Statistical Mechanics Approaches to Study Classical Liquids

Statistical Mechanics, Spring 2018

Ceriotti and Stellacci

Outline about this class

Important Concept from Previous Classes

What is a ‘classical fluid’ in Statistical Mechanics?

Partition Function for a Classical Fluid

$$Q = \sum_R \left\{ \sum_{i(R)} \exp\left[-\beta E_{R,i(R)}\right] \right\}$$

$$\equiv \sum_R \exp\left[-\beta \tilde{E}_R\right],$$

Classical Particles in Phase Space

Partition Function In Phase Space

$$Q = (?) \int dr^N \int dp^N \exp\left[-\beta \mathscr{H}(r^N, p^N)\right],$$

Normalization Constant

$$Q = (?)V^N \left[\int d\mathbf{p} \exp\left(-\beta p^2/2m\right) \right]^N.$$

Complete Partition Function

$$Q = \frac{1}{N!\, h^{3N}} q^N_{\text{quantum}}(\beta) \int dr^N \int dp^N \exp\left[-\beta \mathcal{H}_{\text{classical}}\right],$$

Probability Distribution

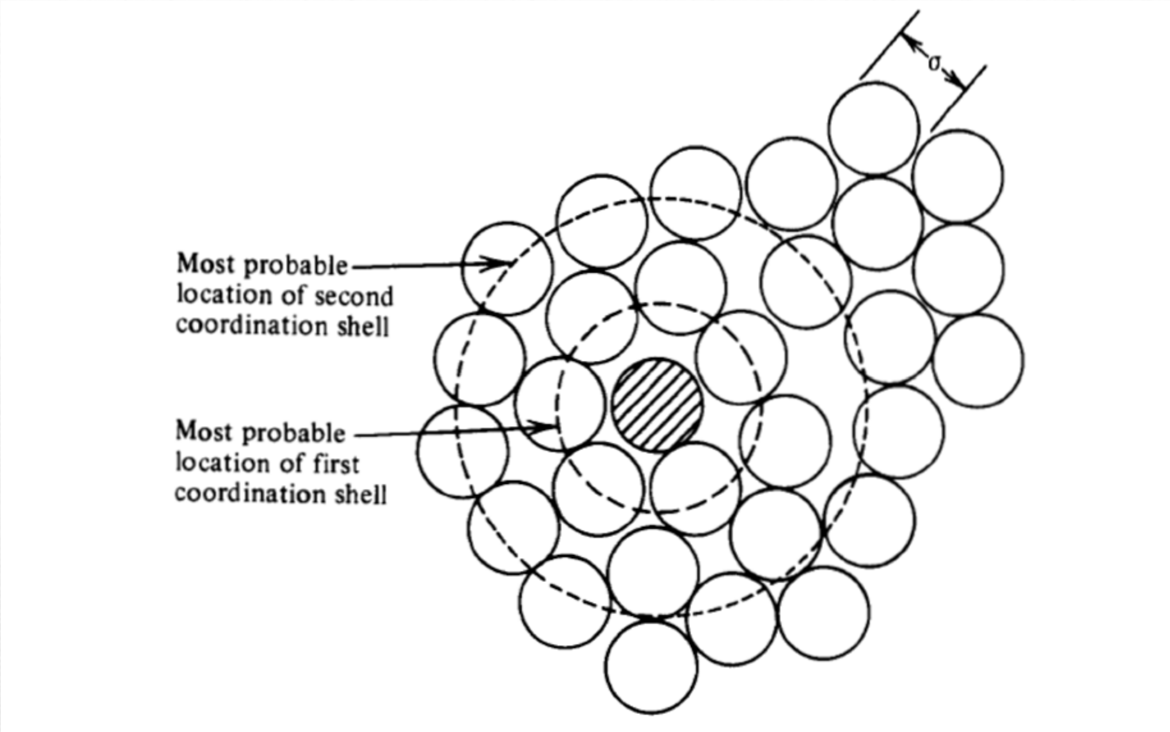
$$f(r^N, p^N) = \exp\left[-\beta\mathscr{H}(r^N, p^N)\right] \Big/ \int dr^N \int dp^N \exp\left[-\beta\mathscr{H}(r^N, p^N)\right].$$

