

# Short Course on Molecular Dynamics Simulation

## Lecture 8: Static Properties

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# High Level Course Outline

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1. MD Basics
2. Potential Energy Functions
3. Integration Algorithms
4. Temperature Control
5. Boundary Conditions
6. Neighbor Lists
7. Initialization and Equilibrium
8. Extracting Static Properties
9. Extracting Dynamic Properties
10. Non-Equilibrium MD

# Static Properties

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- ❑ Thermodynamic properties
  - Simple functions of the Hamiltonian
  - Response functions
  - Entropic properties
- ❑ Static Structure
  - Radial distribution function

# Simple Thermodynamic Properties

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- Internal energy and temperature

$$H(\vec{r}^N, \vec{p}^N) = \text{const}$$

$$H = E_k + U$$

$$\langle E_k \rangle = \frac{3}{2} NkT = \frac{1}{2mt_\infty} \sum_{t'=1}^{t_\infty} \sum_{i=1}^N \vec{p}_i(t'\Delta t) \cdot \vec{p}_i(t'\Delta t)$$

$$\langle U \rangle = \frac{1}{t_\infty} \sum_{t'=1}^{t_\infty} \sum_{\vec{\alpha}} \sum_i^N \sum_{j>i}^N u\left(\left|\vec{r}_{ij}(t'\Delta t) - \vec{\alpha}L\right|\right)$$

# Simple Thermodynamic Properties

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## □ Pressure

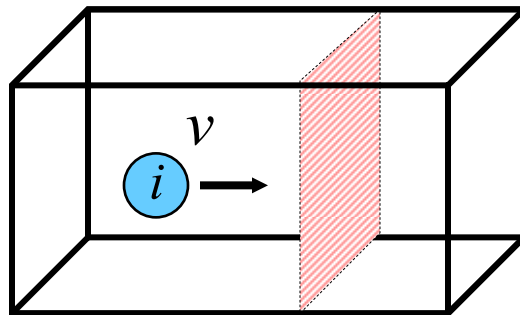
- The continuum concepts of stress or pressure do not translate directly to the discrete particles of an MD simulation
- Pressure is typically calculated using the pressure virial (also called the Irving-Kirkwood equation)
- This expression is obtained by considering stress / pressure to be a momentum flux across an area

$$P = \frac{\text{force}}{\text{area}} = \frac{1}{\text{area}} \frac{d(mv)}{dt}$$

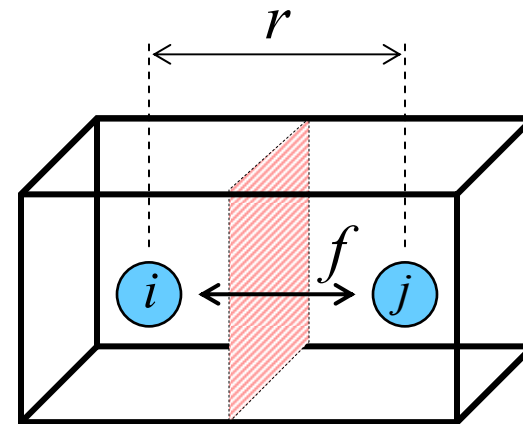
# Simple Thermodynamic Properties

- Momentum transferred via two mechanisms

1. Carried across an area by a moving atom



2. Interaction between atoms on opposite sides of an area



$$P = \frac{1}{\text{volume}} \left[ \sum_i m_i v_i^2 + \sum_i \sum_{j>i} r_{ij} \cdot f_{ij} \right]$$

# Simple Thermodynamic Properties

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- Irving Kirkwood / Pressure Virial
  - Used for all components of the stress tensor

$$\sigma_{\alpha\beta} = -\frac{1}{V} \left\langle \sum_i^N m_i u_{i\alpha} u_{i\beta} + \sum_i^N \sum_{j>i}^N \mathbf{r}_{ij\alpha} \mathbf{F}_{ij\beta} \right\rangle$$

# Simple Thermodynamic Properties

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- Mean square force
  - Gives information about the shape of the repulsive part of the pair potential
  - Obtainable experimentally for comparison

