

Liquids: Cells, The Radial Distribution Function and Thermodynamic Properties.

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Liquids

- Liquids are much more difficult to theoretically describe.
- Interatomic forces are constantly present, essentially making the configuration integral functionally complex.
- Two theoretical approaches have been cell based and distribution function based.
- Molecular dynamics is a computational approach.



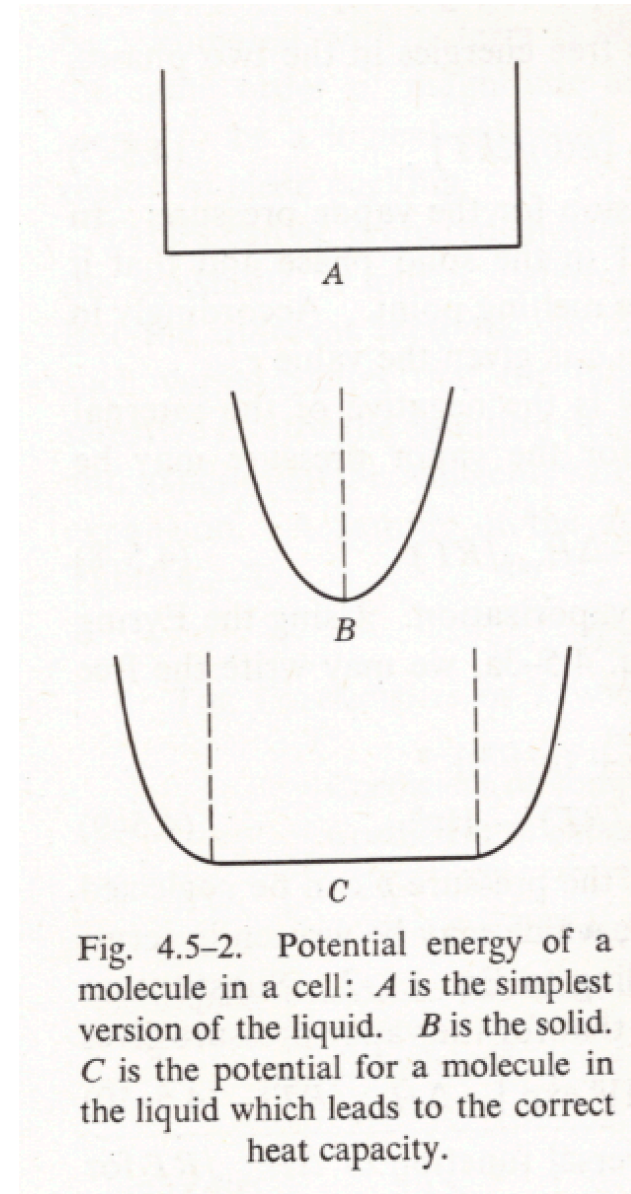
Cell Theories

- Cell theories are based on the idea that molecules in a liquid are restricted in their motion.
- Define a cell that is several collision diameters across.
- Then assume that the molecule behaves like a particle in a box.



Cell Theories

- This diagram from HCB illustrates the idea of cells.
- It shows the potential energy for a simple square cell, a solid crystal, and more appropriate approximation for a liquid.



Distribution Function Methods

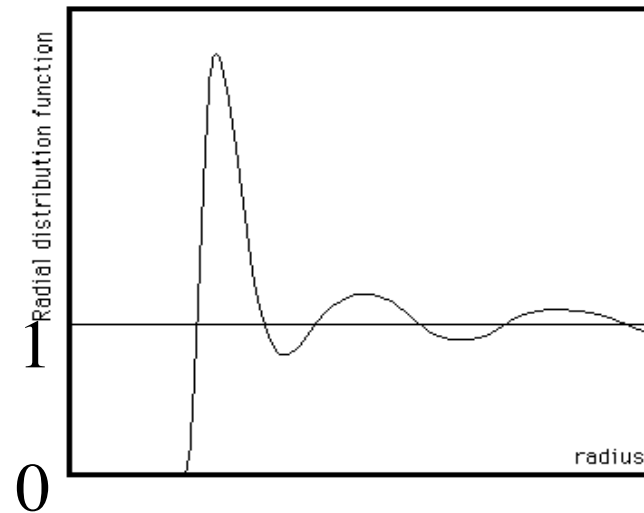
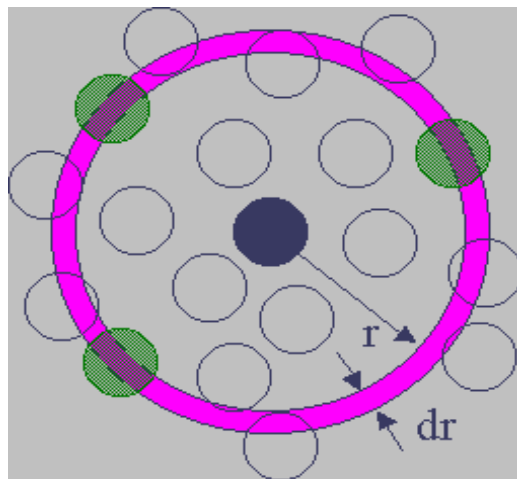
- These are based on evaluating the configuration integral using statistical distributions.
- The key idea is that a distribution function can describe the liquid structure in an average way.
- Experimentally one can determine the radial distribution function using x-ray scattering.



Radial Distribution Function

- The radial distribution function is:

$$g(r) = \rho(r)/\rho$$



- Note $\int_0^{\infty} \rho g(r) 4\pi r^2 dr = N - 1 \approx N$

Relation of Thermodynamic Functions to $g(r)$

- One can show that if we assume that the total potential energy of the N-body system is pair-wise additive, i.e.

$$U_N(r_1, \dots, r_N) = \sum_{i < j} u(r_{ij})$$

- Then all thermodynamic functions can be written in terms of $g(r)$.



- Now

$$4\pi r^2 \frac{N}{V} g(r) dr$$

is the number density of molecules with centers between r and $r + dr$ relative to a specific molecule.

- For spherically symmetric pair-wise potential function it follows that

$$4\pi r^2 u(r) \frac{N}{V} g(r) dr$$

is the intermolecular potential energy between the central molecular and other molecules with centers between r and $r + dr$



- Energy

$$U = \frac{3}{2} N k_B T + \frac{N}{2} \rho \int_0^{\infty} u(r) g(r, \rho, T) 4\pi r^2 dr$$

- Pressure

$$p = \rho k_B T - \frac{\rho^2}{6} \int_0^{\infty} r u'(r) g(r) 4\pi r^2 dr$$