Limits in Classical Description

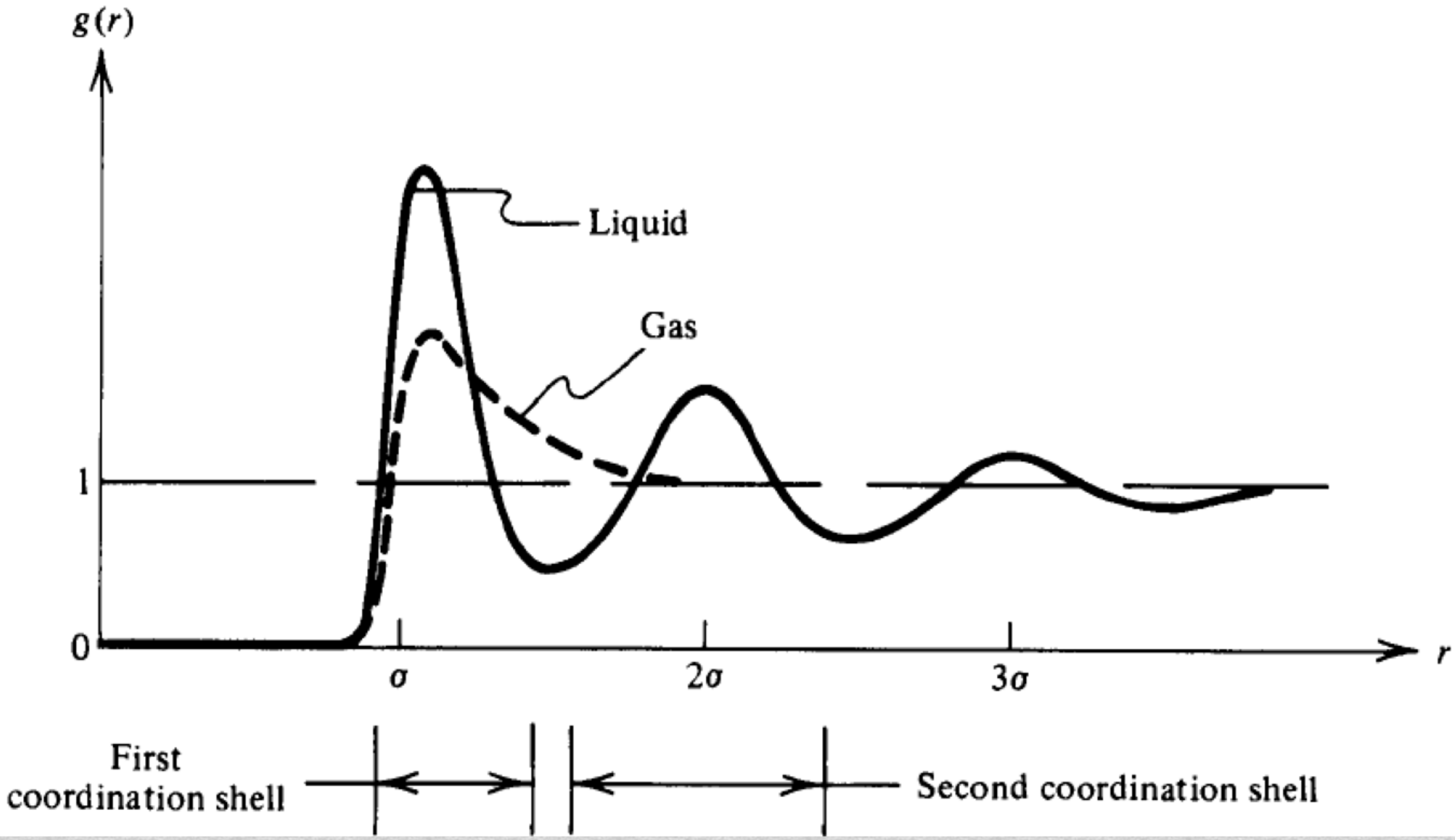
Reduced Configurational Distribution Functions

