Introduction to Molecular Simulations

Mario G. Del Pópolo

Atomistic Simulation Centre
Queen's University Belfast

e-mail: m.del-popolo@qub.ac.uk

Belfast, 5th of December 2011

Outline

1. General Overview
2. Interatomic Forces
3. Thermodynamics and Statistical Mechanics
   - Thermodynamics in a nutshell
   - Ensembles of particles
4. Sampling Methods
   - Molecular Dynamics
   - Monte Carlo Methods
5. What can we calculate ?
   - Thermodynamical properties
   - Microscopic structure
   - Dynamical properties

Outline

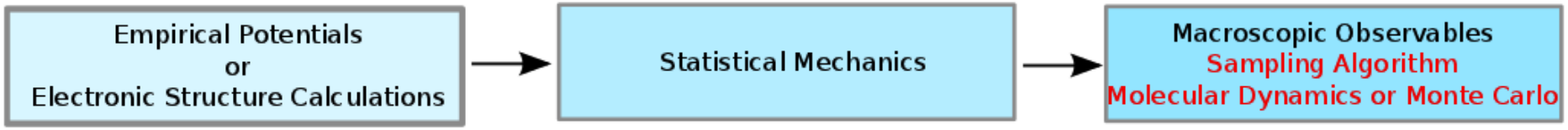
1. General Overview
2. Interatomic Forces
3. Thermodynamics and Statistical Mechanics
   - Thermodynamics in a nutshell
   - Ensembles of particles
4. Sampling Methods
   - Molecular Dynamics
   - Monte Carlo Methods
5. What can we calculate ?
   - Thermodynamical properties
   - Microscopic structure
   - Dynamical properties

Computer simulations

Nowadays numerical simulations are used across the whole spectrum of sciences

(probably the fastest growing branch of applied mathematics)

- Optimization methods and calculus of variations
- Solving ordinary and partial differential equations
- Statistics and stochastic processes
- Agents-based simulations



Outline

1. General Overview
2. Interatomic Forces
3. Thermodynamics and Statistical Mechanics
   - Thermodynamics in a nutshell
   - Ensembles of particles
4. Sampling Methods
   - Molecular Dynamics
   - Monte Carlo Methods
5. What can we calculate ?
   - Thermodynamical properties
   - Microscopic structure
   - Dynamical properties

Some inter-atomic potentials

$$u_{12}(r_{ij}) = 4\epsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right] \qquad \textbf{Lennard} - \textbf{Jones potential} \tag{1}$$

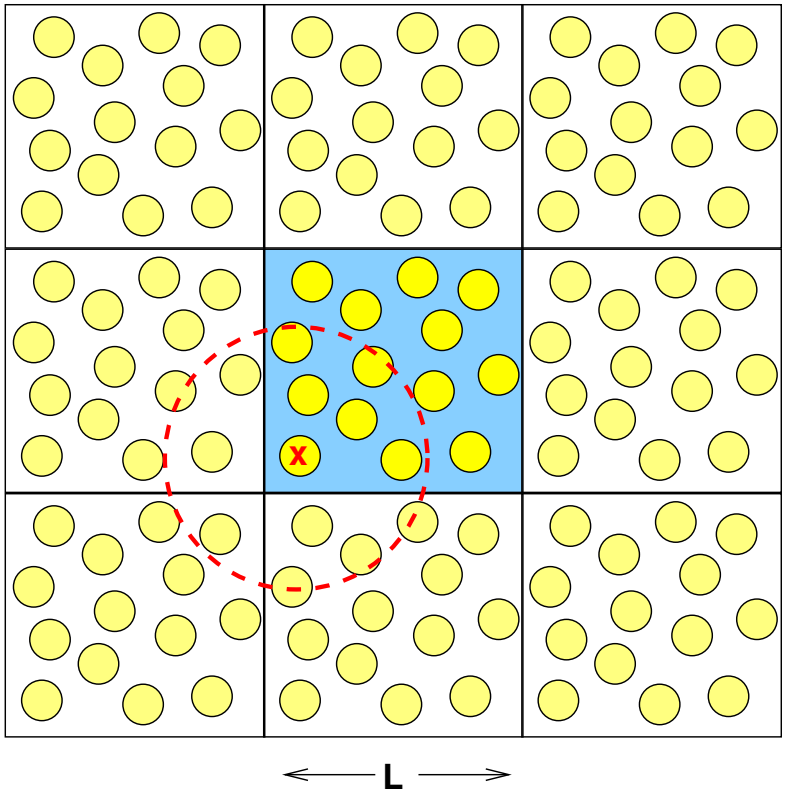
$$u_{i,\alpha} = F_{\alpha}\left[\sum_{i\neq j}\rho_{\beta}(r_{ij})\right] + \frac{1}{2}\sum_{i\neq j}\phi_{\alpha\beta}(r_{ij}) \qquad \textbf{Embedded Atom Method} \tag{2}$$

$$\begin{aligned}\mathcal{U} = &\sum_{b}\frac{k_{r,\,b}}{2}(r_b - r_{0,\,b})^2 + \sum_{a}\frac{k_{\theta,a}}{2}(\theta_a - \theta_{0,\,a})^2 \\ &+ \sum_{d}\sum_{m=1}^{n}\frac{V_{m,\,d}}{2}[1 + (-1)^{m+1}\cos(m\varphi_d)] \\ &+ \sum_{i}\sum_{j}\left\{4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \frac{1}{4\pi\epsilon_0}\frac{q_i q_j}{r_{ij}}\right\}\end{aligned} \tag{3}$$