On one atom:  $\langle F_1^2 \rangle = \left\langle \sum_{j \neq 1} (\nabla U(r_{1j}))^2 \right\rangle$

On all atoms:  $\langle F^2 \rangle = \frac{2}{MN} \sum_{k=1}^M \sum_{\bar{\alpha}} \sum_{i < j} (\nabla U [\vec{r}_{ij}(k\Delta t) - \bar{\alpha}L])^2$



# Response Functions

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- How do simple thermodynamic properties response to changes
  - Temperature
  - Pressure
- Two general methods
  - Use several simulations to determine values of a quantity as functions of the changing variable
  - Evaluate the derivative analytically using statistical mechanics

# Response Functions

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- Example: Constant volume heat capacity

$$C_v = \left( \frac{\partial U}{\partial T} \right)_{V=const}$$

- Method 1
  - Begin with an initial configuration
  - Run simulation at temperature T1
  - Measure the internal energy U1
  - Repeat process at T2, T3, ....
  - Empirically fit simulation results for U(T)
  - Numerically or analytically take derivative

# Response Functions

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## □ Method 2

$$C_v = \frac{1}{kT^2} \langle (\partial U)^2 \rangle$$

$$\partial U = U - \langle \partial U \rangle$$

Fluctuation of internal energy about its average

$$\langle (\partial U)^2 \rangle = \langle (U - \langle \partial U \rangle)^2 \rangle = \langle U^2 \rangle - \langle U \rangle^2$$

Mean-square fluctuation of internal energy

## □ Advantages

- Only requires a single simulation

## □ Disadvantages

- Typically less accurate than Method 1
  - Round off / small differences in big numbers

# Response Functions

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- ▣ Similar approaches are possible for

- Adiabatic compressibility  $\kappa = \frac{-1}{V} \left( \frac{\partial V}{\partial P} \right)_{S=const}$

- Thermal pressure coefficient  $\gamma = \left( \frac{\partial P}{\partial T} \right)_{V=const}$

- Etc.

# Entropic Properties

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- Entropic properties are not simple time averages over a phase-space trajectory
  - Entropy
  - Gibbs free energy
  - Helmholtz free energy
  - Chemical potential
- Methods
  - Thermodynamic integration
  - Test particle method
  - Coupling parameter method

# Entropic Properties

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- Thermodynamic integration

$$dS = \frac{dU}{T} + \frac{P}{T}dV - \frac{\mu}{T}dN$$

← Chemical potential

- Fix  $N$  and  $V$ , vary  $U$ , measure  $T$

$$dS = \left( \frac{dU}{T} \right)_{N,V=const} \quad S(U_2) - S(U_1) = \int_{U_1}^{U_2} \frac{dU}{T}$$

- Fix  $N$  and  $V$ , vary  $T$ , measure  $U$

$$S(T_2) - S(T_1) = \int_{T_1}^{T_2} \frac{1}{T} \left( \frac{dU}{T} \right) dT$$

# Entropic Properties

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- Thermodynamic integration
  - Fix two quantities, vary another, and measure the response of the last
  - For example,
    - Fix N and V
    - Perform a series of simulations at fixed energy
    - Calculate average temperature each time

$$S(U_2) - S(U_1) = \int_{U_1}^{U_2} \frac{dU}{T}$$

- Typically very accurate method, but extremely time consuming because of the large number of simulations to obtain a single entropy difference

# Entropic Properties

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- Test Particle Method
  - Instead of varying the energy, temperature, or volume, alternatively vary the number of particles
  - Randomly insert a particle,
    - If it does overlap (i.e. large positive energy), its effect is ignored
    - If the placement is ok, we can measure the change in energy that results
  - Disadvantages
    - Implementation rather complex
    - Less successful at high densities (most insertions fail)