The Radial Distribution Function

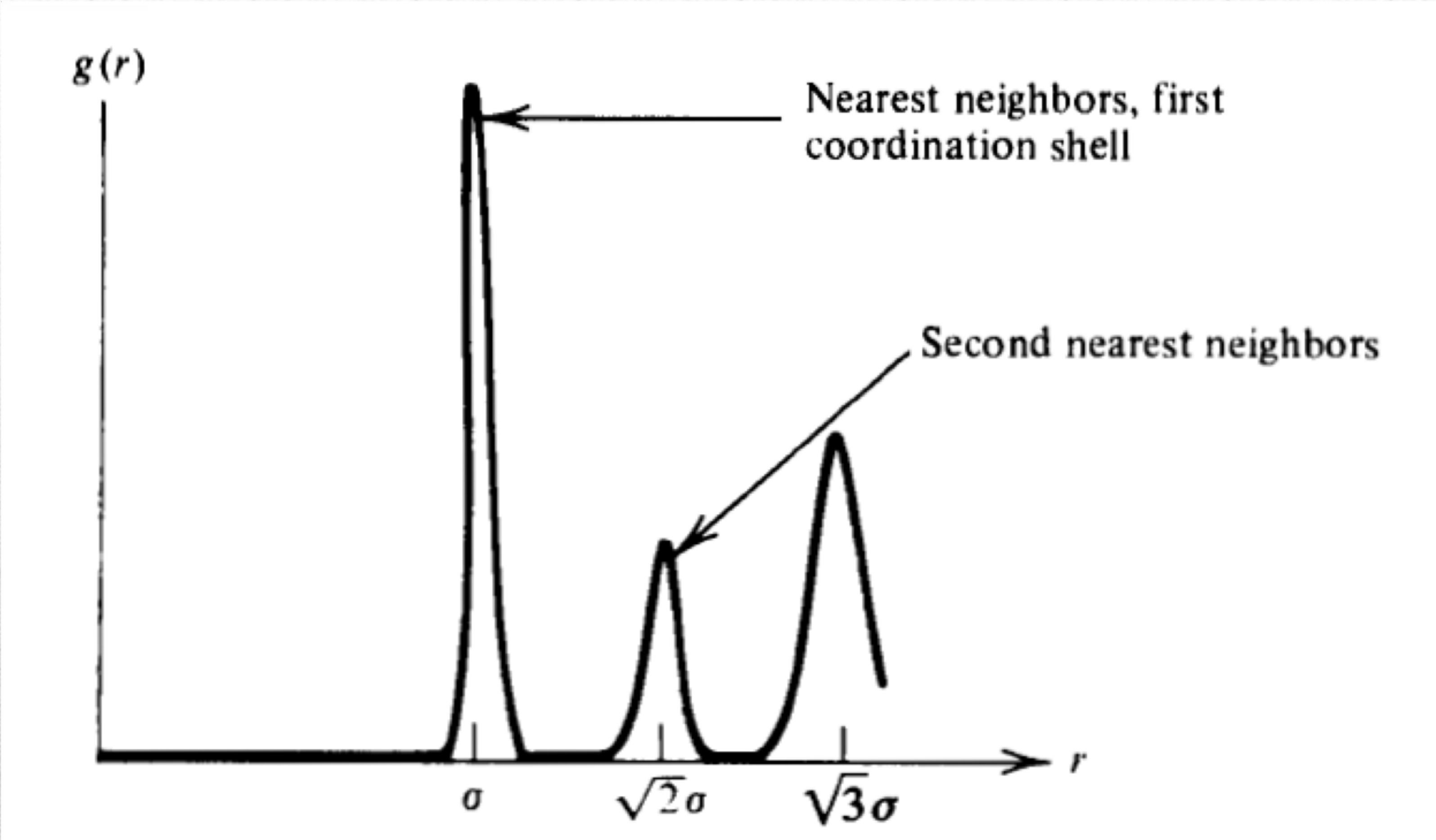
Meaning of g(r)



