Correlations in Fluids

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The effects of intermolecular interactions upon the mechanical and thermal equations of state are studied for classical fluids. The temperature dependence of the second virial coefficient, which governs these effects for dilute systems, is derived for realistic potentials and explained using a model from which one can also derive the van der Waals equation. Next we discuss the measurement of the pair correlation function in denser systems using X-ray or neutron scattering. Finally, the relationship between correlations and density fluctuations is developed.

Classical configurational partition function

If we assume that the classical Hamiltonian for a system of N identical particles can be separated into kinetic, potential, and internal contributions of the form

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \mathcal{U}[\vec{r}_1 \cdots \vec{r}_N] + H_{\text{int}}$$

where $\mathcal{U}$ depends only on the particle positions and H_{int} depends only on internal degrees of freedom, then the classical partition function

$$Z = Z_p Z_r Z_{\text{int}}$$

can be expressed in terms of three independent factors where $Z_p = \lambda_B^{-3N}$ pertains to the kinetic energy, Z_{int} governs (unspecified) internal excitations, and

$$Z_r = \int \frac{d^{3N} r}{N!} e^{-\beta \mathcal{U}}$$

is the spatial or *configurational* partition function. The factor $(N!)^{-1}$ is based upon the Gibbs prescription for permutation symmetry among identical particles and is only valid in the limit of small quantum concentration. The notation

$$d^{3N} r = \prod_{i=1}^{N} d^3 r_i$$

indicates a $3N$ dimensional volume in configuration space. The canonical probability that particles are found within such a volume at the positions $\{\vec{r}_1 \cdots \vec{r}_N\}$ is then

$$\rho_N[\vec{r}_1 \cdots \vec{r}_N] \, d^{3N} r \; = \; \frac{\text{Exp}[-\beta \, \mathcal{U}[\vec{r}_1 \cdots \vec{r}_N]]}{Z_r} \; \frac{d^{3N} r}{N!}$$

and is normalized to unity according to

$$\int d^{3N} r \, \rho_N[\vec{r}_1 \cdots \vec{r}_N] \; = \; 1$$

The potential energy $\mathcal{U}$ must be invariant with respect to permutations of the particle labels because one cannot distinguish between identical particles. Thus, the N-particle density ρ_N requires only that particles are near the specified locations and is also invariant with respect to permutations of labels.

Suppose that we seek to evaluate the ensemble average of a single-particle function of position democratically summed over indistinguishable particles according to

$$\hat{A}_1 \; = \; \sum_{i=1}^{N} A_1[\vec{r}_i]$$

The ensemble average is obtained from the configurational probability distribution following the usual procedure, whereby

$$\langle \hat{A}_1 \rangle \; = \; \int d^{3N} r \, \rho_N \, \hat{A}_1 \; = \; \sum_{i=1}^{N} \int d^{3N} r \, \rho_N[\vec{r}_1 \cdots \vec{r}_N] \, A_1[\vec{r}_i]$$

Due to the permutation symmetry of ρ_N, the sum contains N identical terms such that

$$\langle \hat{A}_1 \rangle \; = \; \int d^3 r \, \rho_1[\vec{r}] \, A_1[\vec{r}]$$

where

$$\rho_1[\vec{r}_1] \; = \; N \int d^{3(N-1)} r \, \rho_N \; = \; N \int \prod_{i=2}^{N} d^3 r_i \; \rho_N[\vec{r}_1 \cdots \vec{r}_N]$$

is the single-particle density distribution obtained by integrating over the coordinates of $N-1$ particles. The average number of particles per unit volume found at $\vec{r}$ is given by $\rho_1[\vec{r}] \, d^3 r$, which may also be obtained as an ensemble average of the $\sum_i \delta[\vec{r} - \vec{r}_i]$, such that

$$\rho_1[\vec{r}] \; = \; \left\langle \sum_{i=1}^{N} \delta[\vec{r} - \vec{r}_i] \right\rangle \; = \; \sum_{i=1}^{N} \int d^{3N} r \, \rho_N[\vec{r}_1 \cdots \vec{r}_N] \, \delta[\vec{r} - \vec{r}_i] \; = \; N \int \prod_{i=2}^{N} d^3 r_i \; \rho_N[\vec{r}, \, \vec{r}_2 \cdots \vec{r}_N]$$

Each delta function in the summation asks whether particle i is at position $\vec{r}$ and the integration over $d^3 r_i \, \rho_N$ returns the probability that it is within volume $d^3 r$. Therefore, summation over N identical particles produces the average number of particles per unit volume at $\vec{r}$.

Similarly, a two-particle function of position summed over all pairs of particles takes the form

$$\hat{A}_2 = \frac{1}{2} \sum_{i,j \neq i} A_2[\vec{r}_i, \vec{r}_j] \; = \; \sum_{i,j<i} A_2[\vec{r}_i, \vec{r}_j]$$

The ensemble average of a two-particle function then becomes

$$\langle \hat{A}_2 \rangle = \int d^{3N} r \, \rho_N \, \hat{A}_2 =$$

$$\frac{1}{2} \sum_{i,j\neq i} \int d^{3N} r \, \rho_N[\vec{r}_1 \cdots \vec{r}_N] \, A_2[\vec{r}_i, \vec{r}_j] = \frac{N(N-1)}{2} \int d^3 r_1 \, d^3 r_2 \, A_2[\vec{r}_1, \vec{r}_2] \prod_{i=3}^{N} d^3 r_i \, \rho_N[\vec{r}_1 \cdots \vec{r}_N]$$

and can be expressed in terms of the two-particle density

$$\rho_2[\vec{r}, \vec{r}\,'] = \left\langle \sum_{i,j\neq i} \delta[\vec{r} - \vec{r}_i] \, \delta[\vec{r}\,' - \vec{r}_i] \right\rangle = N(N-1) \int \prod_{i=3}^{N} d^3 r_i \, \rho_N[\vec{r}, \vec{r}\,', \vec{r}_3 \cdots \vec{r}_N]$$

as

$$\langle \hat{A}_2 \rangle = \frac{1}{2} \int d^3 r \, d^3 r' \, \rho_2[\vec{r}, \vec{r}\,'] \, A_2[\vec{r}, \vec{r}\,']$$

The factor $N(N-1)$ arises because there are N equivalent choices of the first particle and $N-1$ equivalent choices of the second.

