Integral equations and perturbation theories of liquids.

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If you find a mistake, kindly report it to the author :-)

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Summary of thermodynamic functions from $g(r)$

\[
\frac{\mu}{k_B T} = \ln(\rho \Lambda^3) + \frac{\rho}{k_B T} \int_0^1 \int_0^\infty u(r) g(r, \xi) 4\pi r^2 dr d\xi
\]

\[
\frac{E}{Nk_B T} = \frac{3}{2} + \frac{\rho}{2k_B T} \int_0^\infty u(r) g(r, \rho, T) 4\pi r^2 dr
\]

\[
\frac{p}{k_B T} = \rho - \frac{\rho^2}{6V k_B T} \int_0^V \int r \frac{du(r)}{dr} g(r) 4\pi r^2 dr
\]

- We can now express all other thermodynamic functions
- Knowledge of $u(r)$ and $g(r)$ is sufficient to determine them
- At present no exact solution available
- But several very good approximations exist
The Kirkwood integral equation (1930s)

Starting from

\[
\rho^{(n)}(1, 2, \ldots, n; \xi) = \frac{N!}{(N - n)!} \frac{\int \cdots \int e^{-\beta U_N(\xi)} d\mathbf{r}_{n+1} \cdots d\mathbf{r}_N}{Z_N}
\]

where \( \xi \) is the coupling parameter, we express

\[
k_B T \left( \frac{\partial \rho^{(n)}(1, 2, \ldots, n; \xi)}{\partial \xi} \right) = \ldots
\]

after a series of manipulations (see textbook) we arrive at

\[
-k_B T \ln g^{(2)}(1, 2, \xi) = \xi u(r_{12}) +
\]

\[
+ \rho \int_0^\xi \int_V u(r_{13}) \left( \frac{g^{(3)}(1, 2, 3, \xi')}{g^{(2)}(1, 2, \xi')} - g^{(2)}(1, 3, \xi') \right) d\mathbf{r}_3 d\xi'
\]

- Expression for \( g^{(2)}(1, 2, \xi) \) in terms of \( u(\mathbf{r}) \) and \( g^{(3)}(1, 2, 3, \xi) \)
- Hierarchy of integral equations: \( g^{(n)}(1, \ldots, n, \xi) \) in terms of \( g^{(n+1)}(1, \ldots, (n + 1), \xi) \)
Potential of mean force

Let us define a function $w^{(n)}$ as:

$$e^{-\beta w^{(n)}(r_1, \ldots, r_n)} = g^{(n)}(1, \ldots, n) = \frac{\rho^{-n} N!}{(N - n)! Z_N} \int_V e^{-\beta U_N} \, dr_{n+1} \cdots dr_N$$

Then

$$-\nabla_j w^{(n)} = \frac{\int \cdots \int e^{-\beta U_N} (-\nabla_j U_N) \, dr_{n+1} \cdots dr_N}{\int \cdots \int e^{-\beta U_N} \, dr_{n+1} \cdots dr_N}, \quad j = 1, 2, \ldots, n$$

- $f_j^{(n)} = -\nabla_j w^{(n)}$ is the force acting on particle $j$ averaged over the remaining $N - n$ particles
- $w^{(n)}$ is the potential of mean force
- $w^{(2)}(r_{12})$ interaction between two particles at a fixed distance, averaged over all other particles
Example of $w(r)$

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.
Closure for the Kirkwood equation

Superposition approximation – assume pairwise additivity of $w$:

$$w^{(3)}(1, 2, 3) \approx w^{(2)}(1, 2) + w^{(2)}(1, 3) + w^{(2)}(2, 3)$$

This implies

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

The above provides a closure relation to the infinite hierarchy of equations – the Kirkwood equation for $g(r)$:

$$-k_B T \ln g(r_{12}, \xi) = \xi u(r_{12}) + \rho \int_0^\xi \int_V u(r_{13})g(r_{13}, \xi') (g(r_{23}) - 1) \, dr_3 \, d\xi'$$

Note that $\lim_{\rho \to 0} g(r_{12}) = \exp\left(-\beta \xi w(r_{12})\right)$
Other integral equations

Just an overview (derivations lengthy and mathematically involved)

Similar approach to Kirkwood:

