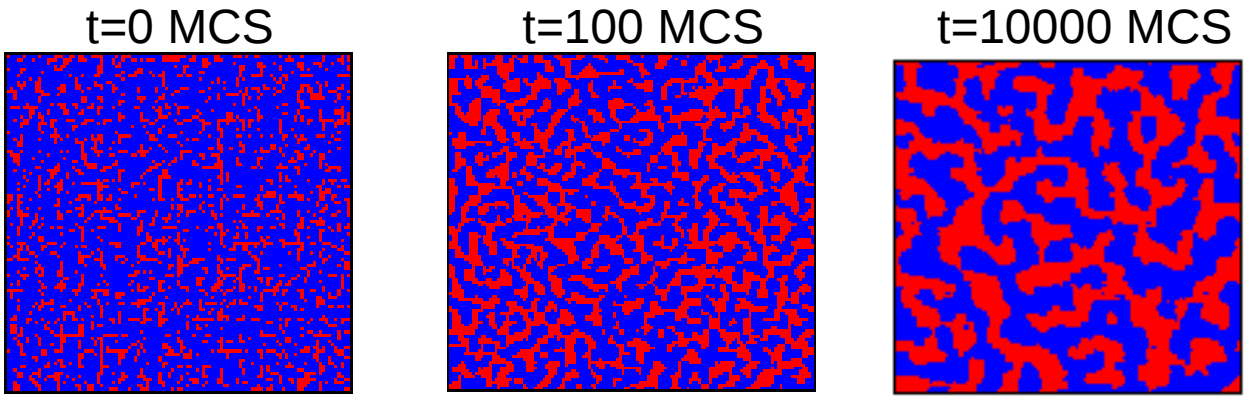
One straight-forwardly solves Newton's equations of motion and hydrodynamics is automatically inbuilt.

(Sutapa Roy and **SKD**)

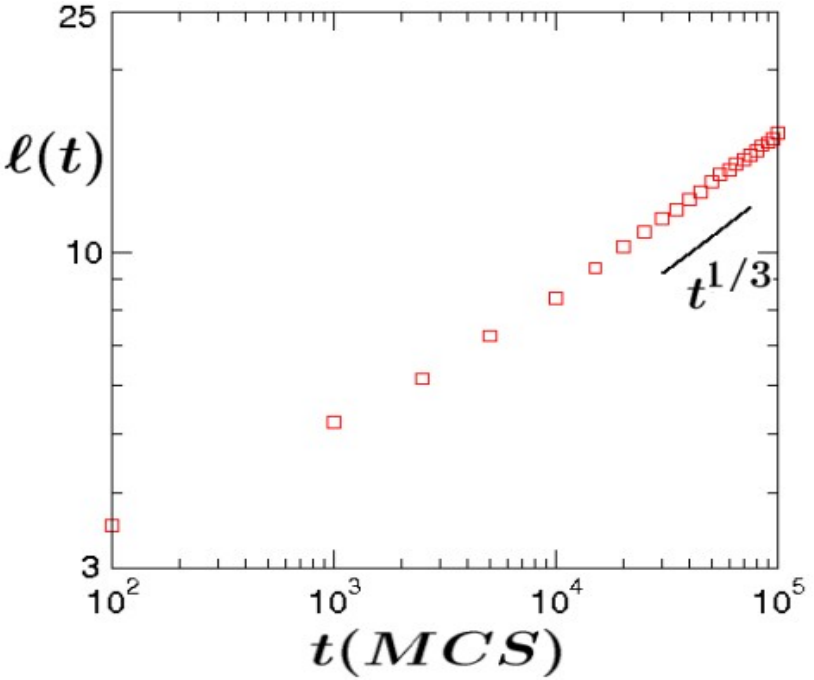
Non-equilibrium Dynamics

Important example : Kinetics of Phase separation





System is minimizing energy via reduction of interface region $\ell(t) \sim t^{\alpha}$



One prepares the system at high temperature and then quenches below T_c

where,

to keep temperature constant, one needs a thermostat

→ Canonical (NVT) ensemble

Study of Phase Separation

- In fluid one needs right thermostat that preserves hydrodynamics

Different Thermostats ⟹ Andersen, Nosé-Hoover, Dissipative Particle dynamics, etc

Andersen ⟹
- Particles randomly collide with heat bath
- Stochastic in nature
- Results similar to Monte Carlo

Nosé-Hoover: Deterministic molecular dynamics at constant temperature based on extended Lagrengian that contains additional artificial variables