This procedure can obviously be extended to n-particle densities by defining

$$\rho_n[\vec{r}_1 \cdots \vec{r}_n] = \frac{N!}{(N-n)!} \left\langle \prod_{i=1}^{n} \delta[\vec{r}_i - \vec{r}_i\,'] \right\rangle = \frac{N!}{(N-n)!} \int d^{3(N-n)} r \, \rho_N[\vec{r}_1 \cdots \vec{r}_N]$$

such that

$$\hat{A}_n = \frac{1}{n!} \sum_{\text{clusters}} A_n[\vec{r}_1 \cdots \vec{r}_n] \implies \langle \hat{A}_n \rangle = \frac{1}{n!} \int d^{3n} r \, \rho_n[\vec{r}_1 \cdots \vec{r}_n] \, A_n[\vec{r}_1 \cdots \vec{r}_n]$$

where $\hat{A}_n$ includes all n-particle clusters and where the notations

$$d^{3(N-n)} r \equiv \prod_{i=n+1}^{N} d^3 r_i \qquad d^{3n} r \equiv \prod_{i=1}^{n} d^3 r_i$$

divide the configuration space into participants and spectators. The N-particle density is thus seen to be the same as the configurational probability distribution,

$$\rho_N[\vec{r}_1 \cdots \vec{r}_N] = \left\langle \prod_{i=1}^{N} \delta[\vec{r}_i - \vec{r}_i\,'] \right\rangle$$

and the n-particle densities, ρ_n for $n < N$, may be called reduced distribution functions. These functions are invariant with respect to permutations of their arguments and are normalized to the total number of n-particle clusters, such that

$$\int d^{3n} r \, \rho_n[\vec{r}_1 \cdots \vec{r}_n] = \frac{N!}{(N-n)!}$$

There is also a useful relationship between ρ_{n-1} and ρ_n

$$\int d^3 r_n \, \rho_n[\vec{r}_1 \cdots \vec{r}_n] = (N-n+1) \, \rho_{n-1}[\vec{r}_1 \cdots \vec{r}_{n-1}]$$

which takes the form

$$\int d^3 r_2 \, \rho_2[\vec{r}_1, \vec{r}_2] \; = \; (N-1) \, \rho_1[\vec{r}_1]$$

$$\int d^3 r_1 \, d^3 r_2 \, \rho_2[\vec{r}_1, \vec{r}_2] \; = \; N \, (N-1)$$

for these important special cases.

To understand the physical meaning of n-particle densities, we consider again the two-particle density as an ensemble average of a product of density operators

$$\rho_2[\vec{r}, \vec{r}'] \; = \; \left\langle \sum_{i, j \neq i} \delta[\vec{r} - \vec{r}_i] \, \delta[\vec{r}' - \vec{r}_j] \right\rangle$$

Thus, $\rho_2[\vec{r}, \vec{r}'] \, d^3 r \, d^3 r'$ is the product of the numbers of particles simultaneously at $\vec{r}$ and $\vec{r}'$ within volumes $d^3 r$ and $d^3 r'$. Since the average number of particles per unit volume at $\vec{r}$ is simply $\rho_1[\vec{r}]$, we can interpret $(\rho_2[\vec{r}, \vec{r}'] / \rho_1[\vec{r}]) \, d^3 r'$ as the average number of particles within volume $d^3 r'$ at $\vec{r}'$ given that we know that there already is a particle at $\vec{r}$. Therefore, the ratio $\rho_2[\vec{r}, \vec{r}'] / \rho_1[\vec{r}]$ is a measure of the spatial correlations within the system or, in other words, the influence of a particle upon the distribution of its neighbors. Since these distributions are democratic (invariant wrt permutations), we can define a pair distribution function $g_2[\vec{r}, \vec{r}']$ by

$$\rho_2[\vec{r}, \vec{r}'] = \rho_1[\vec{r}] \, \rho_1[\vec{r}'] \, g_2[\vec{r}, \vec{r}']$$

In the absence of correlations, the presence of one particle does not affect the distributions of its neighbors, so that one expects $g_2[\vec{r}, \vec{r}'] \to 1$ without correlations. Furthermore, on physical grounds we do not expect spatial correlations to persist to very large distances, at least in classical fluids, so that

$$|\vec{r} - \vec{r}'| \to \infty \implies g_2[\vec{r}, \vec{r}'] \to 1$$

for separations large compared with the interaction range. (Crystals possess long-range order and do not share this property.) Finally, for a homogeneous isotropic system we expect

$$\text{homogeneous} \implies \rho_1[\vec{r}] = \frac{N}{V}$$
$$\text{isotropic} \implies g_2[\vec{r}, \vec{r}'] = g[\, |\vec{r} - \vec{r}'| \,]$$
$$\text{homogeneous \& isotropic} \implies \rho_2[\vec{r}, \vec{r}'] = \left(\frac{N}{V}\right)^2 g[\, |\vec{r} - \vec{r}'| \,]$$

Our normalization conventions then require

$$\int d^3 s \, g[s] \; = \; \frac{N-1}{N} \, V$$

which reduces to the volume in the thermodynamic limit ($N \gg 1$).