- Born-Green-Yvon (BGY), 1930s–1940s

\[- \frac{\partial}{\partial r} \left( k_B T \ln r(r, \xi) + \xi u(r) \right) = \pi \xi \rho \int_0^\infty u'(s) g(s, \xi) ds \int_0^{r+s} \frac{(s^2 + r^2 - R^2)}{r^2 |r-s|} \frac{R g(R) dR}{R} \]

Equations based on direct correlation function:

- Hypernetted Chain (HNC)
- Percus-Yevick (PY)
- Mean spherical approximation (MSA)
Generalization of $\rho^{(n)}$ to open systems

$$\rho^{(n)} = \sum_{N \geq n} \rho^{(n)}_N P_N,$$

$$P_N = \frac{e^{\beta N \mu} Q(N, V, T)}{\Xi(\mu, V, T)} = \frac{z^N Z_N}{N! \Xi}.$$

$$\rho^{(n)}(\mathbf{r}_1, \ldots, \mathbf{r}_n) = \frac{1}{\Xi} \left( z^n e^{-\beta U_n} + \sum_{N=n+1}^{\infty} \frac{z^N}{(N-n)!} \int \cdots \int e^{-\beta U_N} d\mathbf{r}_{n+1} \cdots d\mathbf{r}_N \right).$$

$$\int \cdots \int \rho^{(n)}(\mathbf{r}_1, \ldots, \mathbf{r}_n) d\mathbf{r}_1 \cdots d\mathbf{r}_n = \frac{1}{\Xi} \sum_{N=n+1}^{\infty} \frac{z^N Z_N}{(N-n)!} = \sum_{N=n+1}^{\infty} P_N \frac{N!}{(N-n)!} = \left\langle \frac{N!}{(N-n)!} \right\rangle.$$
The compressibility equation

Integrals of distribution functions take the form of moments:

\[
\int \int \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \, d\mathbf{r}_1 d\mathbf{r}_2 = \langle N(N - 1) \rangle = \bar{N}^2 - \bar{N}
\]

\[
\int \int \rho^{(1)}(\mathbf{r}_1) \rho^{(1)}(\mathbf{r}_2) \, d\mathbf{r}_1 d\mathbf{r}_2 = (\bar{N})^2
\]

Subtracting the two, we arrive at

(Recall Lecture 2: \( \sigma_N^2 / \bar{N} = \rho k_B T \kappa \) with \( \kappa = -\frac{1}{V} (\frac{\partial p}{\partial V})_{N,T} \))

\[
\frac{1}{\rho V} \int \int \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) - \rho^{(1)}(\mathbf{r}_1) \rho^{(1)}(\mathbf{r}_2) \, d\mathbf{r}_1 d\mathbf{r}_2 = \frac{\bar{N}^2 - \bar{N}^2}{\bar{N}} - 1 = \rho k_B T \kappa - 1
\]

Substituting \( g(r) \), we obtain the compressibility equation

\[
k_B T \left( \frac{\partial \rho}{\partial p} \right) = 1 + \rho \int (g(r) - 1) \, d\mathbf{r}
\]

- Does not assume pairwise additive \( U_N(\mathbf{r}) \) (unlike the pressure eq.).
Direct correlation function and OZ equation

- \( h(r_{12}) = (g(r_{12}) - 1) \): total influence of 2 on 1 at separation \( r_{12} \).

- **Ornstein-Zernike (OZ):** split \( h(r_{12}) \) to a direct and indirect term

\[
h(r_{12}) = c(r_{12}) + \rho \int c(r_{13}) h(r_{23}) \, dr_3
\]

- \( c(r_{12}) \) is the **direct correlation function**

- Fourier transform of \( h(r) \) is the **structure factor**:

\[
\int h(r_{12}) e^{i \mathbf{k} \cdot r_{12}} \, dr_1 \, dr_2 = \int c(r_{12}) e^{i \mathbf{k} \cdot r_{12}} \, dr_1 \, dr_2
\]

\[
+ \rho \int \int \int c(r_{13}) h(r_{23}) e^{i \mathbf{k} \cdot r_{12}} \, dr_1 \, dr_2 \, dr_3
\]