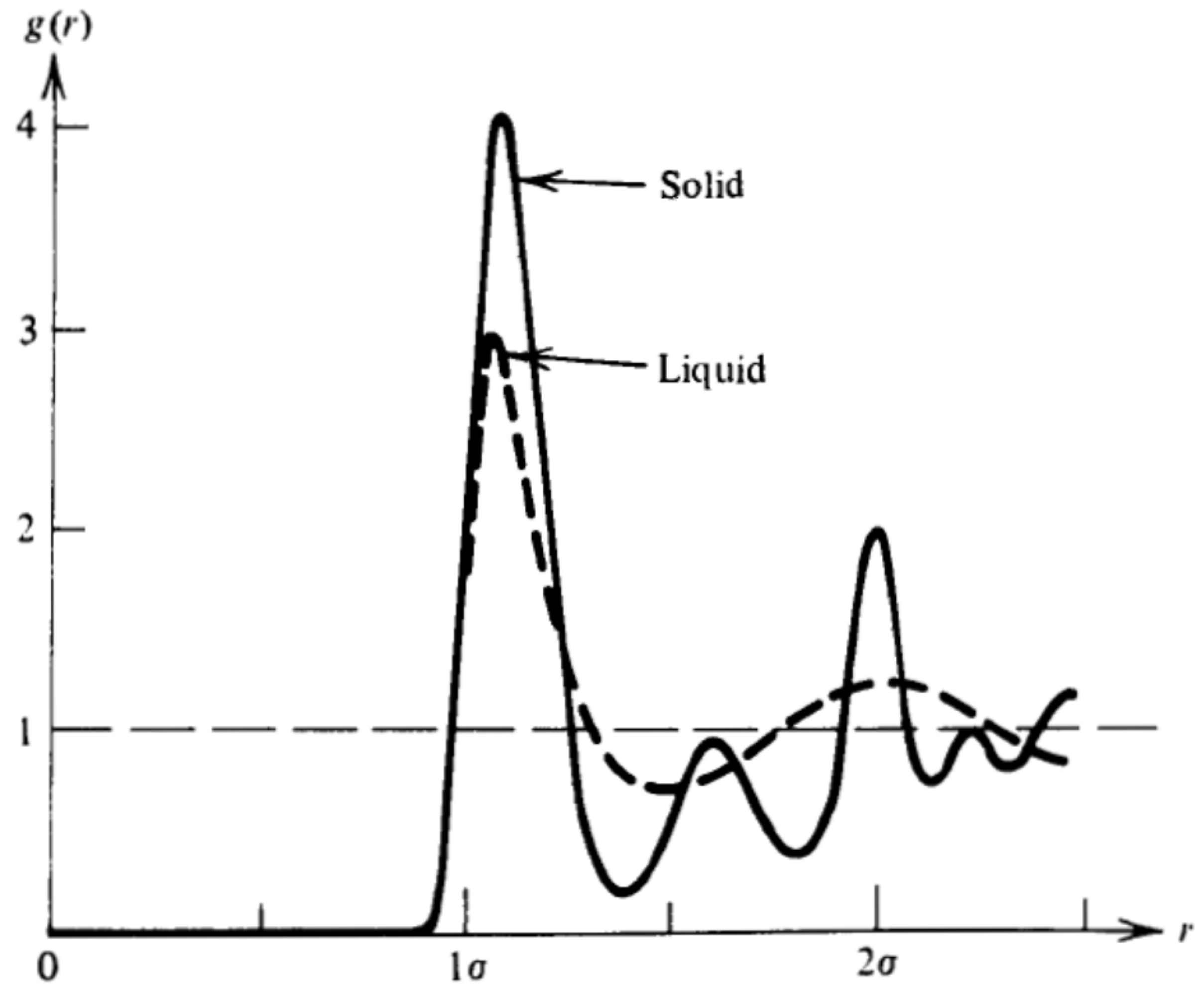
Interpretation of g(r)