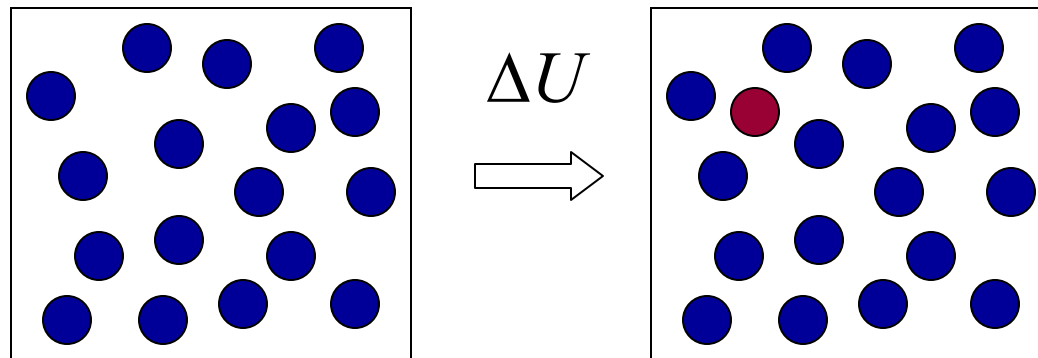


# Entropic Properties

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- Test Particle Method
  - Estimate the change in entropy due to a change in the number of particles, vary  $N$

$$\mu = -T \left( \frac{dS}{dN} \right)_{U, V = \text{const}}$$



# Entropic Properties


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- Coupling parameter method
  - Redefine the potential energy as a function of both position and a “coupling parameter”

$$U = U(\vec{r}^N, \lambda)$$

- Parameter determines how strongly the atoms are coupled via the potential function
- It varies between  $\lambda_0$  which is a reference conditions (typically an ideal gas state) and  $\lambda_f$  which is the potential at its full strength

$$\lambda_0 < \lambda < \lambda_f$$



Reference State  
(Ideal Gas)

Full Strength

# Entropic Properties

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- Coupling parameter method
  - Can obtain an expression for the change in entropy between different values of  $\lambda$  which can in turn be related to density and temperature
  - Then systematically vary  $\lambda$  to get entropy
  - Method preferred over the test particle method because it does not fail in the high density limit

$$U = U(\vec{r}^N, \lambda)$$

$$S(\lambda_f) - S(\lambda_0) = -k \left( \frac{3N}{2} - 1 \right) \int_{\lambda_0}^{\lambda_f} \left\langle \frac{1}{E_k} \left( \frac{dU}{d\lambda} \right)_{NVE} \right\rangle d\lambda$$

# Static Structure

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- ▣ Radial distribution function,  $g(r)$ 
  - Measure of how atoms organize themselves around one another
  - Plays an important role in many statistical mechanics methods
  - Can be extracted from x-ray and neutron diffraction