- Denote Fourier transform of \( h(r) \) and \( c(r) \) as \( \hat{h}(\mathbf{k}) \) and \( \hat{c}(\mathbf{k}) \):

\[
\hat{h}(\mathbf{k}) = \hat{c}(\mathbf{k}) + \rho \hat{h}(\mathbf{k}) \hat{c}(\mathbf{k})
\]
Direct correlation function and OZ equation

- Ornstein-Zernike (OZ) relation (1914)

\[ \hat{h}(k) = \hat{c}(k) + \rho \hat{h}(k) \hat{c}(k) \quad \stackrel{\rho \neq 0}{\longrightarrow} \quad 1 = \left( 1 + \rho \hat{h}(k) \right) \left( 1 - \rho \hat{c}(k) \right) \]

- Compressibility equation

\[ k_B T \left( \frac{\partial \rho}{\partial p} \right) = 1 + \rho \int (g(r) - 1) \, dr \]

- Compressibility equation in terms of \( c(r) \)

\[ \frac{1}{k_B T} \left( \frac{\partial p}{\partial \rho} \right) = \frac{1}{1 + \rho \int h(r) \, dr} = \frac{1}{1 + \rho \hat{h}(0)} = 1 - \hat{c}(0) \]

\[ = 1 - \rho \int c(r) \, dr \]
Example of $c(r)$

- $c(r)$ is short-ranged
- Integrals with $c(r)$ converge much faster than with $g(r)$

*Figure from McQuarrie: Statistical Mechanics, University Science Books (2000)*
Approximations for $c(r)$ (late 1950s and 1960s)

- Approximations based on $c(r)$ perform better than Kirkwood or BGY
- Hypernetted Chain (HNC) and Percus-Yevick (PY) approximations
- Mean spherical approximation (MSA)
- Analytical solutions for PY for hard spheres ($y$ is packing fraction):

\[
\frac{p}{\rho k_B T} = 1 + 2y + 3y^2 \quad (1 - y)^2
\]

from pressure equation

\[
\frac{p}{\rho k_B T} = 1 + y + y^2 \quad (1 - y)^3
\]

from compressibility equation

- Exact solution would yield the same forms
- All yield correct $B_i$ for $i < 4$, differ in approximations for $i \geq 4$.

*If interested, see textbook for details on PY and HNC equations*
Comparison with simulations – hard spheres

Figure 13–6. (a) Equation of state of hard spheres calculated from the Born-Green-Yvon and Kirkwood integral equations compared with the results of molecular dynamics calculations. $v_0$ is the closest-packing volume, $N\sigma^3/\sqrt{2}$. (b) Equation of state of hard spheres calculated from the HNC and Percus-Yevick integral equations compared with the results of molecular dynamics calculations. (From D. Henderson, *Ann. Rev. Phys. Chem.*, 15, p. 31, 1964.)
Comparison with simulations – Lennard-Jones

Figure 13–10. The compressibility and virial equations of state for the Lennard-Jones 6–12 potential. The BGY, HNC, and PY results are those of D. Levesque (Physica, 32, p. 1985, 1966) and A. A. Broyles et al. (J. Chem. Phys., 37, p. 2462, 1962) and the Monte Carlo results are due to Wood and Parker (J. Chem. Phys., 27, p. 720, 1957).

Figures from McQuarrie: Statistical Mechanics, University Science Books (2000)

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Comparison with simulations – superposition


Figures from McQuarrie: Statistical Mechanics, University Science Books (2000)

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Lecture 8: Integral equations and perturbation theories of liquids.
Comparison with simulations – $g(r)$

Figure 13–11. The radial distribution function from the Percus-Yevick equation for the Lennard-Jones 6–12 potential. (From F. Mandel, R. J. Bearman, and M. Y. Bearman, J. Chem. Phys., 52, p. 3315, 1970.)
Perturbation theories of liquids

Motivation:

1. $g(r)$ of dense real fluids and hard sphere systems are similar.
2. Structure of a dense system is determined by the repulsion (excluded volume).
3. Attractive part of the potential has little effect on the structure.
4. Treat the attraction as a perturbation to the reference system.
5. As a reference choose a well understood system.
6. Develop approximations for the perturbation
7. Approximations more straightforward than in the integral equations
8. Van der Waals equation as one special case
Background of the perturbation theories