Solid vs. Liquids



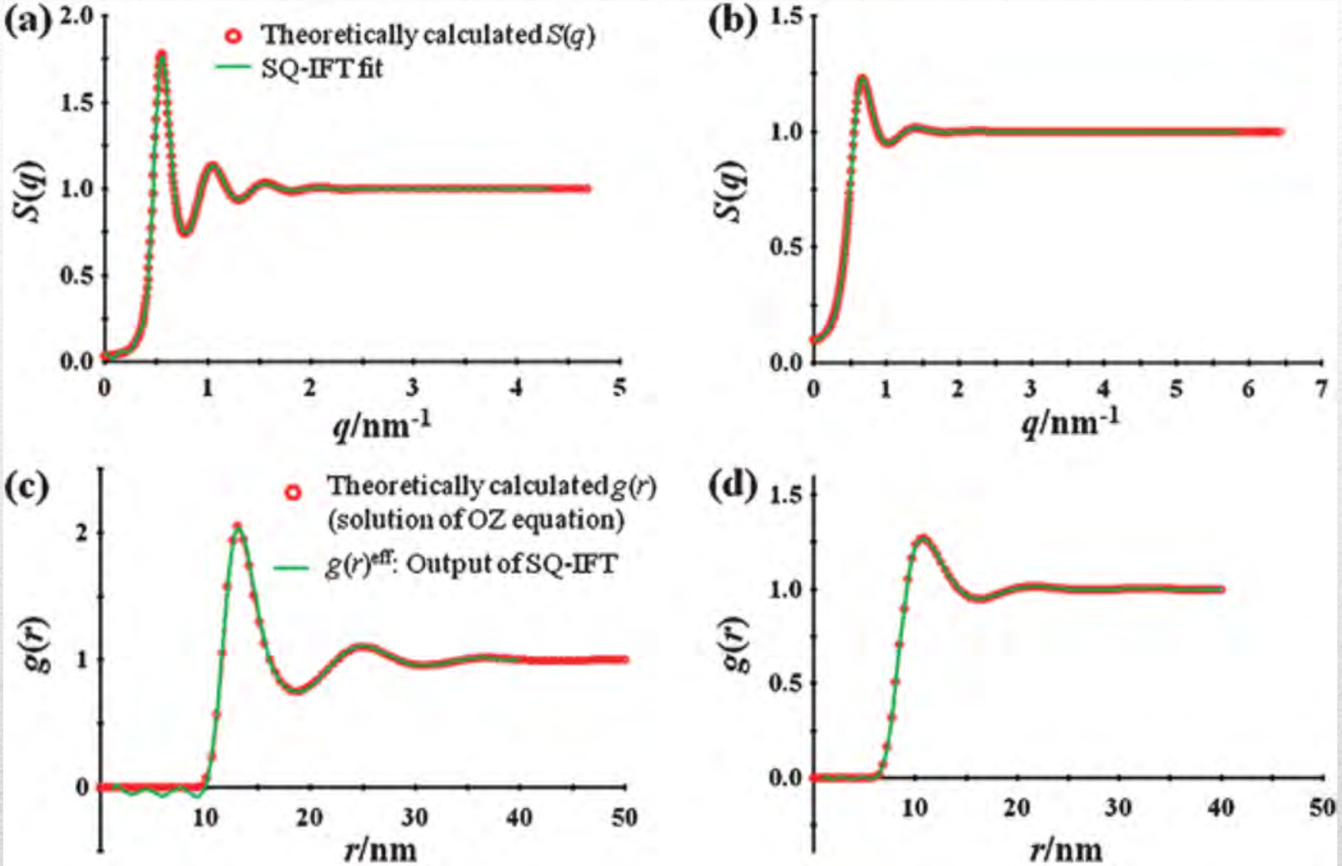
Solid vs. Liquids



Experimental g(r)

$$S(k) = N^{-1} \left\langle \sum_{l,j=1}^{N} \exp\left[i\mathbf{k} \cdot (\mathbf{r}_l - \mathbf{r}_j)\right] \right\rangle.$$

Examples



Versatile application of indirect Fourier transformation to structure factor analysis: from X-ray diffraction of molecular liquids to small angle scattering of protein solutions

Toshiko Fukasawa[a] and Takaaki Sato*[b]

The Reversible Work Theorem

$$g(r) = e^{-\beta w(r)}$$

Thermodynamics Properties from g(r)

$$\langle E \rangle / N = \frac{3}{2} k_B T + \frac{1}{2} \rho \int d\mathbf{r}\, g(r) u(r).$$