Simulation of molecular systems

Boundary conditions

- Periodic boundary conditions:
  - Avoid surface effects
  - Warning: periodicity introduces correlations
- System size N:
  - Finite size effects depend on correlation length and range of interactions
  - Dependence on cell symmetry and shape
- Configurational energy:
  - The Ewald method (truly periodic b.c.)
  - Truncation of the intermolecular forces: Minimum image plus cutoff



Outline

1. General Overview
2. Interatomic Forces
3. Thermodynamics and Statistical Mechanics
   - Thermodynamics in a nutshell
   - Ensembles of particles
4. Sampling Methods
   - Molecular Dynamics
   - Monte Carlo Methods
5. What can we calculate ?
   - Thermodynamical properties
   - Microscopic structure
   - Dynamical properties

Thermodynamic systems and state variables

- **Thermodynamics:** Phenomenological theory that describes equilibrium states of macroscopic systems
- **Thermodynamic system:** Macroscopic sample whose properties can be fully described by a reduced number of observables called **state variables:**
  - **Extensive** variables (additive): proportional to the amount of matter (energy E, volume V, etc.)
  - **Intensive** variables: independent of sample size (temperature T, chemical potential, μ, etc.)
  - Number of independent variables dictated by Gibbs phase rule: $\mathbf{F} = \mathbf{K} + \mathbf{2} - \mathbf{P}$.
    - For pure homogeneous substance $F = 2$
- **Standard thermodynamic systems:** **Isolated** (N, V, E), **closed** (N, V, T), **isobaric-isothermal** (NPT), **open systems** (μ, V, T)

First and Second Law of Thermodynamics

First law

In any infinitesimal transformation the variation of the system's internal energy U is given by the sum of work and heat exchanged with the surroundings:

$$dU = đQ + đW \Rightarrow đQ - PdV + \gamma dA + \mu dN \tag{4}$$

Second law

In any infinitesimal transformation involving heat exchange đQ with a reservoir at temperature T, the entropy variation of the system,dS, obeys:

$$dS \geq \frac{đQ}{T} \tag{5}$$

where the equality applies to reversible transformations

Thermodynamic potentials

- Combining the first and second laws we obtain:

$$dU = TdS - PdV + \mu dN \quad \text{(reversible transformation)} \tag{6}$$

- For an isolated system, $U = U(S, V, N)$ is a thermodynamic potential which attains its **global minimum** at thermodynamic equilibrium
- Since dU is an exact differential, we can write:

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,N} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N} dV + \left(\frac{\partial U}{\partial N}\right)_{U,V} dN \tag{7}$$

which, when compared to equation 6, leads to three **equations of state**:

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N} \quad -P = \left(\frac{\partial U}{\partial V}\right)_{S,N} \quad \mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}$$

Thermodynamic potentials

Legendre transformations of $U(S, V, N)$ generate different **thermodynamic potentials** or **free energies**

Transforming: $S \to T$

$$F(N, V, T) = U(S, V, N) - S\left(\frac{\partial U}{\partial S}\right)_{V,N} = U - ST \quad \text{(Helmholtz F.E.)}$$

Note: F is minimum at equilibrium for (N, V, T) systems

Further transformation: $N \to \mu$, gives

$$\Omega(\mu, V, T) = F(N, V, T) - N\left(\frac{\partial F}{\partial N}\right)_{V,T} = F - N\mu = -PV \quad \text{(Grand Potential)}$$

Note: Ω is minimum at equilibrium for (μ, V, T) systems

Equations of state - EoS

- Obtained as derivatives of thermodynamic potentials. For example, given:

$$dF = -SdT - PdV + \mu dN \tag{8}$$

the corresponding EoS are:

$$S = \left(\frac{\partial F}{\partial T}\right)_{V,N} \quad -P = \left(\frac{\partial F}{\partial V}\right)_{T,N} \quad \mu = \left(\frac{\partial F}{\partial N}\right)_{V,T}$$