Suppose that the configurational potential energy consists of pairwise interactions, such that

$$\mathcal{U} = \frac{1}{2} \sum_{i, j \neq i} v_{i,j} \implies \langle \mathcal{U} \rangle = \frac{1}{2} \int d^3 r \, d^3 r' \, \rho_2[\vec{r}, \vec{r}'] \, v[\vec{r}, \vec{r}']$$

For a homogeneous isotropic system we would then obtain

$$\langle \mathcal{U} \rangle = \frac{N^2}{2 \, V} \int d^3 s \, g[s] \, v[s] \; = \; 2 \pi \frac{N^2}{V} \int ds \, s^2 \, g[s] \, v[s]$$

where $s = |\vec{r} - \vec{r}'|$ is the separation between a pair of interacting particles. Since the mean kinetic energy is given by the equipartition theorem, we can evaluate the internal energy of a nonideal gas as

$$\langle H \rangle = \frac{3}{2} N k_B T + \langle H_{\text{int}} \rangle + 2\pi \frac{N^2}{V} \int ds\, s^2\, g[s]\, v[s]$$

The isochoric heat capacity is then

$$C_V = \frac{3}{2} N k_B + \frac{\partial}{\partial T} \langle H_{\text{int}} \rangle + 2\pi \frac{N^2}{V} \int ds\, s^2\, \frac{\partial g}{\partial T}\, v[s]$$

where we must recognize that $g[s]$ depends implicitly upon both temperature and density.

In the absence of correlations we would find

$$g[s] \to 1 \implies \langle \mathcal{U} \rangle = 2\pi \frac{N^2}{V} \int ds\, s^2\, v[s]$$

such that the mean potential energy per particle is proportional to density and to the volume integral of the pair potential. To obtain a more realistic estimate, we must consider the correlations produced by the pair potential even for dilute systems. The interatomic potential for simple monatomic gases typically features a strong short-range potential followed by a modest longer-range attractive tail. Since the probability that two particles will be found within the repulsive core is small, a better approximation to the pair distribution function is $g[r] = \Theta[r - r_c]$ where r_c is the range of the repulsive core and where the truth function $\Theta[x]$ is defined to be unity for $x > 0$ and zero otherwise. Under these circumstances

$$g[s] = \Theta[r - r_c] \implies \langle \mathcal{U} \rangle = 2\pi \frac{N^2}{V} \int_{r_c}^{\infty} ds\, s^2\, v[s]$$

we find that the mean potential energy per particle is proportional to density and to the volume integral of the attractive part of the pair potential. We will soon show that an even better estimate of pair distribution function is provided by a Boltzmann factor based upon the pair potential energy, such that

$$\frac{N}{V} \text{ small} \implies g[s] \approx e^{-\beta v[s]} \implies C_V \approx \frac{3}{2} N k_B + 2\pi \frac{N^2}{k_B T^2 V} \int ds\, s^2\, e^{-\beta v}\, v^2$$

or

$$C_V \approx \frac{3}{2} N k_B \left(1 + \frac{N}{V} \beta^2 \frac{4\pi}{3} \int ds\, s^2\, e^{-\beta v}\, v^2 \right)$$

for structureless ($H_{\text{int}} = 0$) atoms. For higher densities we must include the effect of multiparticle clusters also.

Virial equation of state

Consider a collection of particles confined to finite volume by strong forces $\vec{F}_i^{\text{wall}}$ near the walls of their container and suppose that their mutual interactions are pairwise forces $\vec{F}_{i,j}$ such that

$$\vec{F}_i = \vec{F}_i^{\text{wall}} + \sum_{j \neq i} \vec{F}_{i,j} = \vec{F}_i^{\text{wall}} - \sum_{j \neq i} \vec{\nabla} v[\,|\vec{r}_i - \vec{r}_j|\,]$$

is the net forces acting on particle i and $v[\,|\vec{r}_i - \vec{r}_j\,|\,]$ is an intermolecular potential that depends upon the separation between two particle. According to the virial theorem , the ensemble average of Clausius virial for nonrelativistic particles is related to temperature by

$$\left\langle \sum_i \vec{r}_i \cdot \vec{F}_i \right\rangle = -3\,N\,k_B\,T$$

The pressure p exerted by the wall upon the fluid is produced by forces acting at the surface of the container, such that

$$\left\langle \sum_i \vec{r}_i \cdot \vec{F}_i^{\text{wall}} \right\rangle = -p \int d\vec{A} \cdot \vec{r} = -3\,p\,V$$

where $d\vec{A}$ is an outward element of surface area and $\vec{r}$ is the coordinate vector for a particle at the surface of the container. Assuming that the system is homogeneous and isotropic, the contribution to the Clausius virial by pairwise forces becomes

$$\left\langle \sum_{j \ne i} \vec{r}_i \cdot \vec{F}_{i,j} \right\rangle = -\frac{1}{2}\left(\frac{N}{V}\right)^2 \int d^3r_1\, d^3r_2\, g[s]\, s\, \frac{\partial v}{\partial s} = -2\,\pi\,\frac{N^2}{V} \int ds\, s^3\, g[s]\, \frac{\partial v}{\partial s}$$

where $s = |\vec{r} - \vec{r}'\,|$ is the separation between a pair of interacting particles, $\frac{1}{2}\,N(N-1) \approx \frac{1}{2}\,N^2$ is the number of pairs, and $g[s]$ is the pair correlation function. Combining these two contributions, the mechanical equation of state becomes

$$p\,V = N\,k_B\,T - \frac{2\,\pi}{3}\,\frac{N^2}{V} \int ds\, s^3\, g[s]\, \frac{\partial v}{\partial s}$$

where the effect of pairwise interactions depends upon the pair correlation function and the intermolecular potential. Of course, the pair correlation function also depends implicitly upon both density and temperature.