Molecular Liquids

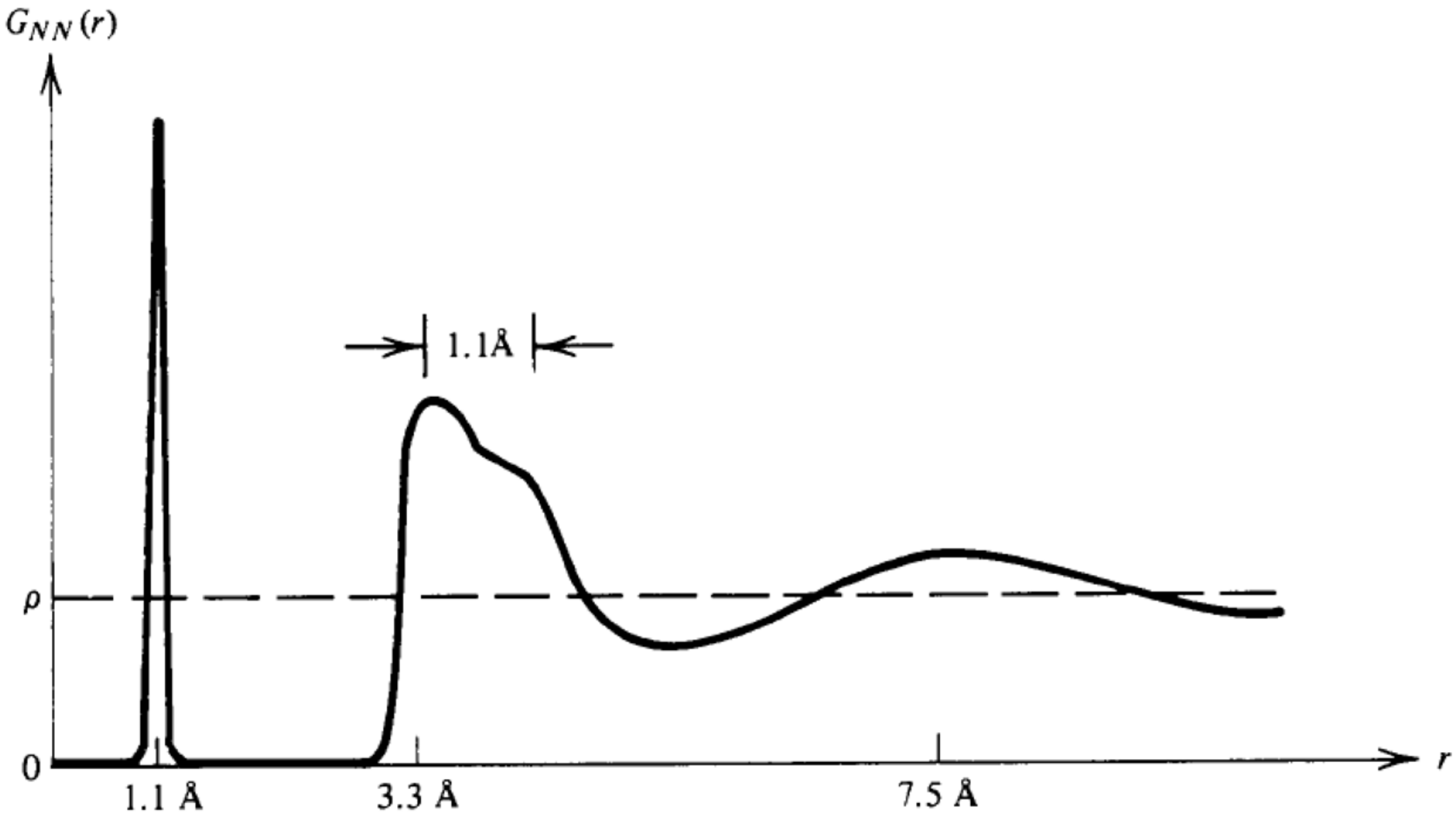