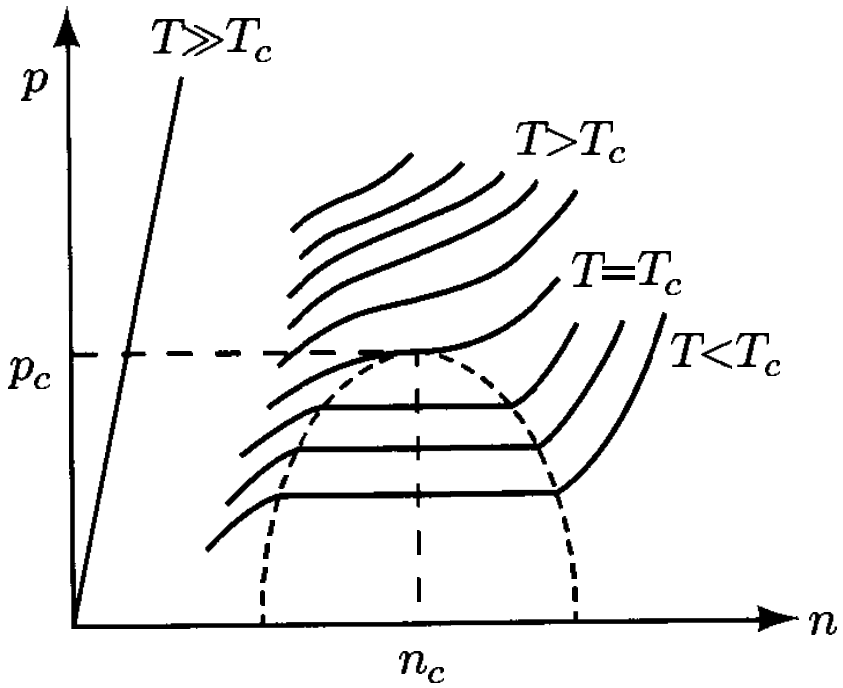
- Examples:

$$PV = Nk_BT \quad or \quad \left(P + a\frac{N}{V}\right)\left(\frac{V}{N} - b\right) = k_bT \tag{9}$$

- EoS can only be obtained via: **experimental measurements**, or **statistical mechanics** or **computer simulation**
- The full set of EoS can be used to construct the free energy function of the system by integration

Model phase diagram

- Equations of state give access to the phase diagram of the system.
- **Figure:** Phase diagram of a one component fluid. Pressure, P, as a function of density, n, at different temperatures, T, i.e. $P = f(n, T)$
- For each value of n there is a unique value of P for each T
- For $T < T_c$ there are two possible values of P at fixed T. Coexistence of liquid and gas at the same μ, T and P
- At T_c both phases have equal densities



Thermodynamic stability

How do equilibrium systems respond to external perturbations ?. Regression of spontaneous fluctuations (Le Chatelier's principle) and response functions.

- Globally **stable systems** return to equilibrium after occurrence of arbitrarily large fluctuations
- **Metastable states** might have long life-times but move towards genuine equilibrium sates upon large perturbation (locally stable - globally unstable)
- **Unstable systems** change macroscopically in response to the slightest perturbation or fluctuation

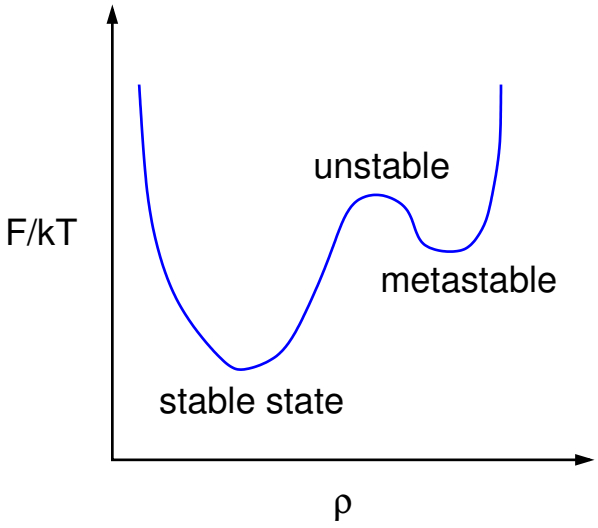


Figure: Free energy curve showing stable, metastable and unstable sates

Response functions: second derivatives of free energy

$$\left(\frac{\partial^2 F}{\partial V^2}\right)_{N,T} = \frac{1}{V\kappa_T} \geq 0 \tag{10}$$

κ_T is the **isothermal compressibility**

Classical many-particle systems

Consider: system composed of N classical particles interacting via pairwise potentials and in the presence of an external field.

$$\text{Hamiltonian} \rightarrow \quad \mathcal{H}(\mathbf{r}^N, \mathbf{p}^N) = K_N(\mathbf{p}^N) + V_N(\mathbf{r}^N) + \phi_N(\mathbf{r}^N) \tag{11}$$

$$K_N(\mathbf{p}^N) = \sum_{i=1}^{N} \frac{|\mathbf{p}_i|^2}{2m} \qquad \text{Kinetic Energy} \tag{12}$$

$$V_N(\mathbf{r}^N) = \sum_{i=1}^{N} \sum_{j>i} u(|\mathbf{r}_{ij}|) \qquad \text{Potential Energy} \tag{13}$$

$$\Phi(\mathbf{r}^N) \qquad \rightarrow \text{Spatially varying external field} \tag{14}$$