Equations of motion →

$$\ddot{r}(t) = \frac{\vec{f}_i}{m_i} - \zeta(t)\,\vec{p}_i$$

$$\dot{\zeta}(t) = \frac{1}{Q}\left(\Sigma_{i=1}^{N} m_i \vec{v}_i^{\,2} - 3Nk_B T\right)$$

$Q \longrightarrow$ Fictitious mass

$Q \to \infty,\ \zeta(t) = 0$

Perfect preservation of momentum and energy (NVE)

Verlet algorithm is applied to solve them

Basic discussion on kinetics of fluid phase separation

Domain grows as: $\ell(t) \sim t^{\alpha}$

Regimes of Growth

a) Diffusive: Interface velocity scales as

$$v_\ell \sim \nabla |\mu| \sim \sigma / \ell$$

$$\Rightarrow \quad \frac{d\ell(t)}{dt} = \sigma / \ell(t)^2 \longrightarrow \ell(t) \sim t^{1/3}$$

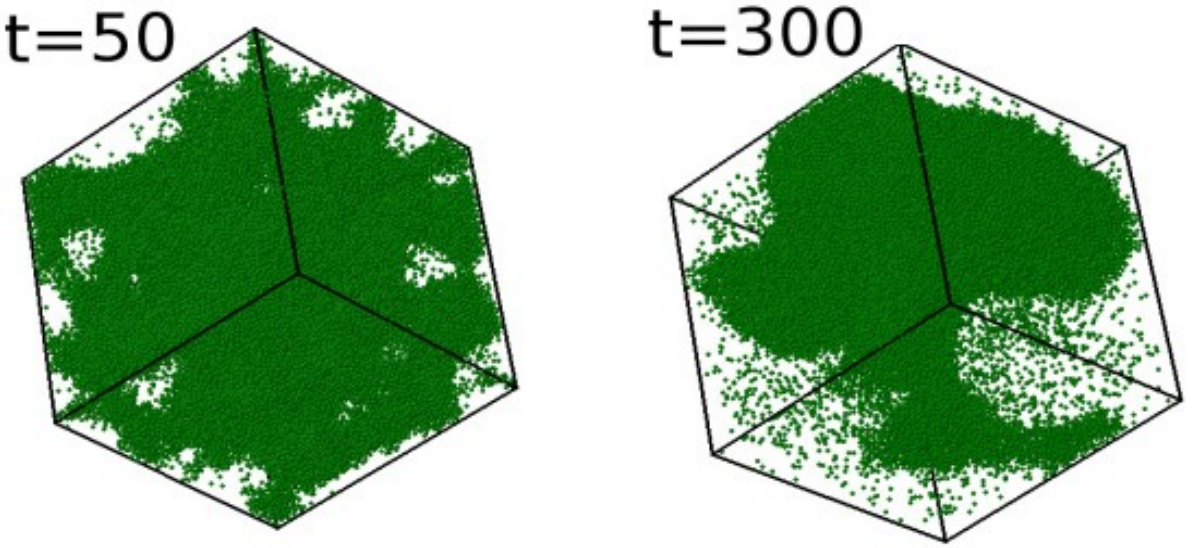
b) Viscous hydrodynamic: Surface energy $(\sigma/\ell) = 6\pi\eta v_\ell/\ell$ (Viscous stress) density

$$\Rightarrow \quad \frac{d\ell(t)}{dt} = v_\ell = \sigma/\eta \longrightarrow \ell(t) \sim t$$

c) Inertial hydrodynamic: Surface energy $(\sigma/\ell) = \rho v_\ell^2$ (Kinetic energy density) density

$$\Rightarrow \quad \frac{d\ell(t)}{dt} = \frac{1}{\ell(t)^{1/2}} \longrightarrow \ell(t) \sim t^{2/3}$$