- Zwanzig (1954)
- Total potential = reference + perturbation

\[ U_N = U_N^{(0)} + U_N^{(1)} \]

\[ Z_N = \int \cdots \int e^{-\beta(U_N^{(0)} + U_N^{(1)})} \, d\mathbf{r}_1 \cdots d\mathbf{r}_N \]

\[ = \int \cdots \int e^{-\beta U_N^{(0)}} \, d\mathbf{r}_1 \cdots d\mathbf{r}_N \int \cdots \int e^{-\beta U_N^{(1)}} \, d\mathbf{r}_1 \cdots d\mathbf{r}_N \]

\[ = Z_N^{(0)} \langle e^{-\beta U_N^{(1)}} \rangle_{(0)} \]

- Expand the exponential

\[ \langle e^{-\beta U_N^{(1)}} \rangle_{(0)} = 1 - \beta \langle U_N^{(1)} \rangle_{(0)} + \frac{\beta^2}{2!} \langle U_N^{(1)} \rangle_{(0)}^2 + \cdots \]

\[ \langle \cdots \rangle_0 \] denotes average in the reference (unperturbed) system
Background of the perturbation theories

- **Helmholtz free energy**

  \[ A = -k_B T \ln Q, \quad Q = Z_N/(N!\Lambda^{3N}) \]

  \[-\beta A = \ln \left( \frac{Z_N^{(0)}}{N!\Lambda^{3N}} \right) + \ln \left\langle e^{-\beta U_N^{(1)}} \right\rangle_{(0)} + \cdots = -\beta A_0 - \beta A^{(1)} + \cdots\]

- **Perturbation (excess) free energy**

  \[ A^{(1)} = -k_B T \ln \left\langle e^{-\beta U_N^{(1)}} \right\rangle_{(0)} \]

- **Express** \( A^{(1)} \) **as a power series in** \( \beta \):

  \[ A^{(1)} = \sum_{n=1}^{\infty} \frac{\omega_n}{n!} (-\beta)^{n-1}, \quad \exp(-\beta A^{(1)}) = \exp \left( \sum_{n=1}^{\infty} \frac{\omega_n}{n!} (-\beta)^{n-1} \right) \]

  \[ e^{-\beta A^{(1)}} = \left\langle e^{-\beta U_N^{(1)}} \right\rangle_{(0)} = \sum_{k=0}^{\infty} \frac{-\beta^k}{k!} \left\langle U_N^{(1)k} \right\rangle_{(0)} \]
Background of the perturbation theories

Compare the expansions in powers of $\beta$ of

$$\exp\left(\sum_{n=1}^{\infty} \frac{\omega_n}{n!} (-\beta)^{n-1}\right) \quad \text{and} \quad \langle \exp(-\beta U_N^{(1)}) \rangle_{(0)}$$

and collect the coefficients before like powers of $\beta^n$ to obtain

$$\omega_1 = \langle U_N^{(1)} \rangle_{(0)}$$

$$\omega_2 = \langle (U_N^{(1)})^2 \rangle_{(0)} - \langle U_N^{(1)} \rangle_{(0)}^2$$

$$\omega_3 = \langle (U_N^{(1)})^3 \rangle_{(0)} - 3 \langle (U_N^{(1)})^2 \rangle_{(0)} \langle U_N^{(1)} \rangle_{(0)}^2 - \langle U_N^{(1)} \rangle_{(0)}^3$$

To the second order we have

$$A^{(1)} = \omega_1 + \frac{\beta \omega_2}{2} + O(\beta^2) \approx \langle U_N^{(1)} \rangle_{(0)} + \frac{\beta}{2} \left( \langle (U_N^{(1)})^2 \rangle_{(0)} - \langle U_N^{(1)} \rangle_{(0)}^2 \right)$$
Background of the perturbation theories