The dynamical state of the system is specified by the 6N-dimensional **phase vector:** $\Gamma(t) = [\mathbf{r}_1(t), \cdots, \mathbf{p}_N(t)]$

Time averages and ensemble averages

- **Observable mechanical properties**, correspond to the expectation value of functions $B(\mathbf{r}^N, \mathbf{p}^N)$ of coordinates $\{\mathbf{r}^N\}$ and momenta $\{\mathbf{p}^N\}$. Examples: U, P, etc.
- At equilibrium, such averages are independent of time
- The instantaneous value of $B(\mathbf{r}^N, \mathbf{p}^N)$ fluctuates as $[\mathbf{r}^N(t), \mathbf{p}^N(t)]$ evolves according to Hamilton's equations
- The observable $\langle B \rangle_{obs}$ is a time average over the dynamical history of the system

$$\langle B \rangle_t = \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^\tau B[\mathbf{r}^N(t), \mathbf{p}^N(t)] dt \quad (15)$$

$$\approx \frac{1}{N_{obs}} \sum_{i=1}^{N_{obs}} B(i \times \delta t) \quad (16)$$

Temperature as time average

Example:

The thermodynamic temperature is related to the time average of the instantaneous kinetic energy, $K_N(t) = \sum_{i=1}^{N} |\mathbf{p}_i(t)|^2/2m$

$$\mathcal{T}(t) = \frac{2}{3Nk_B} K_N(t) = \frac{1}{3Nk_B m} \sum_{i=1}^{N} |\mathbf{p}_i(t)|^2 \quad \text{Instantaneous temperature} \tag{17}$$

$$T \equiv \langle \mathcal{T} \rangle_t = \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^{\tau} \mathcal{T}(t) dt \quad \text{Average (observable) temperature} \tag{18}$$

Statistical ensembles

Statistical ensemble

Large collection of copies of a particular macrostate, each described by a different state point, Γ, in phase space

The equilibrium ensemble average of $B(\mathbf{r}^N, \mathbf{p}^N)$ is given by

Ensemble average

$$\langle B \rangle_e = \int \int B(\mathbf{r}^N, \mathbf{p}^N) f_0^{[N]}(\mathbf{r}^N, \mathbf{p}^N) d\mathbf{r}^N d\mathbf{p}^N \tag{19}$$

For example, the themodynamic internal energy is the ensemble average of the Hamiltonian

$$U \equiv \langle \mathcal{H} \rangle_e = \int \int \mathcal{H}(\mathbf{r}^N, \mathbf{p}^N) f_0^{[N]}(\mathbf{r}^N, \mathbf{p}^N) d\mathbf{r}^N d\mathbf{p}^N \tag{20}$$

The form of $f_0^{[N]}$ depends on the macroscopic parameters defining the ensemble

The microcanonical ensemble

First postulate

All microstates with the same values of N, V and E are equally likely (equal a priori probabilities)

- Macroscopic parameters: (N, V, E). **Isolated system**
- Equilibrium probability density:

$$f_0^{[N]}(\mathbf{r}^N, \mathbf{p}^N) d\mathbf{r}^N d\mathbf{p}^N = C\delta\left[\mathcal{H}(\mathbf{r}^N, \mathbf{p}^N) - E\right] d\mathbf{r}^N d\mathbf{p}^N \quad \textit{uniform distribution} \tag{21}$$

- **Partition function** (normalisation constant):

$$C = \frac{1}{\Omega(N, V, E)} \tag{22}$$

- $\Omega(N, V, E)dE$= number of micro-states with total energy in $[E, E + dE]$

The microcanonical ensemble

Second postulate

Time averages and ensemble averages are identical if the system is *ergodic*, i.e. if the phase trajectory spends the same time in every phase-space volume element

$$\langle B \rangle_e = \langle B \rangle_t \quad \textit{Ergodic dynamics} \tag{23}$$

- Connection with thermodynamics: **Entropy**

$$S = k_B \ln \left[\Omega(N, V, E)\right] \tag{24}$$

and the equations of states are obtained from:

$$\left(\frac{\partial \ln[\Omega]}{\partial E}\right)_{N,V} = \frac{1}{k_B T} \;\; ; \;\; \left(\frac{\partial \ln[\Omega]}{\partial V}\right)_{U,N} = \frac{P}{k_B T} \;\; ; \;\; \left(\frac{\partial \ln[\Omega]}{\partial N}\right)_{U,V} = \frac{\mu}{k_B T}$$

- In general the entropy associated to $f_0^{[N]}$:

$$S = -k_B \int f_0^{[N]}(\mathbf{r}^N, \mathbf{p}^N) \ln f_0^{[N]}(\mathbf{r}^N, \mathbf{p}^N) d\mathbf{r}^N d\mathbf{p}^N \tag{25}$$