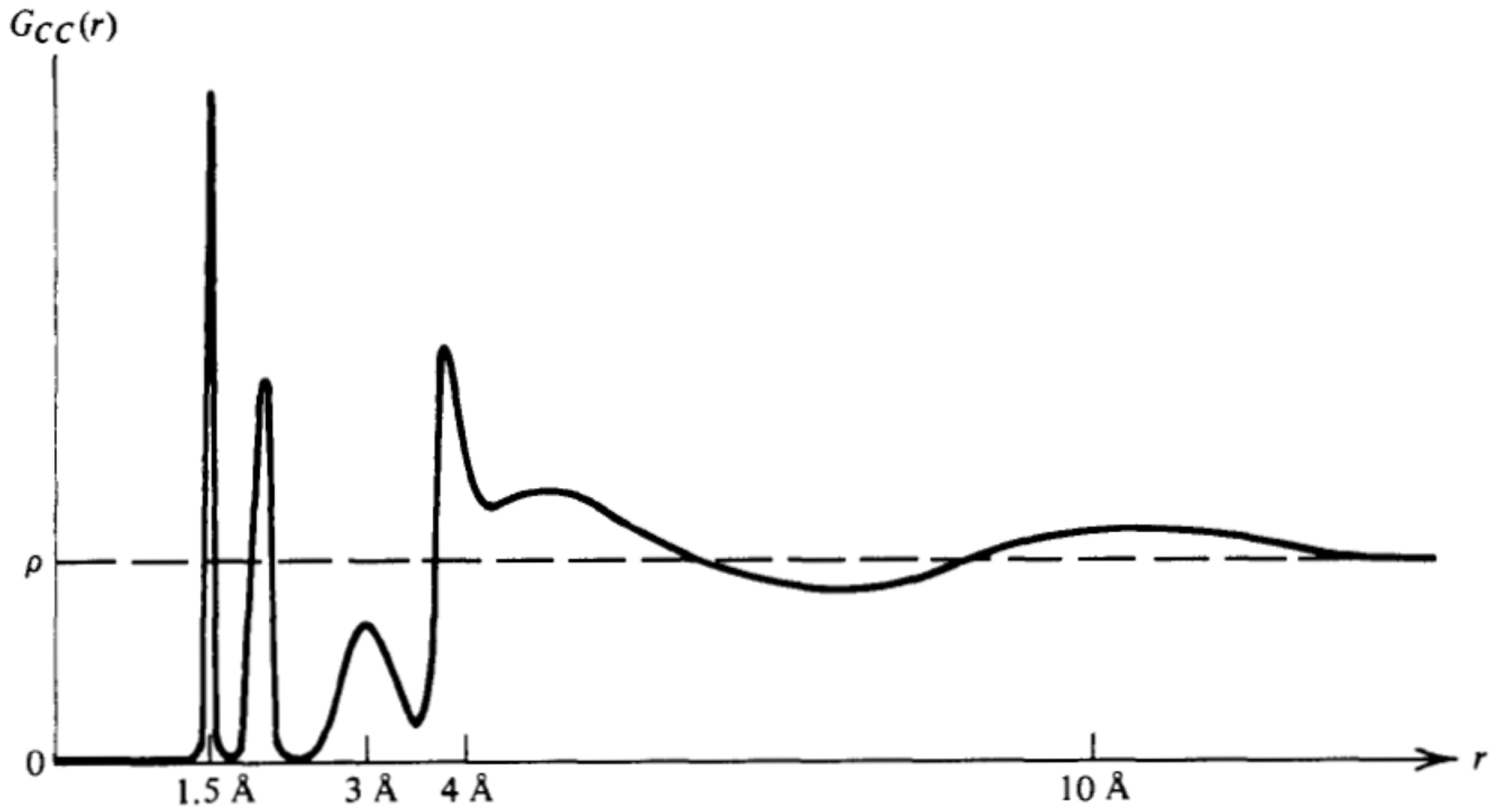
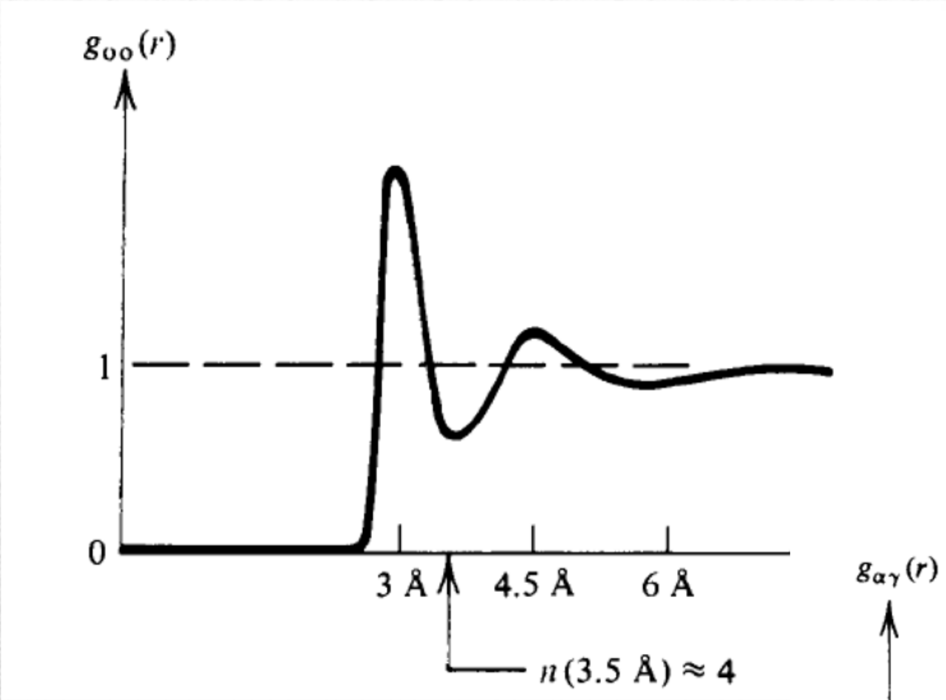


