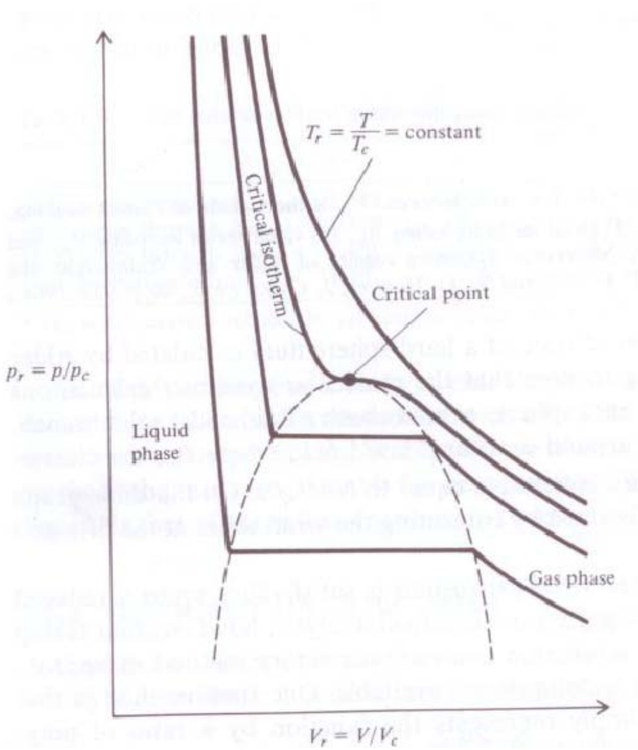
Distribution Functions



Pressure-volume isotherms of a real fluid.
(from McQuarrie)

Virial expansion fails for liquids

prob particle 1 is in dr_1 at r_1 , particle 2 is in dr_2 at r_2, etc.

$$P^{(N)}\left(r_1,\ldots,r_N\right)dr_1\ldots dr_N = \frac{e^{-\beta U_N}dr_1\ldots dr_N}{Z_N}$$

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prob particle 1 in dr_1 at r_1, … particle n is in dr_n at r_n, with no restrictions on particles r_{n+1}, … r_N

$$P^{(n)}\left(r_1,\ldots r_n\right) = \frac{\int e^{-\beta u_N}dr_{n+1}\ldots dr_N}{Z_N}$$

prob any molecule is in dr_1 at r_1, …, and any molecule is in dr_n at r_n.

$$\rho^{(n)}\left(r_1,\ldots,r_n\right) = \frac{N!}{\left(N-n\right)!}P^{(n)}\left(r_1,\ldots,r_n\right)$$

$$\rho^{(1)}(r_1)\,dr_1 =$$ prob any molecule is in dr_1

find:

$$\frac{1}{V}\int \rho^{(1)}(r_1)\,dr_1 = \frac{N}{V} = \rho$$ (fluid)

$$\rho^{(1)}(r_1) = NP^{(1)}(r_1)$$
$$= \frac{N}{V}\int \frac{dr_1}{V} \rightarrow \frac{N}{V}$$

using $Z_1 = V$

Now define

$$\rho^{(n)}(r_1,\ldots,r_n) = \rho^n \underbrace{g^{(n)}(r_1,\ldots,r_n)}_{\text{correlation function}}$$

$$g^{(n)} \approx V^n \frac{\int e^{-\beta u_N}\,dr_{n+1}\ldots dr_N}{Z_N}$$

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

molecules between *r* and *r* + *dr* about some other molecule

$$\rho^{(1)}(r) = \rho g(r)$$

$$g^{(1)} = g$$
$$g \to 0 \text{ as } r \to 0$$
$$g \to 1 \text{ as } r \to \infty$$

g(r) = radial distribution function

If *U* is pair-wise additive, all thermodynamic quantities can be calculated in terms of *g(r)*

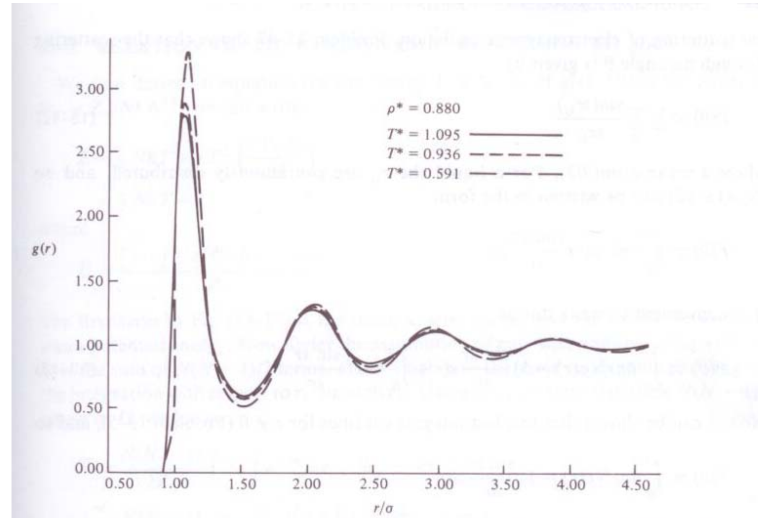

Figure 13–3. **The radial distribution function of a fluid of molecules obeying a Lennard-Jones 6–12 potential from molecular dynamics calculations.** $T^* = kT/\varepsilon$ **and** $\rho^* = \sigma^3\rho$.