The canonical ensemble

- Independent thermodynamic variables: (N, V, T). System in contact with heat bath at temperature T
- Equilibrium probability density:

$$f_0^{[N]}(\mathbf{r}^N, \mathbf{p}^N) = \frac{1}{h^{3N} N!} \frac{\exp(-\beta \mathcal{H})}{Q_{N,V,T}} \tag{26}$$

$$\textit{with} \tag{27}$$

$$Q_{N,V,T} = \frac{1}{h^{3N} N!} \int \int \exp(-\beta \mathcal{H}) d\mathbf{r}^N d\mathbf{p}^N \tag{28}$$

- Helmholtz free energy $\Rightarrow$ F=-k$_B T \ln(Q_{N,V,T})$
  - From thermodynamics we know $dF = -SdT - PdV + \mu dN$
  - Equations of state

$$S = -\left(\frac{\partial F}{\partial T}\right)_{N,V} \quad P = -\left(\frac{\partial F}{\partial V}\right)_{N,T} \quad \mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} \tag{29}$$

The canonical ensemble

- Thermodynamic relations can be expressed in terms of $Q_{N,V,T}$

$$U = \langle E \rangle = \frac{1}{h^{3N} N! Q_{N,V,T}} \int \int \mathcal{H} \exp\left(-\beta \mathcal{H}\right) d\mathbf{r}^N d\mathbf{p}^N \quad (30)$$

$$= -\left(\frac{\partial \ln\left(Q_N\right)}{\partial \beta}\right)_{V,N} \quad (31)$$

and, similarly

$$P = k_B T \left(\frac{\partial \ln\left(Q_N\right)}{\partial V}\right)_{T,N} \quad (32)$$

- Energy fluctuations:

$$\left\langle (\Delta E)^2 \right\rangle = \left\langle E^2 \right\rangle - \langle E \rangle^2 = -\left(\frac{\partial U}{\partial \beta}\right)_{N,V}$$

$$= k_B T^2 \left(\frac{\partial U}{\partial T}\right)_{N,V} = k_B T^2 C_V \geq 0$$

Outline

1. General Overview
2. Interatomic Forces
3. Thermodynamics and Statistical Mechanics
   - Thermodynamics in a nutshell
   - Ensembles of particles
4. Sampling Methods
   - Molecular Dynamics
   - Monte Carlo Methods
5. What can we calculate ?
   - Thermodynamical properties
   - Microscopic structure
   - Dynamical properties

The simplest integrator

In Molecular Dynamics we integrate equations of motion numerically

Finite differences with **time step** τ: In the Verlet algorithm (1967) particle positions are advanced in time according to the rule:

$$\mathbf{r}_i(t+\tau) = 2\mathbf{r}_i(t) - \mathbf{r}_i(t-\tau) + \frac{\mathbf{f}_i(t)}{m_i}\tau^2 \tag{33}$$

where $\mathbf{f}_i = -\left(\frac{\partial \mathcal{V}}{\partial \mathbf{r}_i}\right)$ is the force on particle i and m_i is its mass.

Velocities needed to calculate kinetic energy (check energy conservation and calculate temperature)

$$\mathbf{v}_i(t) = \frac{\mathbf{r}_i(t+\tau) - \mathbf{r}_i(t-\tau)}{2\tau} \tag{34}$$

Considerations on MD

Integrators must satisfy the following conditions:

- Computational speed (the bottleneck is the calculation of $\mathbf{f}_i$)
- Low memory demand
- Accuracy
- Stability (energy conservation, no drift)
- Time reversibility
- Symplectic: each step in the simulation constitutes the volume of phase space

It is possible to add thermostats and barostats (extended Hamiltonians) in order to sample *NVT* and *NPT* ensembles

Evaluating ensemble averages

Example: canonical internal energy

$$\langle \mathcal{H} \rangle = \int \int \mathcal{H}(\mathbf{r}^N, \mathbf{p}^N) f_0^C(\mathbf{r}^N, \mathbf{p}^N) d\mathbf{r}^N d\mathbf{p}^N$$

How to evaluate $\langle \mathcal{H} \rangle$ numerically (6N-dimensional integral)?$\rightarrow$ quadrature unfeasible

Solution $\rightarrow$ Importance sampling: generate random configurations according to a distribution $\rho(\mathbf{r}^N)$, so that

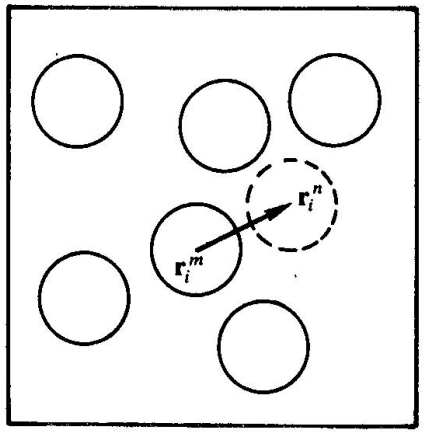
$$\langle \mathcal{H} \rangle = \frac{\int \mathcal{H}(\mathbf{r}^N) f_0^c(\mathbf{r}^N) d\mathbf{r}^N}{\int f_0^c(\mathbf{r}^N) d\mathbf{r}^N} = \frac{\int \mathcal{H}(\mathbf{r}^N) \frac{\rho(\mathbf{r}^N)}{\rho(\mathbf{r}^N)} f_0^c(\mathbf{r}^N) d\mathbf{r}^N}{\int \frac{\rho(\mathbf{r}^N)}{\rho(\mathbf{r}^N)} f_0^c(\mathbf{r}^N) d\mathbf{r}^N} = \frac{\langle \mathcal{H}/\rho \rangle_\rho}{\langle 1/\rho \rangle_\rho}$$