Gas-liquid phase separation in single component fluid



Domain growth snapshots

Model

Lennard-Jones
inter-particle interaction

$$U(r_{ij}) = 4\epsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right]$$

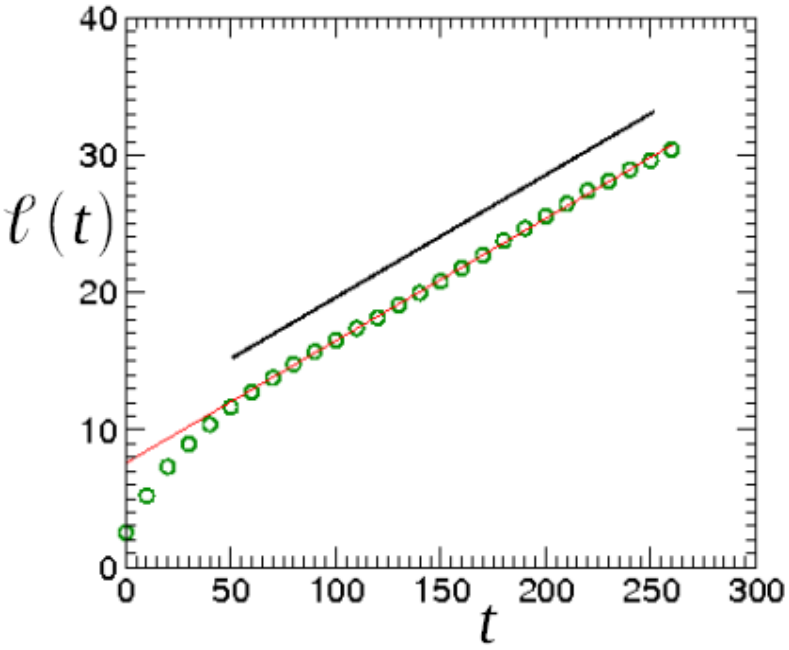
Nosé-Hoover MD

153600 particles and L=80

$\rho = 0.3$

System quenched to :

$T = 0.7\mathrm{T}_c$



Data confirms the viscous hydrodynamic growth

Suman Majumder and **SKD**

Liquid-Liquid Phase Separation in a Binary Fluid

Lennard-Jones potential :

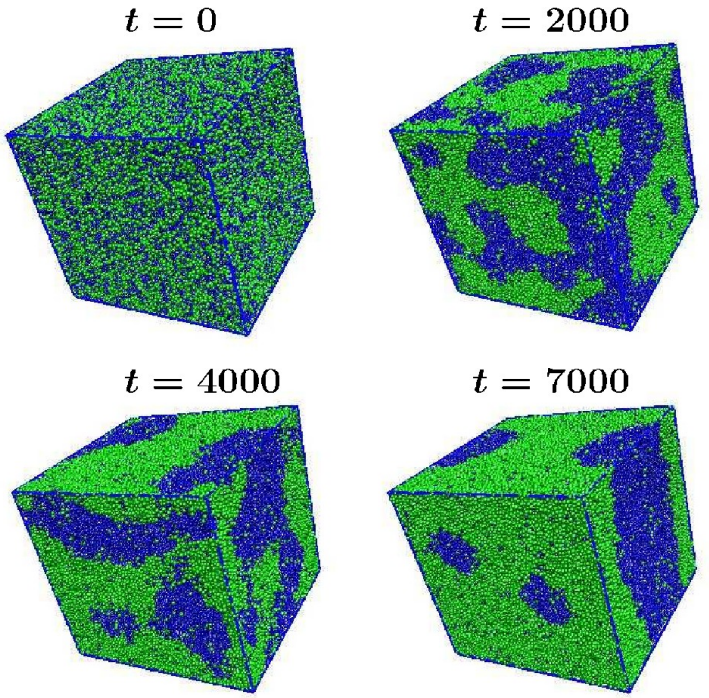
$$V(r_{ij}) = U(r_{ij}) - U(r_c) - (r_{ij} - r_c)\frac{dU(r_{ij})}{dr_{ij}}\Big|_{r_{ij}=r_c}$$

where,

$$U(r_{ij}) = 4\epsilon_{\alpha\beta}\left[(\sigma_{\alpha\beta}/r_{ij})^{12} - (\sigma_{\alpha\beta}/r_{ij})^{6}\right]$$