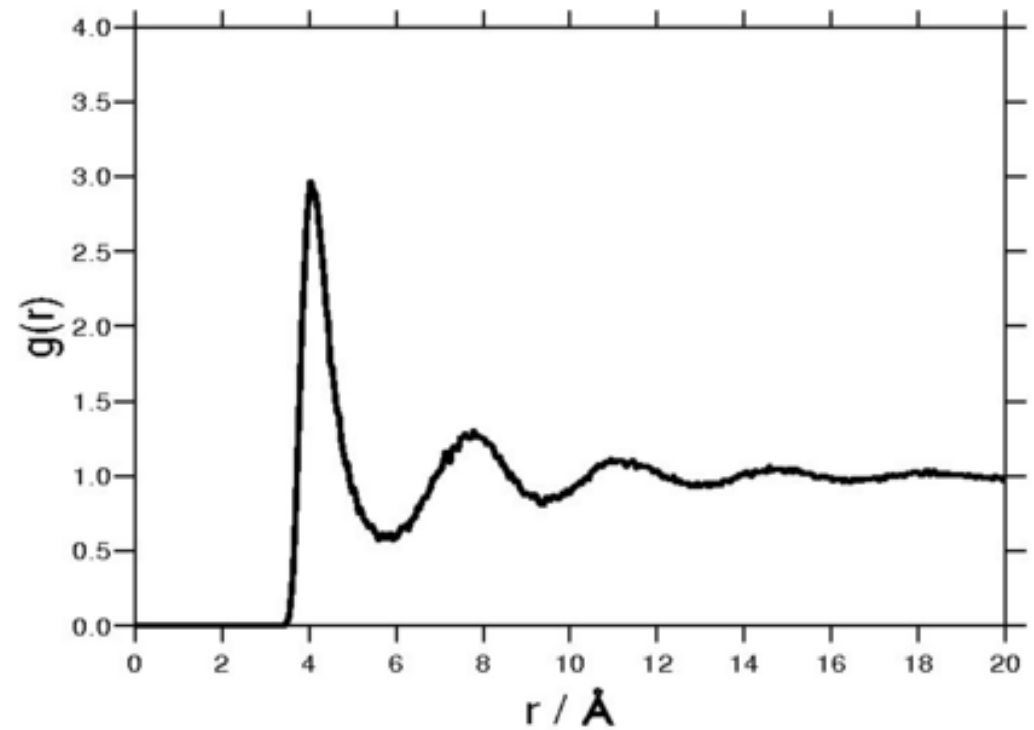
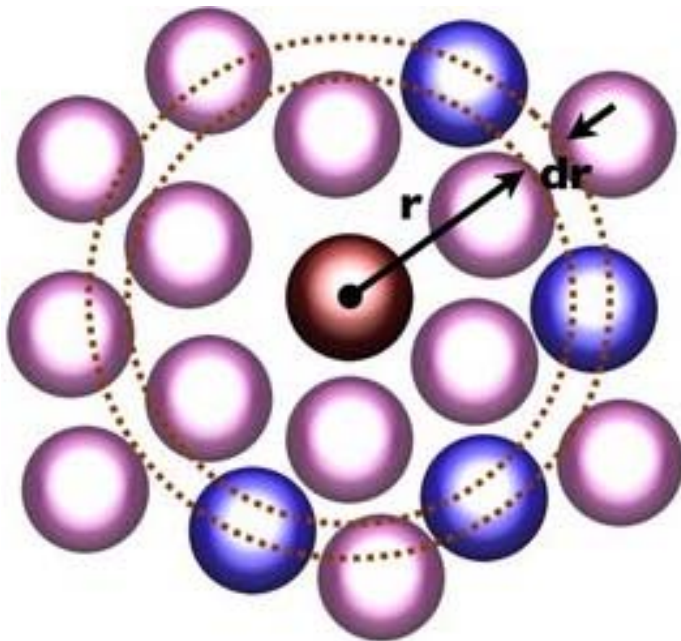
Ratio between the average number density at a given distance from any atom to the density at the same distance in an ideal gas

Necessarily,  $g(r)=1$  in an ideal gas

# Static Structure

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- Radial distribution function



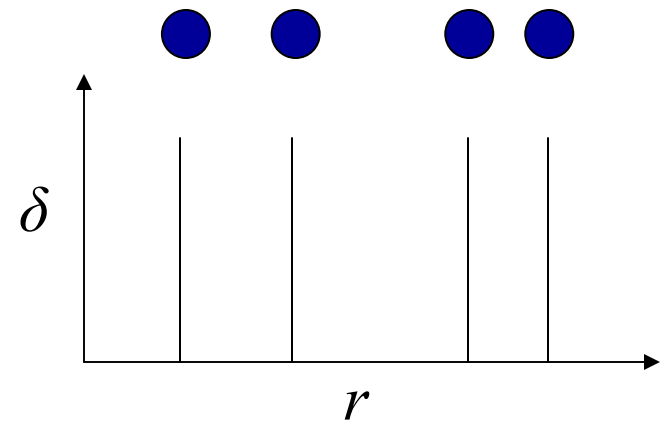
# Static Structure

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- Radial distribution function from MD

$$\rho g(r) = \frac{1}{N} \left\langle \sum_i^N \sum_{j \neq i}^N \delta[r - r_{ij}] \right\rangle$$

$$\rho g(r) = \frac{2}{N} \left\langle \sum_i^N \sum_{j < i}^N \delta[r - r_{ij}] \right\rangle$$



- Integrate over all possible two atom separations

$$\rho \int g(r) dr = \frac{2}{N} \left\langle \sum_i^N \sum_{j < i}^N \int \delta[r - r_{ij}] dr \right\rangle$$