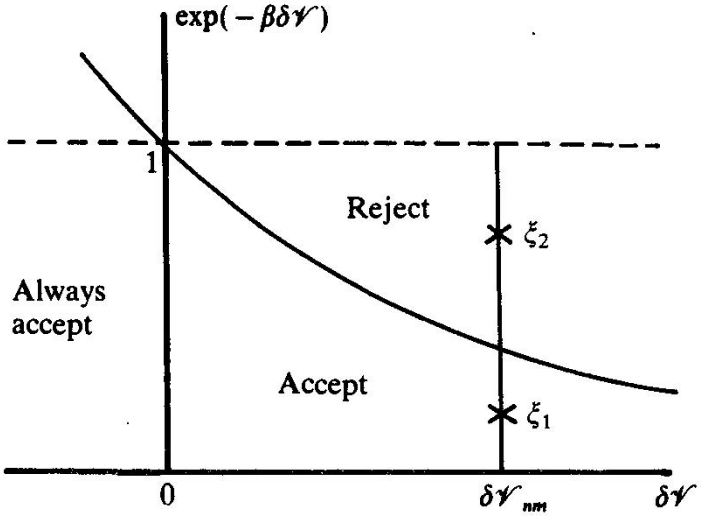
- **Good choice** $\rightarrow \rho(\mathbf{r}^N) = f_0^c(\mathbf{r}^N)$
- The problem has been rephrased: How to generate a series of random configurations so that each state occurs with probability $\rho(\mathbf{r}^N) = f_0^c(\mathbf{r}^N)$?
- Generate a **random walk**, $\Gamma_n \equiv (\mathbf{r}_n^N)$, with a limiting distribution $f_0^c(\mathbf{r}^N)$

Metropolis Monte Carlo in practice

Metropolis algorithm

- Pick particle at random
- Alter position $\mathbf{r}_i$ by displacements chosen randomly from interval $-\Delta r_{max} \leq \Delta r \leq \Delta r_{max}$ (trial move)
- Calculate resulting change in potential energy: $\delta\mathcal{V} = \mathcal{V}_n - \mathcal{V}_o$
- Accept move with probability $\min(1, \exp(-\beta\delta\mathcal{V}))$
  - If $\delta\mathcal{V} \leq 0$ accept new configuration
  - If $\delta\mathcal{V} > 0$ generate random number $0 \leq \mathcal{R} \leq 1$
  - If $\mathcal{R} \leq \exp(-\beta\delta\mathcal{V})$
  - If $\mathcal{R} > \exp(-\beta\delta\mathcal{V})$ reject and retain old configuration





Outline

1. General Overview
2. Interatomic Forces
3. Thermodynamics and Statistical Mechanics
   - Thermodynamics in a nutshell
   - Ensembles of particles
4. Sampling Methods
   - Molecular Dynamics
   - Monte Carlo Methods
5. What can we calculate ?
   - Thermodynamical properties
   - Microscopic structure
   - Dynamical properties

Thermodynamics

- Phase diagrams (big challenge)
- Free energy differences and potentials of mean force

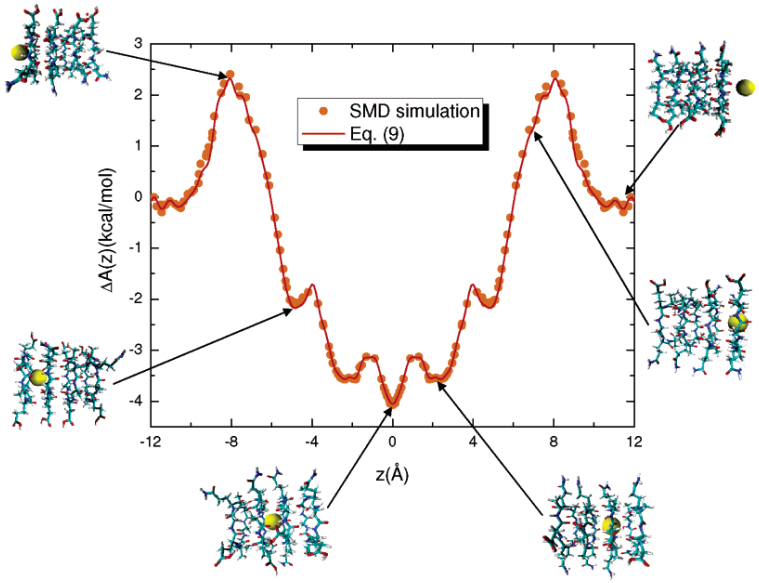


Figure: Potential of mean force, calculated by molecular dynamics, for a sodium ion moving across a cyclic peptide nanotube in water. Hwang et al., J. Phys. Chem. B, 2006, 110, 26448.