The mechanical equation of state for a nonideal gas can be represented as an expansion in powers of the density which takes the form

$$\frac{p\,V}{N\,k_B\,T} = 1 + \sum_{k=2}^{\infty} B_k[T]\left(\frac{N}{V}\right)^{k-1} \implies \frac{p}{k_B\,T} = \sum_{k=1}^{\infty} B_k[T]\left(\frac{N}{V}\right)^{k}$$

where $B_1 \equiv 1$ and $B_k[T]$ for $k \ge 2$ are called *virial coefficients*. Recognizing that $p = -\left(\frac{\partial F}{\partial V}\right)_T$, we can express $F[T, V]$ as an expansion of the form

$$F = F_0 + N\,k_B\,T \sum_{k=2}^{\infty} \frac{B_k[T]}{k-1}\left(\frac{N}{V}\right)^{k-1}$$

where F_0 is the free energy for an ideal gas. Similarly, using $C_V = \left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_v = -T\left(\frac{\partial^2 F}{\partial T^2}\right)_V$, we find

$$U = U_0 - N\,k_B\,T^2 \sum_{k=2}^{\infty} \frac{1}{k-1}\left(\frac{N}{V}\right)^{k-1} \frac{\partial B_k[T]}{\partial T}$$

$$C_V = C_{V,0} - N\,k_B\,T \sum_{k=2}^{\infty} \frac{1}{k-1}\left(\frac{N}{V}\right)^{k-1} \frac{\partial^2\,(T\,B_k[T])}{\partial T^2}$$

where U_0 and $C_{V,0}$ are the internal energy and heat capacity of an ideal gas in the limit $\frac{N}{V} \to 0$. For structureless monatomic gases $U_0 = \frac{3}{2}\,N\,k_B\,T$ and $C_{V,0} = \frac{3}{2}\,N\,k_B$, but larger values are obtained for gases with internal structure even when

dilute enough to neglect intermolecular interactions. Empirical values for the temperature dependence of the lowest few virial coefficients can be extracted from measurements of the mechanical and thermal response functions.

If we truncate the virial expansion at B_2, the mechanical response functions become

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{1}{T}\frac{1 + \frac{N}{V}\frac{d(T\,B_2)}{dT}}{1 + 2\,B_2\,\frac{N}{V}} \approx \frac{1}{T}\left(1 - \frac{N}{V}\,T^2\,\frac{d}{dT}\left(\frac{B_2}{T}\right) + \cdots\right)$$

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = \frac{V}{N\,k_B\,T}\left(1 + 2\,B_2\,\frac{N}{V}\right)^{-1} \approx \frac{V}{N\,k_B\,T}\left(1 - 2\,B_2\,\frac{N}{V} + \cdots\right)$$

after some straightforward algebra. Finally, the difference between principal heat capacities reduces to

$$C_p - C_V = V\,T\,\frac{\alpha^2}{\kappa_T} = N\,k_B\,\frac{\left(1 + \frac{N}{V}\frac{d(T\,B_2)}{dT}\right)^2}{\left(1 + 2\,\frac{N}{V}\,B_2[T]\right)} \approx N\,k_B\left(1 + 2\,\frac{N}{V}\,T\,B_2'[T]\right)$$

For very dilute systems,

$$g[s] \to 1 \implies p\,V \to N\,k_B\,T + 2\,\pi\,\frac{N^2}{V}\int ds\,s^2\,v[s] \implies B_2[T] \to \frac{2\,\pi}{k_B\,T}\int ds\,s^2\,v[s]$$

the second virial coefficient is proportional to the volume integral of the potential and inversely proportional to temperature. If the potential is attractive overall, such that its volume integral is negative, then B_2 is negative for dilute systems and becomes large for small temperatures. Under these conditions one finds

$$g[s] \to 1 \implies C_V \to C_{V,0}$$

$$B_2 \propto T^{-1} \implies T\,B_2' = -B_2 \implies C_p - C_V = N\,k_B\left(1 - 2\,\frac{N}{V}\,B_2\right)$$

Thus, C_V is insensitive to the intermolecular potential, but C_p is increased for attractive potentials by a term that is proportional to density and inversely proportional to temperature. However, denser systems with nontrivial correlations are sensitive to more detailed properties of the potential. These properties in turn affect the correlation function in a temperature-dependent manner. Thus, the central problem is computation of the temperature and density dependence of the pair correlation function for systems at finite density.

Classical configurational partition function for dilute systems

Consider a classical system of N particles with pairwise interactions for which the configurational partition function becomes

$$\mathcal{U} = \frac{1}{2}\sum_{i,j\neq i} v_{i,j} \implies Z_r = \frac{1}{N!}\int d^{3N}r\prod_{i,j<i} e^{-\beta\,v_{i,j}}$$

In the ideal-gas limit, $v_{i,j} = 0 \implies Z_r = V^N/N!$. For dilute systems the mean separation is large where $v_{i,j}$ is small. Hence, we can evaluate the effect of interactions using an expansion in terms of the *Mayer function*, $f_{i,j}$, defined as

$$f_{i,j} = e^{-\beta\,v_{i,j}} - 1 \implies Z_r = \frac{1}{N!}\int d^{3N}r\prod_{i,j<i}(1 + f_{i,j})$$

where for dilute systems the assumption $f_{i,j} \ll 1$ yields

$$f_{i,j} \ll 1 \implies Z_r = \frac{1}{N!} \int d^{3N} r \left(1 + \sum_{i,j<i} f_{i,j} + \cdots \right) = \frac{1}{N!} \left(V^N + \frac{N(N-1)}{2} V^{N-2} \int d^3 r_1 \, d^3 r_2 \, f_{1,2} + \cdots \right)$$

The first-order term describes the contribution of an interacting pair of particles while higher order terms describe one or more clusters with two or more particles per cluster. Although it is possible to develop a systematic *cluster expansion*, in this section we will be content with the first-order density-dependent correction to equation of state for imperfect gases. Therefore, the configurational partition function for dilute systems reduces to

$$Z_r = \frac{V^N}{N!} \left(1 + \frac{N(N-1)}{2 V^2} \int d^3 r_1 \, d^3 r_2 \, f_{1,2} + \cdots \right)$$

Finally, assuming that $v[\vec{r}_1, \vec{r}_2] = v[\,|\,\vec{r}_1 - \vec{r}_2\,|\,] = v[s]$ and $N(N-1) \approx N^2$ we obtain

$$Z_r \approx \frac{V^N}{N!} \left(1 + 2\pi \frac{N^2}{V} \int ds \, s^2 \, (e^{-\beta v[s]} - 1) \right)$$

to lowest order in the interaction. Higher-order corrections arising from n-particle clusters and described by terms with $n-1$ factors of $f_{i,j}$ will be developed in a separate section.