For pairwise additive $U^{(1)}_N$:

$$U^{(1)}_N = \sum_{i<j} u^{(1)}(r_{ij})$$

$$\omega_1 = \left\langle U^{(1)}_N \right\rangle_0 = \left\langle \sum_{i<j} u^{(1)}(r_{ij}) \right\rangle_0 = \frac{N(N-1)}{2} \left\langle u^{(1)}(r_{12}) \right\rangle_0$$

$$= \frac{N(N-1)}{2} \frac{1}{Z^{(0)}_N} \int \cdots \int e^{\beta U^{(0)}_N} u^{(1)}(r_{12}) dr_1 \cdots dr_N$$

$$= \frac{1}{2} \int \int \frac{u^{(1)}(r_{12})}{V} \rho^{(2)}_0(r_{12}) dr_1 dr_2$$

$$= \frac{\rho^2 V}{2} \int g^{(2)}_0(r_{12}) dr_{12}$$

• Higher order $\omega_n$ are awkward because they require $\rho^{(3)}$ and $\rho^{(4)}$
The Van der Waals equation

- Take a hard sphere fluid as a reference system

\[ Z_N = Z_N^{(0)} \langle e^{-\beta U_N^{(1)}} \rangle_0 \]

- Assume pairwise additive \( u(r) = u^{\text{HS}}(r) + u^{(1)}(r) \)
- Where \( u^{(1)}(r) \) is an arbitrary attractive potential
- Assume \( \beta U_N^{(1)}(r) \) small enough so that

\[ \langle e^{-\beta U_N^{(1)}} \rangle_0 \approx 1 - \beta \langle U_N^{(1)} \rangle_0 \approx \exp \langle -\beta U_N^{(1)} \rangle_0 \]

- Neglect terms \( \mathcal{O}(\beta^2) \) and higher
- We then obtain for \( \langle U_N^{(1)} \rangle_0 \):

\[ \langle U_N^{(1)} \rangle_0 = \frac{\rho^2 V}{2} \int_0^\infty u^{(1)}(r) g^{\text{HS}}(r) 4\pi r^2 dr \]
The Van der Waals equation

- Assume $g^{HS}(r)$ takes the form

$$g^{HS}(r) = \begin{cases} 0 & \text{for } r < \sigma \\ 1 & \text{for } r > \sigma \end{cases}$$

- The expression for $\langle U^{(1)}_N \rangle_0$ then evaluates to

$$\langle U^{(1)}_N \rangle_0 = \frac{\rho^2 V}{2} \int_{\sigma}^{\infty} u^{(1)}(r) 4\pi r^2 \, dr = -aN \rho$$

where

$$a = -2\pi \int_{\sigma}^{\infty} u^{(1)}(r) 4\pi r^2 \, dr$$

$$Z_N = Z_N^{(0)} e^{\beta a \rho N}$$
The Van der Waals equation

- For pressure we then obtain

\[
\frac{p}{k_B T} = \left( \frac{\partial \ln Z_N}{\partial V} \right)_{N,T} = \left( \frac{\partial \ln Z_N^{(0)}}{\partial V} \right)_{N,T} - \frac{a \rho^2}{k_B T} = \frac{p^{(0)}}{k_B T} - \frac{a \rho^2}{k_B T}
\]

- Last assumption:

\[
Z_N^{(0)} = V_{\text{eff}}^N = (V - Nb)^N \quad \text{where} \quad b = \frac{1}{2} \frac{4\pi \sigma^3}{3} = \frac{2\pi \sigma^3}{3}
\]

- Substituting for \( Z_N^{(0)} \) we obtain the Van der Waals equation

\[
\frac{p}{k_B T} = \frac{\rho}{1 - b \rho} - \frac{a \rho^2}{k_B T}
\]
Remarks on the Van der Waals equation

- Parameters $a$ and $b$ obtained from a square well potential disagree with those obtained empirically.
- Assumptions on $g(r)$ and $Z_N^{(0)}$ are very rough.
- Nevertheless, it indicates critical point and condensation within a rudimentary model.
- Also PY and other integral equations possess this feature but require much more involved treatment.
- Straightforward routes for further improvements:
  - Better $g(r)$ – integral equations, Padé approximants, simulations, . . .
  - Better approximation to $Z_N^{(0)}$ – same as above.
  - More realistic $u(r)$ and $u^{(0)}(r)$ – needs good knowledge of $g^{(0)}(r)$.
  - Higher terms in $\beta$ – needs three- and four-body distribution functions.
Barker-Henderson perturbation theory (1960s–1970s)