Structure and correlations in space

- Condensation generates a limitless variety of equilibrium structures
- Structures characterized by **average atomic positions** and/or **inter-particle spatial correlations**

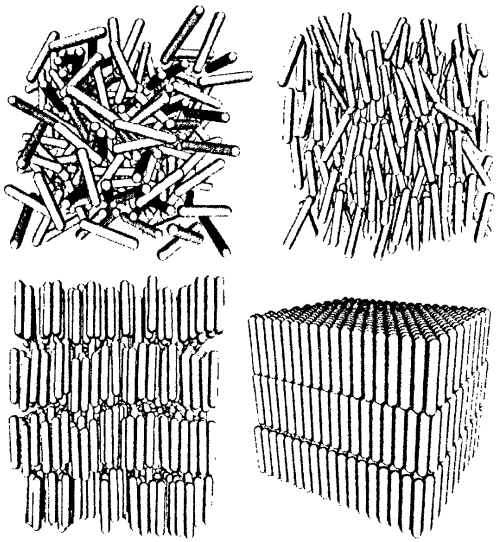
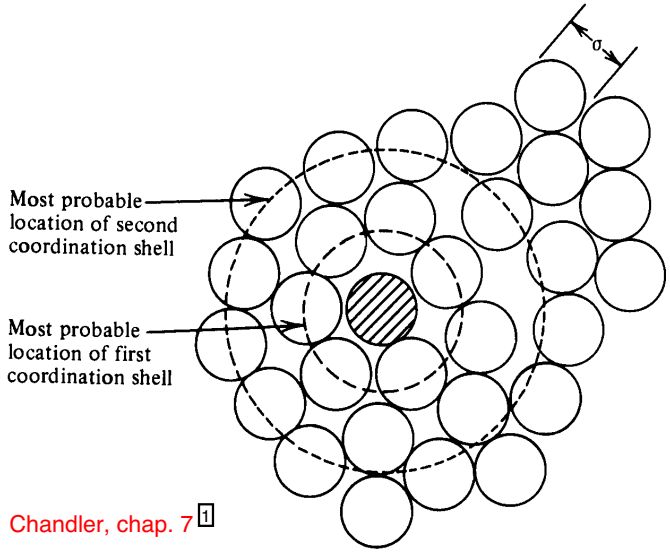
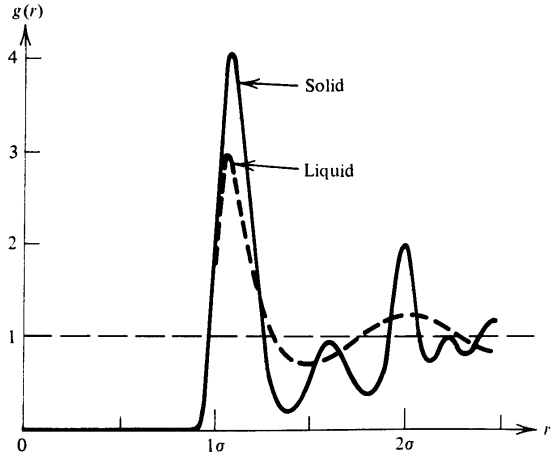


Figure: Different types of mesogenic order: Isotropic, nematic, smectic and crystalline (figure taken from Ref. 5)

The pair distribution function



Chandler, chap. 7 [1]



- $g(r) = \left\langle \frac{1}{N} \sum_{i=1}^{N} \sum_{j \neq i}^{N} \delta(\mathbf{r} - \mathbf{r}_j + \mathbf{r}_i) \right\rangle$ measured by X-ray or neutrons scattering
- **coordination number n_c:**

$$n_c(r) = 4\pi\rho \int_0^r g(r') r'^2 dr' \tag{35}$$

- **Note:** for a liquid,
  - $g(r) \to 1$ as $r \to \infty$. Absence of long-range order
  - $g(r) \to 0$ as $r \to 0$. Repulsive forces at short distances

Connection with thermodynamics

Relations valid for uniform fluids with potential energy given by a sum of pair interactions:

Energy equation:

$$U^{ex}/N = 2\pi\rho \int_0^\infty v(r)g(r)r^2 dr \tag{36}$$

Pressure equation:

$$\frac{\beta P}{\rho} = 1 - \frac{2\pi\beta\rho}{3} \int_0^\infty v'(r)g(r)r^3 dr \tag{37}$$

Reversible work theorem

Under constant (N, V, T) the reversible for work (Helmholtz free energy) necessary to bring two tagged particles from infinite separation to a relative distance r is given by:

$$w(r) = -k_B T \ln(g(r)) \tag{38}$$

Time auto-correlation functions

Time average:

$$C_{AA}(t) = \langle A(t)A(0)\rangle \quad = \quad \lim_{\tau\to\infty} \frac{1}{\tau}\int_0^{\tau} A(t)A(0)dt \tag{39}$$

For a system in equilibrium $f_o(\mathbf{r}^N, \mathbf{p}^N)$ is independent of time and correlation functions only depend on the time lag: $t = t' - t''$.