A typical intermolecular potential features a strong short-ranged repulsive core followed by a weak long-ranged attractive well. A useful parametrization is the *Lennard-Jones potential*

$$v[r] = v_0 \left(\left(\frac{r_0}{r} \right)^{12} - 2 \left(\frac{r_0}{r} \right)^6 \right)$$

where v_0 is the maximum depth of the attractive well at r_0. The long-ranged tail with asymptotic behavior r^{-6} is motivated by the van der Waals force between mutually induced electronic dipole moments while the r^{-12} repulsive core is a convenient and fairly realistic description of the repulsion between overlapping electron distributions. The figure below illustrates this potential and the corresponding Mayer function for a couple of temperatures. For a hard core, $v \to \infty \implies f \to -1$, the value $f \approx -1$ reflects the anticorrelation which keeps the molecules apart. Where the interaction is attractive there is a mild positive correlation that reflects the tendency of particles to spend more time near the potential minimum. At large distances the interaction becomes ineffective and the correlation between them vanishes. At high temperature f becomes quite small except in the immediate vicinity of the hard core, where it still approaches -1. However, the greater the temperature the smaller the volume where the hard core is effective for realistic potentials. The lower the temperature the greater the positive lobe of f and the tendency for particles to linger in the potential well. The effectiveness of the attractive well is a rather strongly decreasing function of temperature.

Lennard−Jones Potential

Mayer Function
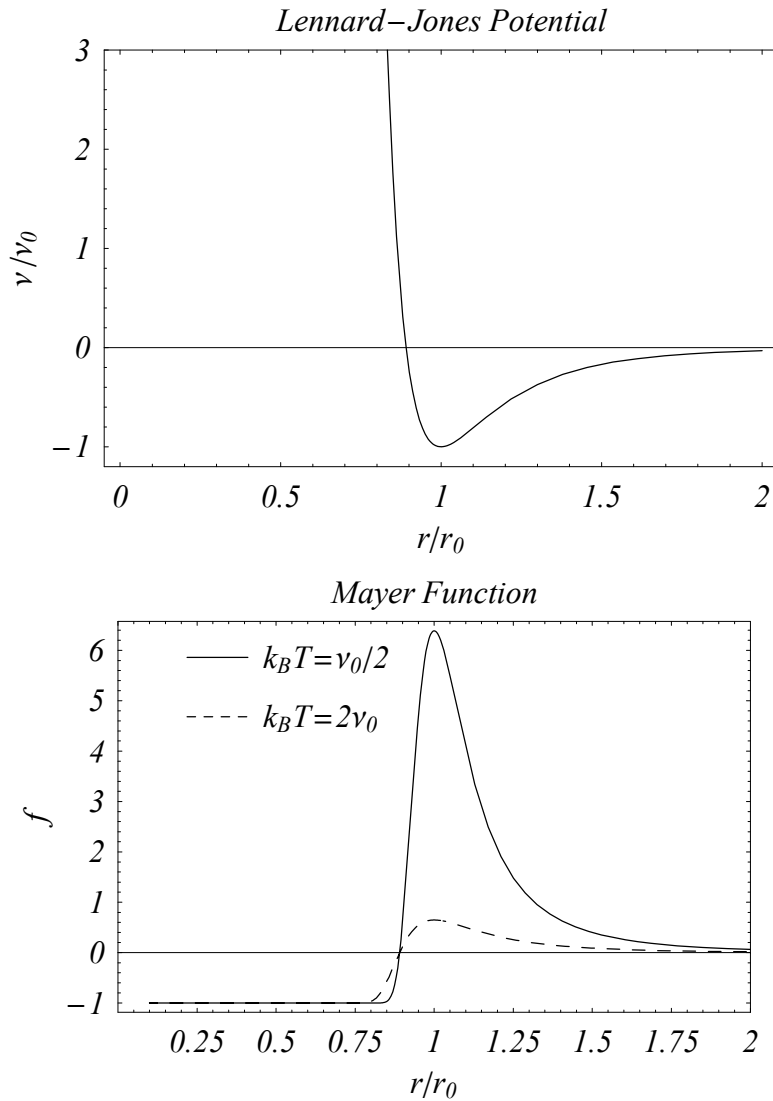
The mechanical equation of state for a simple (monatomic, structureless) gas can now be obtained from the partition function, $Z = Z_p Z_r = \lambda_B^{-3N} Z_r$, as follows:

$$F = -k_B T \ln Z = 3 N k_B T \ln \lambda_B - k_B T \ln Z_r$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = k_B T \frac{\partial \ln Z_r}{\partial V}$$

$$Z_r = \frac{V^N}{N!} \left(1 + \frac{N^2}{2V} b[T]\right) \implies \frac{\partial \ln Z_r}{\partial V} = \frac{N}{V} - \frac{N^2}{2 V^2} \frac{b[T]}{1 + \frac{N^2}{2V} b[T]}$$

We defined

$$b[T] = 4 \pi \int d s \, s^2 \, (e^{-\beta v[s]} - 1)$$

to simplify the algebra. Recognizing that $b[T]$ has dimensions of molecular volume, it is useful to divide a large system into small volumes V that are large compared with the range of the interatomic potentia,l such that $b[T]$ is independent of the size or shape of that volume, but containing a small enough N that

$$\frac{N^2}{2V} b[T] \ll 1 \implies \frac{\partial \ln Z_r}{\partial V} \approx \frac{N}{V} \left(1 - \frac{N}{2V} b[T]\right)$$

For each subsystem we obtain an equation of state of the form

$$\frac{pV}{N k_B T} \approx 1 - 2\pi \frac{N}{V} \int ds \, s^2 \, (e^{-\beta v[s]} - 1)$$

which can be applied to the entire system assuming that the density is uniform and the thermodynamic potentials are extensive. Therefore, the *second virial coefficient* is given by

$$B_2[T] = -2\pi \int_0^\infty ds \, s^2 \, (e^{-\beta v[s]} - 1)$$

A more rigorous derivation uses the grand canonical ensemble to analyze subsystems with variable particle number, using the chemical potential to regulate the convergence of the cluster expansion in a systematic fashion, but gives the same result at this level of approximation.