# Static Structure

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– By definition  $\int \delta[r - r_{ij}] dr = 1$

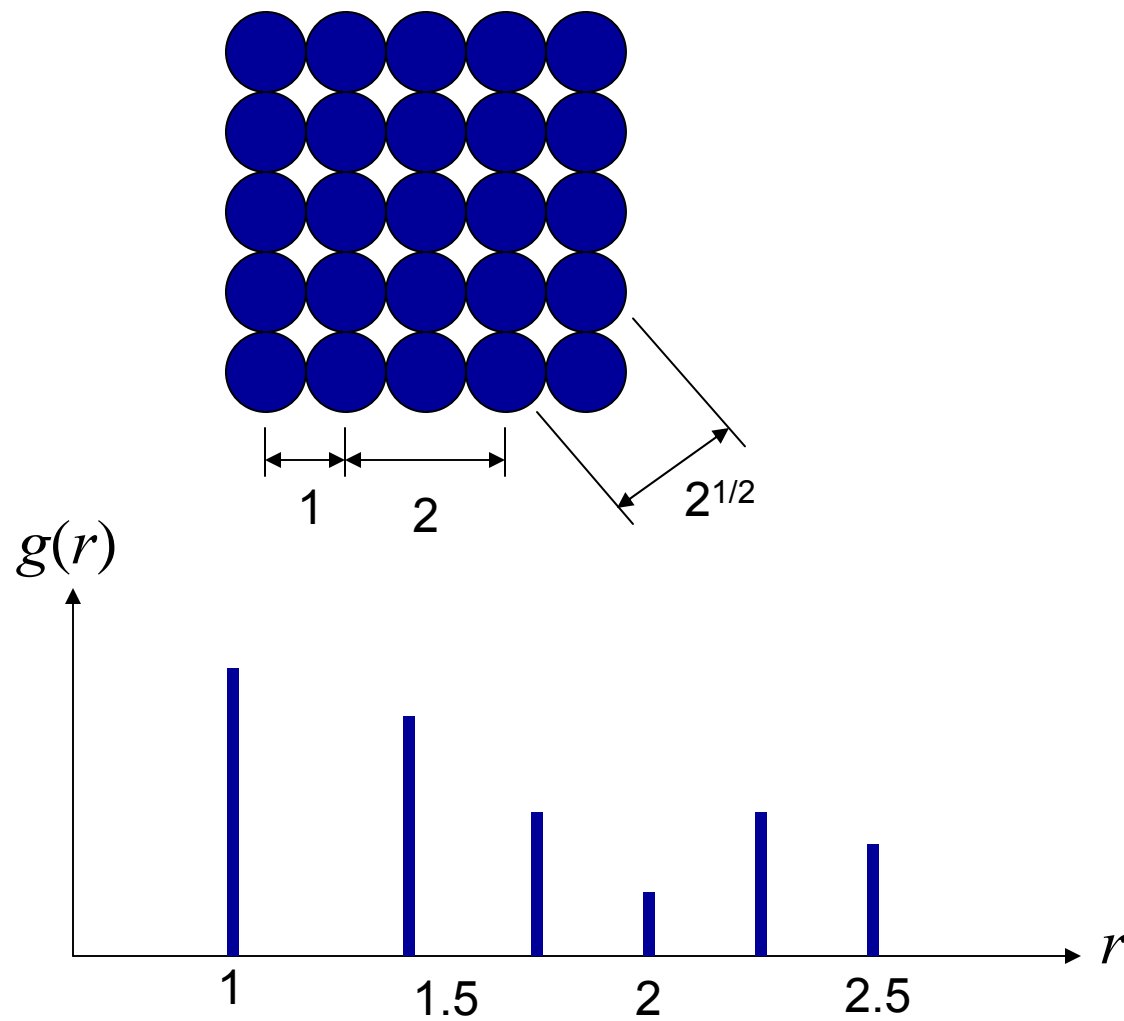
– So  $\rho \int g(r) dr = N - 1 \approx N$