- Higher terms in $\beta$
- HS and also 6-12 fluids
- Approximation to higher order distribution functions
- Macroscopic compressibility approximation

$$\frac{A}{Nk_B T} = \frac{A_0}{Nk_B T} + \frac{\beta \rho}{2} \int u^{(1)}(r) g_0(r) 4\pi r^2 dr$$
\[ - \frac{\beta^2 \rho}{4} \int (u^{(1)}(r))^2 k_B T \left( \frac{\partial \rho}{\partial p} \right) g_0(r) 4\pi r^2 dr + \mathcal{O}(\beta^3) \]

- Local compressibility approximation

$$\frac{A}{Nk_B T} = \frac{A_0}{Nk_B T} + \frac{\beta \rho}{2} \int u^{(1)}(r) g_0(r) 4\pi r^2 dr$$
\[ - \frac{\beta^2 \rho}{4} \int (u^{(1)}(r))^2 k_B T \left( \frac{\partial}{\partial p} \rho g_0(r) \right) 4\pi r^2 dr + \mathcal{O}(\beta^3) \]
Weeks-Chandler-Andersen (WCA) theory (1970s)

- For Lennard-Jones 6-12 fluids
- Barker-Henderson: repulsive core at $r < \sigma$, attractive well at $r > \sigma$
- WCA: repulsive force at $r < 2^{1/6}\sigma$, attractive force at $r > 2^{1/6}\sigma$

$$u_0(r) = \begin{cases} 
  u(r) + \varepsilon & \text{for } r < 2^{1/6}\sigma \\
  0 & \text{for } r > 2^{1/6}\sigma 
\end{cases}$$

$$u^{(1)}(r) = \begin{cases} 
  -\varepsilon & \text{for } r < 2^{1/6}\sigma \\
  u(r) & \text{for } r > 2^{1/6}\sigma 
\end{cases}$$
Weeks-Chandler-Andersen (WCA) theory (1970s)

- **Excess** free energy with respect to the ideal gas
  \[
  \frac{\Delta A}{Nk_B T} = \frac{\Delta A_0}{Nk_B T} + \frac{\beta \rho}{2} \int u^{(1)}(r) g_0(r) 4\pi r^2 \, dr
  \]

- **Problem:** \(g_0(r)\) not well known

- **Solution:** assign an effective hard-sphere diameter \(d\)
  \[g_0(r) \approx y_d(r) e^{-\beta u_0(r)} \quad \text{where} \quad y(r) = e^{\beta u(r)} g(r)\]

- Shape of \(y(r)\) is rather insensitive to details of the potential

- Use the compressibility equation to select \(d\) such that compressibilities of the two systems are equal
  \[
  \frac{1}{\beta} \left( \frac{\partial \rho}{\partial p} \right)_\beta = 1 + \rho \int (g(r) - 1) \, dr
  \]

  \[
  \int (y_d e^{-\beta u_0} - 1) \, dr = \int (y_d e^{-\beta u_d} - 1) \, dr
  \]
Summary of perturbation theories

- Unlike all previous approaches, perturbation theories improve with increasing density.
- Excellent agreement at high density and near critical point.
- WCA lacks a universal reference state but converges rapidly.
- BH possesses a universal reference state but requires higher order terms in $\beta$.
- Very good for short-ranged realistic potentials.
- Similar to previous, they fail for long-ranged potentials like Coulomb.
Comparison with experiment/simulation

Figure 14–3. The equation of state for the 6–12 potential according to Barker and Henderson. The curves are labeled by the value of $T^*$. The points are a mixture of machine calculations and actual experimental data. (From J. A. Barker and D. Henderson, J. Chem. Phys., 47, p. 4714, 1967.)
Figure 14-5. Densities of coexisting phases for the 6-12 potential according to Barker and Henderson. The points are a mixture of machine calculations and actual experimental data. (From J. A. Barker and D. Henderson, *J. Chem. Phys.*, 47, p. 4714, 1967.)
Comparison with experiment/simulation

Figure 14–10. Plot of $h(k)$ for $\rho^* = 0.844$, $T^* = 0.723$. The line represents the use of Eq. (14–36); the circles are the molecular dynamics results of Verlet. (From J. D. Weeks, D. Chandler, and H. C. Andersen, *J Chem. Phys.* 54, p. 5237, 1971.)

Figure from McQuarrie: Statistical Mechanics, University Science Books (2000)