Next, we evaluate the two-particle density

$$\rho_2[\vec{r}_1, \vec{r}_2] = Z_r^{-1} \frac{N(N-1)}{N!} \int d^{3(N-2)} r \, e^{-\beta \mathcal{U}} \approx Z_r^{-1} \frac{N(N-1)}{N!} \int d^{3(N-2)} r \left(1 + \frac{1}{2} \sum_{i,j} f_{i,j}\right)$$

Recognizing that $f_{i,j} = f[\,|\vec{r}_i - \vec{r}_j|, T]$, we can replace any integral over $f_{i,j}$ by a simple function of temperature $b[T] \equiv \int d^3 r_i \, f_{i,j} = \int d^3 r_j \, f_{i,j}$. The only term involving $f_{i,j}$ that is not integrated out is the single term involving $f_{1,2}$. Hence,

$$\int d^{3(N-2)} r \left(1 + \frac{1}{2} \sum_{i,j} f_{i,j}\right) =$$
$$V^{N-2} + \left(\frac{N(N-1)}{2} - 1\right) V^{N-3} b[T] + V^{N-2} f_{1,2}[s] = V^{N-2} \left(1 + f_{1,2}[s] + \frac{(N+1)(N-2)}{2} \frac{b[T]}{V}\right)$$

whereas in the same notation

$$Z_r = \frac{V^N}{N!} \left(1 + \frac{N(N-1)}{2V} b[T]\right)$$

Combining these results and assuming that the correction terms are small, we find

$$\rho_2[\vec{r}_1, \vec{r}_2] \approx \frac{N(N-1)}{V^2} \frac{1 + f_{1,2} + \frac{(N+1)(N-2)}{2} \frac{b[T]}{V}}{1 + \frac{N(N-1)}{2V} b[T]} \approx \frac{N(N-1)}{V^2} \left(1 + f_{1,2} - \frac{b[T]}{V}\right)$$

Finally, using $\frac{b}{V} \ll 1$ and $\frac{b}{V} \ll f$, we obtain

$$\rho_2[\vec{r}_1, \vec{r}_2] \approx \left(\frac{N}{V}\right)^2 e^{-\beta v_{1,2}} \implies g[s] = e^{-\beta v[s]}$$

Therefore, we find that the pair distribution function for a dilute system reduces to a Boltzmann factor based upon the pair potential. Clearly the probability for finding a second particle is reduced in the repulsive and enhanced in the attractive regions of the intermolecular potential.

It is instructive to verify the internal consistency of these results by using this approximation to the pair correlation function to evaluate the more general equation of state

$$p\,V \;=\; N\,k_B\,T \;-\; \frac{2\,\pi}{3}\,\frac{N^2}{V}\,\int d s\; s^3\, g[s]\,\frac{\partial v}{\partial s} \;\approx\; N\,k_B\,T \;-\; \frac{2\,\pi}{3}\,\frac{N^2}{V}\,\int d s\; s^3\, e^{-\beta v[s]}\,\frac{\partial v}{\partial s}$$

Recognizing that

$$e^{-\beta v[s]}\,\frac{\partial v}{\partial s} \;=\;$$
$$-k_B\,T\,\frac{\partial}{\partial s}\,(e^{-\beta v}-1) \;\implies\; \int d s\; s^3\, e^{-\beta v}\,\frac{\partial v}{\partial s} \;=\; -k_B\,T\,\Big(s^3\,(e^{-\beta v}-1)\big|_0^\infty \;-\; 3\int d s\; s^2\,(e^{-\beta v}-1)\Big) \;=\; 3\,k_B\,T$$

such that

$$\int d s\; s^3\, e^{-\beta v[s]}\,\frac{\partial v}{\partial s} \;=\; 3\,k_B\,T\,\int d s\; s^2\,(e^{-\beta v[s]}-1)$$

we obtain

$$\frac{p\,V}{N\,k_B\,T} \;\approx\; 1 \;-\; 2\,\pi\,\frac{N}{V}\,\int d s\; s^2\,(e^{-\beta v[s]}-1)$$

as before. Similarly, the internal energy and heat capacity become

$$U = \frac{3}{2}\,N\,k_B\,T \;+\; 2\,\pi\,\frac{N^2}{V}\,\int d s\; s^2\, g[s]\, v[s] \;\approx\; \frac{3}{2}\,N\,k_B\,T\left(1 \;+\; \frac{4\,\pi}{3}\,\frac{N}{V}\,\int d s\; s^2\, e^{-\beta v[s]}\,\frac{v[s]}{k_B\,T}\right)$$
$$C_V = \frac{3}{2}\,N\,k_B \;+\; 2\,\pi\,\frac{N^2}{V}\,\int d s\; s^2\,\frac{\partial g}{\partial T}\, v[s] \;\approx\; \frac{3}{2}\,N\,k_B\left(1 \;+\; \frac{4\,\pi}{3}\,\frac{N}{V}\,\int d s\; s^2\, e^{-\beta v[s]}\left(\frac{v[s]}{k_B\,T}\right)^2\right)$$

when internal degrees of freedom are neglected or subtracted. Thus, we are now able to evaluate the first-order effects of intermolecular interactions upon the thermodynamics of dense gases.

Second virial coefficient

A very simple model of the intermolecular interaction in simple gases (which do not bind) can be constructed from a hard-core repulsion combined with a square-well attraction.