– Probabilistic interpretation

$$\frac{\rho}{N-1} g(r) V(r, \Delta r) = \text{probability that an atomic center lies in a spherical shell of radius } r \text{ and thickness } \Delta r \text{ with the shell centered on another atom}$$

# Static Structure

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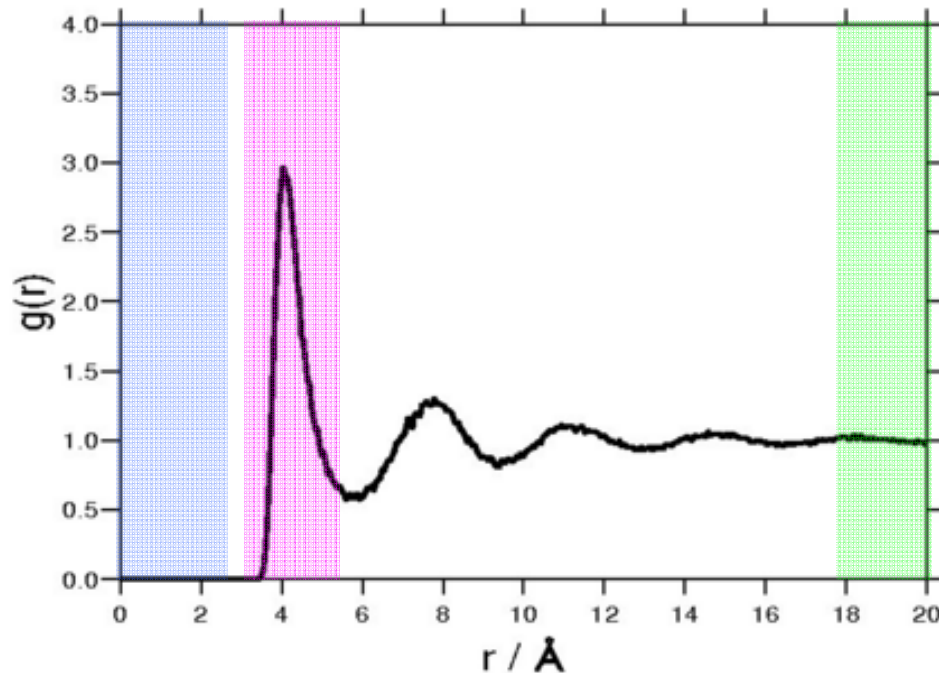
# Static Structure

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Zero at distances less than an atomic diameter due to the strong repulsive forces

Largest peak  $\sim 3.7$  where there is 3 times more likely to be an atom (than ideal gas)

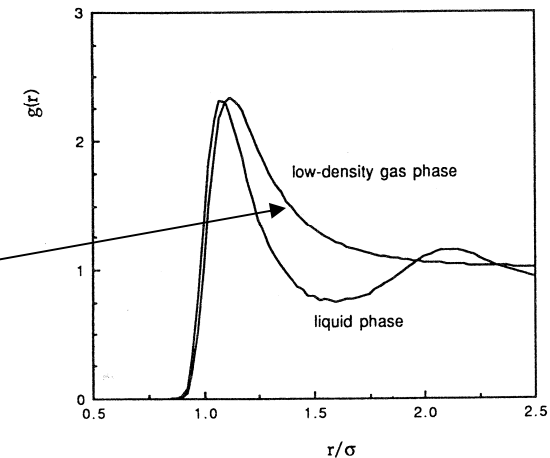
At large distances the system approaches an ideal gas; no long-range order



# Static Structure

- Radial distribution function
  - In the low density (gas) limit

$$\lim_{\rho \rightarrow 0} g(r) = \exp\left[-\frac{U(r)}{kT}\right]$$



- Discriminate between crystal structures
  - FCC lattice has fewer atomic pairs separated by  $\sqrt{2}$  and more atomic pairs separated by  $\sqrt{3}$  than a simple cubic lattice
- Near fluid-solid boundaries,  $g(r)$  used to determine phase
  - Crystalline solids will exhibit deeper valleys and higher, narrower secondary peaks liquids or amorphous solids