g(r) can be determined from x-ray or neutron scattering measurements

What is actually measured is $\hat{h}(s)$, the structure factor

$$h(r) = g(r) - 1$$

$$\hat{h}(s) = \underbrace{\rho \int h(r) e^{isr} dr}_{\text{Fourier transform}}$$

$$s = \frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right)$$

$$\theta = \text{scattering angle}$$

$$E = 3/2NkT + kT^2\left(\frac{\partial \ell n Z_N}{\partial T}\right)_{N,V}$$

$$= 3/2NkT + \bar{U}$$

$$\bar{U} = \frac{\int U e^{-\beta U} dr_1 ... dr_N}{Z_N}$$

$$= \frac{N^2}{2V}\int_0^\infty u(r)g(r)4\pi r^2 dr$$

$$p = kT\left(\frac{\partial \ell n Z_N}{\partial V}\right)_{N,T}$$

prime

$$\frac{p}{kT} = \rho - \frac{\rho^2}{6kT}\int_0^\infty r u'(r)4\pi r^2 dr$$

$$Q_N = \frac{Z_N}{N!\Lambda^{3N}}$$

$$\frac{p}{kT} = \rho - \frac{\rho^2}{6kT}\int_0^\infty r u'(r)\, g(r)\, 4\pi r^2 dr$$

$$g = g_0 + \rho g_1 + \rho^2 g_2 + \ldots$$

$$\frac{p}{kT} = \rho - \frac{\rho^2}{6kT}\sum_{j=0} \rho^j \int_0^\infty r u'(r) g_j(r,T)\, 4\pi r^2 dr$$

$$= \rho - \frac{\rho^2}{6kT}\int_0^\infty r u'(r) g_0\, 4\pi r^2 dr + \ldots$$

low density $g_0 \sim e^{-\beta u(r)}$

$$\frac{\mu}{kT} = \ell n \rho \Lambda^3 + \frac{\rho}{kT}\int_0^1\int_0^\infty u(r) g(r,\xi)\, 4\pi r^2 dr d\xi$$

ξ Is a coupling parameter: *$\xi\mu(r)$*

Kirkwood

$$-kT\,\ell n g^{(2)}(1,2,\xi) = \xi\mu(r_{12}) + \rho\int_0^{\xi}\int_V u(r_{13})\left[\frac{g^{(3)}(1,2,3,\xi)}{g^{(2)}(1,2,\xi)} - g^{(2)}(1,2,\xi)\right]dr_3\,d\xi$$

$g^{(2)}$ depend on $g^{(3)}$ which depends on $g^{(4)}$, etc.

define $g^{(n)} = e^{-\beta\omega^{(n)}}$

$\omega^{(n)} =$ potential of mean force

$\omega^{(2)}(r_{1,2})$ potential between particles 1 and 2 averaging over interactions of all other atoms/molecules

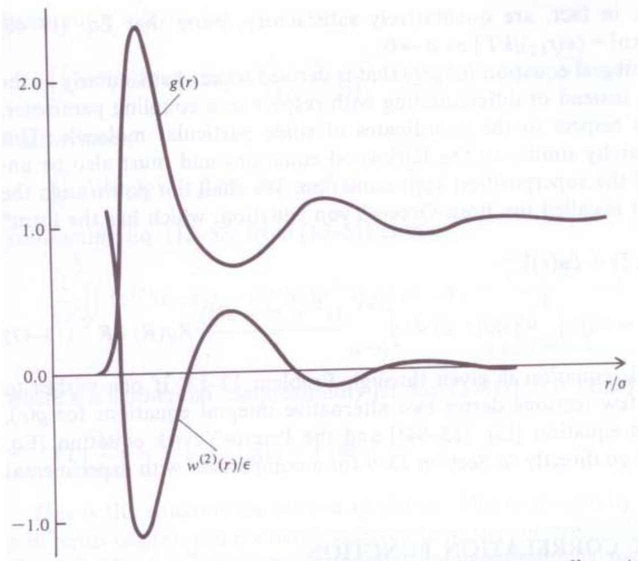

Figure 13–4. **The radial distribution function $g(r)$ and the corresponding potential of mean force $w^{(2)}(r)$ for a dense fluid. Note that $w^{(2)}(r)$ has minima where $g(r)$ has maxima and vice versa.**

$$f_j^{(n)} = -\nabla_j \omega^{(n)}$$

$\omega_j^{(n)}$ is the potential that gives the mean force on *j*
of special interest is $\omega^{(2)} = \omega(r)$

$$\omega(r) \to u(r) \text{ as } \rho \to 0$$

Although hard sphere potential has no attraction, the corresponding potential of mean force does have minima! Resembles $\omega(r)$ of real systems.

Assume $\omega^{(3)}(1,2,3) = \omega^{(2)}(1,2) + \omega^{(2)}(1,3) + \omega^{(2)}(3,3)$

$$\Rightarrow g^{(3)}(1,2,3) = g^{(2)}(1,2)\, g^{(2)}(1,3)\, g^{(2)}(2,3)$$

Plug with Kirkwood equation

$$\underbrace{-kTg(r_{12},\xi) = \xi u(r_{12}) + \rho \int_0^{\xi} \int_V u(r_{13})\, g(r_{13},\xi')\left[g(r_{23})-1\right] dr_3 d\xi'}_{\text{non-linear integral equation}}$$

There are several other integral equations, but we will not pursue these here.