Toy Model of Intermolecular Potential
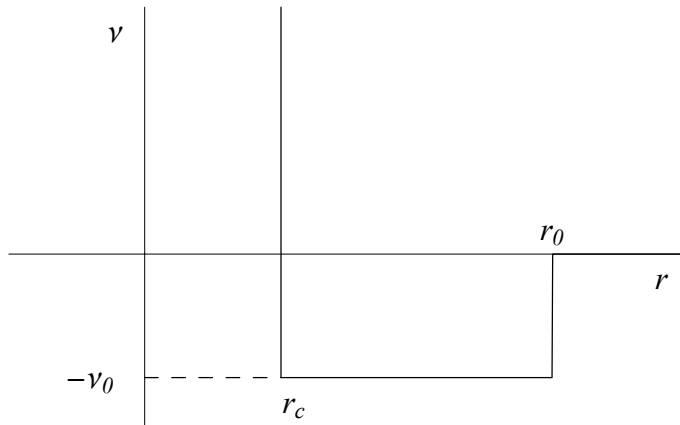
The second virial coefficient

$$B_2[T] = -2\pi \int_0^\infty ds\, s^2 \left(e^{-\beta v[s]} - 1\right)$$

can be evaluated easily for this model, whereby

$$B_2[T] = \frac{2\pi}{3} r_c^3 \left(\left(\frac{r_0}{r_c}\right)^3 + \left(1 - \left(\frac{r_0}{r_c}\right)^3\right) e^{v_0/k_B T} \right)$$

$$T \to \infty \implies B_2 \to \frac{2\pi}{3} r_c^3 \left(1 - \frac{v_0}{k_B T}\left(\frac{r_0^3 - r_c^3}{r_c^3}\right)\right) \approx \frac{2\pi}{3} r_c^3$$

$$T \to 0 \implies B_2 \to -\frac{2\pi}{3} r_c^3 \left(\frac{r_0^3 - r_c^3}{r_c^3}\right) e^{v_0/k_B T}$$

In the high-temperature limit, $B_2 \to \frac{2\pi}{3} r_c^3$ can be interpreted as the volume per particle excluded by the hard core in the two-particle interaction. For low temperatures the attractive square well produces a strong negative contribution proportional to the volume within the attractive region. For intermediate temperatures we can approximate

$$k_B T \gtrsim v_0 \implies B_2 \approx b - \frac{a}{k_B T} \quad \text{with} \quad b = \frac{2\pi}{3} r_c^3, \quad a = \frac{2\pi}{3}\left(r_0^3 - r_c^3\right) v_0$$

Inserting these parameters into the equation of state, we obtain

$$\frac{pV}{Nk_B T} = 1 + \frac{N}{V}\left(b - \frac{a}{k_B T}\right) \implies \left(p + \frac{a}{v^2}\right)\frac{v^2}{v+b} = k_B T$$

where $v = V/N$ is the volume per particle. Then approximating

$$v \gg b \implies \frac{v^2}{v+b} \approx v - b$$

for a dilute gas, we obtain the *van der Waals* equation of state

$$\boxed{\left(p + \frac{a}{v^2}\right)(v - b) = k_B T}$$

van der Waals equation of state

and can identify b with the volume excluded by the hard core and a with the volume integral of the attractive portion of the intermolecular potential. At this level of approximation

$$B_2 \approx b - \frac{a}{k_B T} \implies C_V \approx C_{V,0} \qquad \frac{C_p - C_V}{N k_B} \approx 1 + 2 \frac{a}{k_B T} \frac{N}{V}$$

we find that C_V is unaffected by the intermolecular potential while C_p is increased slightly.

Note that the van der Waals equation of state and empirical parameters are usually presented in molar form

$$\left(p + \frac{a_m}{v_m^2}\right)(v_m - b_m) = R T$$

where $R = N_A k_B$ as the molar gas constant, $v_m = V N_A / N$ is the molar volume, and the molar parameters are

$$a_m = a N_A^2 \qquad b_m = b N_A$$

and where N_A is Avogadro's number of particles per mole. Of course, the subscript m can be omitted if molar units are used consistently.

The second virial coefficient for more realistic potentials usually must be evaluated numerically. The figure below, constructed in *virial.nb*, compares a numerical calculation for the Lennard-Jones potential with the simple core+well model. The more realistic potential produces a virial coefficient that has the same qualitative features as the approximate potential, but is softer at high temperatures and less attractive at low temperatures. As the temperature increases the volume excluded by realistic potential decreases particles can penetrate further into the repulsive region. At low temperatures the tendency of particles to collect near the bottom of the well reduces the volume integral of the attractive region relative to the simple square well. However, the effectiveness of the attractive portion has an exponential temperature dependence, suggesting that B_2 can become strongly negative. As the density increases, it becomes necessary to include higher-order terms in the virial expansion and to include multiparticle clusters in the evaluation of the correlation function. At some point multiparticle clusters become dominant, droplets form, and the system tends to condense.

Comparison between Lennard−Jones and Toy Model
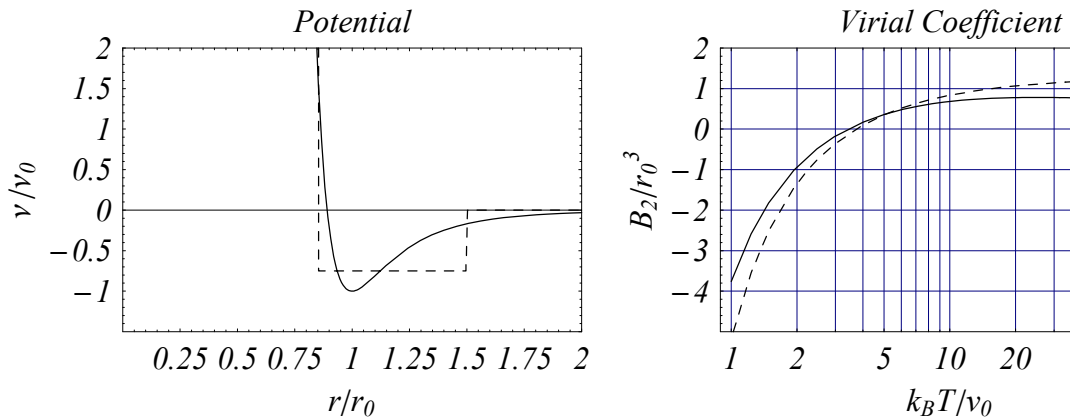
A detailed study of the van der Waals equation of state in vapor, liquid, and coexistence regions is presented in *vdwaals.nb*.