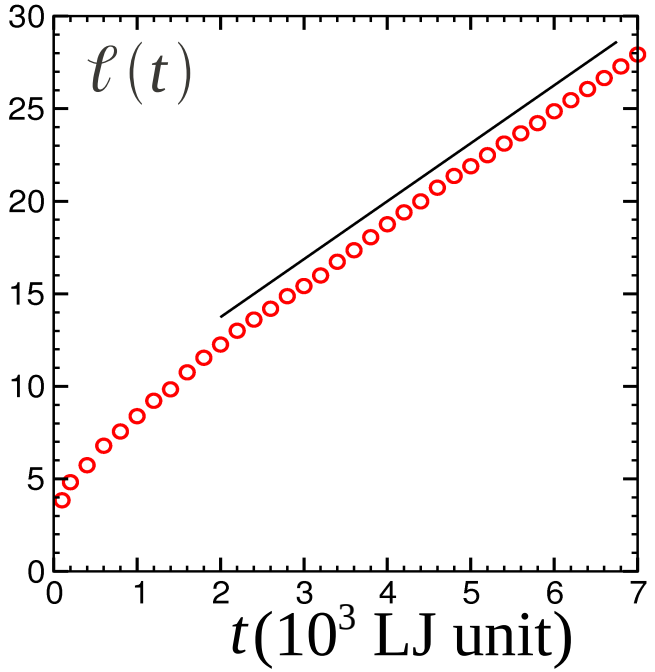
$\alpha, \beta \rightarrow A, B$

- Equal masses (m) for all particles
- $\epsilon_{AA} = \epsilon_{BB} = 2\epsilon_{AB} = \epsilon$
- Incompressible fluid($\rho = 1, T_c = 1.423$) quenched to $T = 1.1$
- 262144 particles, L = 64
- Nosé-Hoover MD



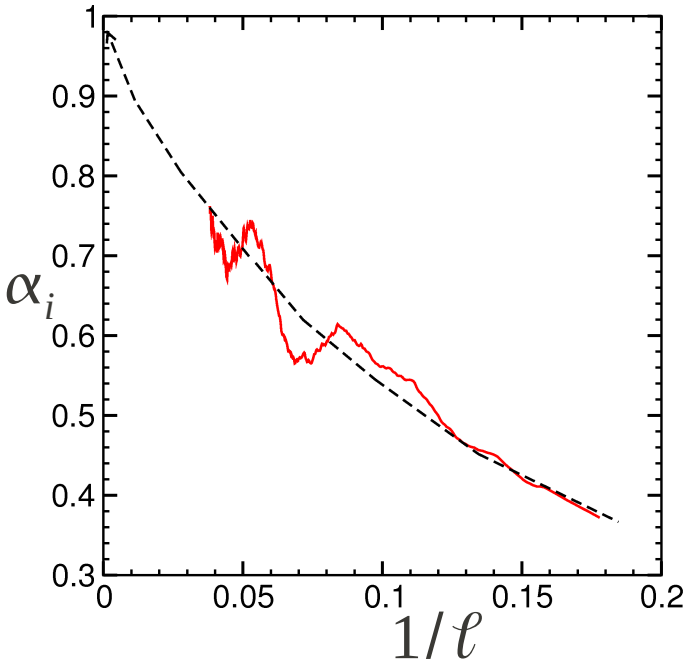
Evolution Snapshots

Length Scale Variation

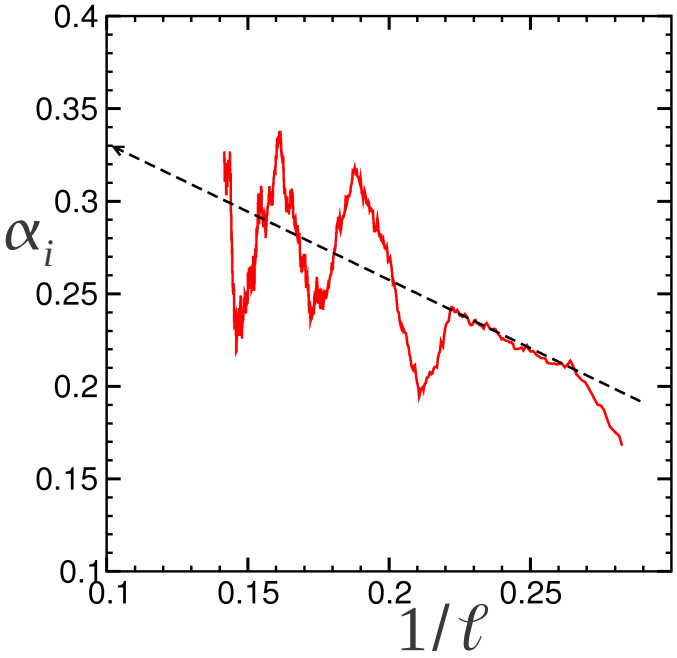


Nosé-Hoover MD

Plots of effective exponent



Nosé-Hoover MD



Andersen MD

Instantaneous exponent $\longrightarrow$ $\alpha_i = \dfrac{d[\ln \ell(t)]}{d[\ln t]}$

As expected, Andersen MD gives diffusive growth for all time, like Monte Carlo.

So: depending upon the study, one needs to choose ensemble and thermostats appropriately.

Shaista Ahmad, **SKD** and Sanjay Puri

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