Fig. 7.9. Pair distribution function for liquid nitrogen.

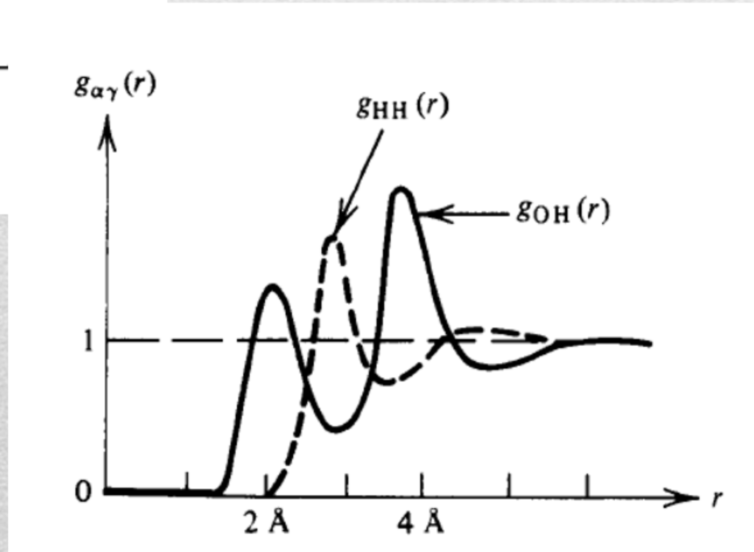
Molecular Liquids



Water



$g_{OO}(r)$
1
0
3 Å
4.5 Å
6 Å
$n(3.5\ Å) \approx 4$



$g_{\alpha\gamma}(r)$
$g_{HH}(r)$
$g_{OH}(r)$
1
0
2 Å
4 Å
r

Principles of Solvation and Chemical Equilibrium

$$Q = Q_S^{(\mathrm{id})} Q_A^{(\mathrm{id})} V^{-(N_A+N_S)} \int dr^{N_A} \int dr^{N_S} \times \exp\left[-\beta U_S(r^{N_S}) - \beta U_{AS}(r^{N_S}, r^{N_A})\right],$$

Principles of Solvation and Chemical Equilibrium

$$\mu_A = \mu_A^{(\mathrm{id})} + \Delta\mu_A,$$

where

$$\Delta\mu_A = \int_0^1 d\lambda \int d\mathbf{r}\, \rho_S g_{AS}(r;\lambda) u_{AS}(r),$$