- **Short- and long-time limits:**

$$\lim_{t\to 0} \langle A(t)A(0)\rangle = \langle AA\rangle \qquad \lim_{t\to\infty} \langle A(t)A(0)\rangle = \langle A\rangle^2 \tag{40}$$

- **It is possible to show that the power absorbed by the system for a mono-cromatic perturbation of frequency ω, is given by:**

$$\boxed{abs(\omega) = \frac{\beta\omega^2|f_\omega|^2}{4}\int_0^{\infty} dt\,\langle\delta A(0)\delta A(t)\rangle\cos(\omega t)} \tag{41}$$

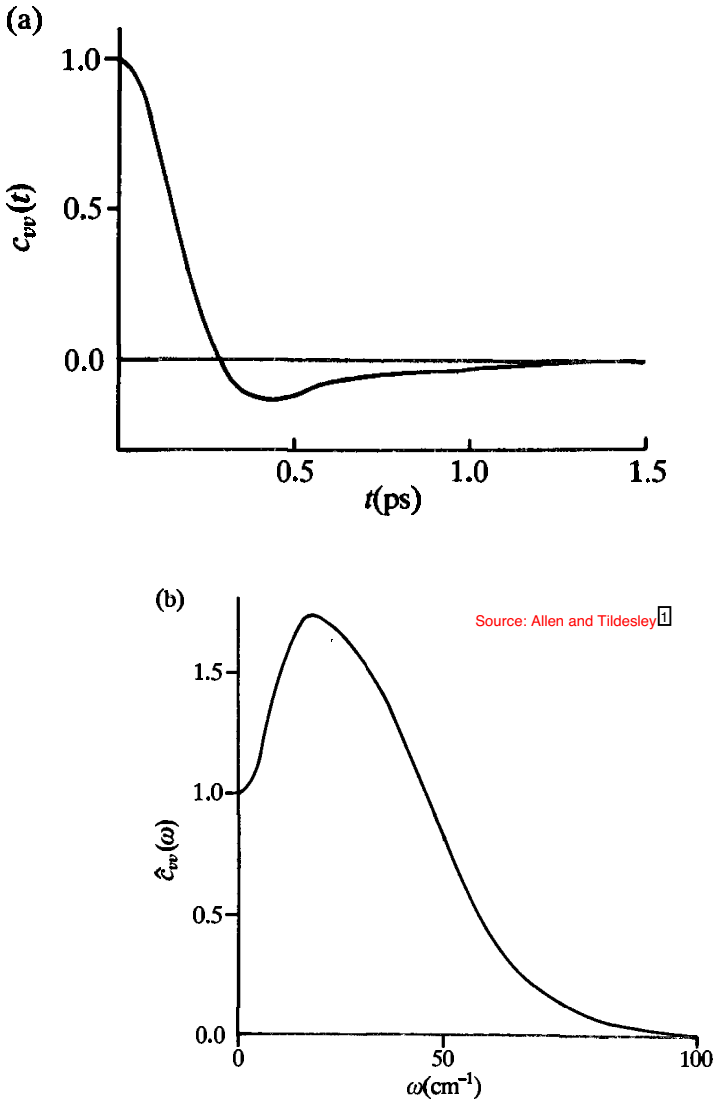
The velocity auto-correlation function

$$\boxed{C_{V_x V_x}(t) = \frac{1}{3}\langle \mathbf{V}(t)\cdot\mathbf{V}(0)\rangle}$$

$$C_{V_x V_x}(0) = \left\langle V_x^2 \right\rangle = \frac{k_B T}{m}$$

$$\lim_{t\to\infty} C_{V_x V_x}(t) = \langle V_x \rangle^2 = 0$$

- $C_{V_x V_x}(t)$ measures the projection of the particle velocity at time t onto its initial value
- Fast initial decay followed by back-scatering



Bibliography

- *"Introduction to Modern Statistical Mechanics"*, by D. Chandler, Oxford University Press, 1987
- *"Theory of Simple Liquids "*, by J-P. Hansen , I. R. McDonald, Academic Press, Third Edition, 2005
- *" Principles of Condensed Matter Physics "*, by P. M. Chaikin and T. C. Lubensky, Cambridge University Press, 1995
- *" Statistical Physics of Particles"*, by M. Kardar, Cambridge University Press, 2007
- *" Basic Concepts for Simple and Complex Liquids "*, by Jean-Louis Barrat and Jean-Pierre Hansen. Cambridge University Press, 2003