Pair distribution function

Once again let us consider the two-particle density. Assuming that the single-particle density is homogenous, at least macroscopically, we can write

$$\rho_2[\vec{r}, \vec{r}'] = \rho^2 \, g[\vec{s}] \; = \; \left\langle \sum_{i,j \neq i} \delta[\vec{r} - \vec{r}_i] \, \delta[\vec{r}' - \vec{r}_j] \right\rangle$$

where $\vec{s} = \vec{r} - \vec{r}'$ is the pair separation and ρ is the average density (without the cumbersome subscript "1"). To retain the possibility of describing solids, we do not necessarily assume that $g[\vec{s}]$ is isotropic and hence retain the vector separation as its argument. Also note that the pair distribution function is so important that we need not retain its subscript either, the "2" being understood. This formulation overlooks the microscopic inhomogeneity of the single-particle density, focusing instead upon its lattice structure. For fluids we can safely assume that the average single-particle density is actually homogeneous without losing any structure information.

Consider the integral

$$\int d^3 r' \, \rho_2[\vec{r}, \vec{r}'] \; = \; \left\langle \sum_{i,j \neq i} \delta[\vec{s} + \vec{r}_j - \vec{r}_i] \right\rangle$$

where we have used $\vec{r} = \vec{r}' + \vec{s}$ over $\delta[\vec{r}' - \vec{r}_j]$ to substitute $\vec{r} \to \vec{s} + \vec{r}_j$. Therefore, we can interpret $g[\vec{s}]$ as the distribution of separation vectors expressed by the ensemble average

$$\boxed{\; \rho \, g[\vec{s}] \; = \; \left\langle \frac{1}{N} \sum_{i,j \neq i} \delta[\vec{s} + \vec{r}_j - \vec{r}_i] \right\rangle \;}$$

For a crystal lattice at low temperature where the vibrations about lattice sites may be neglected, the ensemble average becomes trivial and we find

$$\text{frozen lattice} \implies \rho \, g[\vec{s}] \; = \; \frac{1}{N} \sum_{i,j \neq i} \delta[\vec{s} + \vec{r}_j - \vec{r}_i]$$

Alternatively, for a homogeneous isotropic fluid where all pairs are equivalent, we find

$$\rho \, g[s] \; = \; (N - 1) \langle \, \delta[s - |\vec{r}_1 - \vec{r}_2 |] \, \rangle$$

The correlations in fluids are not strong enough to establish the long-range order characteristic of crystalline solids, but the short-range order is certainly strong enough to distinguish liquids (and dense gases) from dilute (nearly ideal) gases. The most important correlation arises from the hard core and is responsible for the incompressibility of condensed matter. The intermediate range attraction is also important and is responsible for condensation of the liquid phase. At larger distances the oscillations in $g[s]$ shown in the schematic figure below represent the greater degree of order within liquids reflecting rings of increased and decreased density surrounding a particular molecule. The sketch is only intended to be qualitatively accurate. The presence of a molecule tends to keep other molecules further away than the hard core, but the attractive well tends to increase the density for $s \sim r_0$ near the well radius. The molecules in this ring, in turn, clear out another ring within their hard core radius, and then to enhance the density for $s \sim 2 \, r_0$, a structure that is a diminished echo

of the first ring. The second ring promotes a third diminished ring, etc. until the influence of the central molecule diminishes to insignificance. However, it is importance to recognize that the choice of central molecule is not significant — the same basic structure surrounds every molecule in the system. The average density is uniform, but these correlations between the molecules have important effects upon the properties of the system. The size and importance of these correlations tends to decrease as the temperature increases.

Schematic Pair Correlation Function
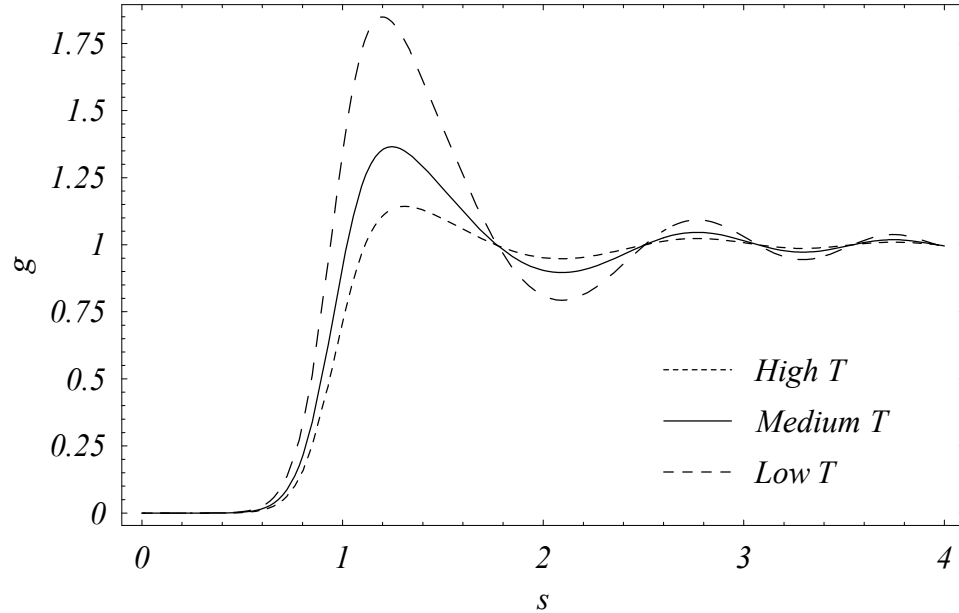
Structure factor

The structure of crystals is revealed with impressive clarity by X-ray diffraction, where the sharp peaks arise from coherent superposition of waves emanating from the highly ordered lattice. Similarly, the spatial correlations in fluids can also be probed, albeit without the sharpness exhibited by crystals, using either X-ray or neutron scattering. Here we provide a schematic derivation of the fundamental principles underlying this technique.

Suppose that a plane wave $\text{Exp}[i\,\vec{k}\cdot\vec{r}]$ is incident upon a small sample. We place a detector at a distance very large compared with the size of the sample and choose an origin within the sample. Each atom acts as a source of outgoing spherical waves. The total wave function consists of the incident plane wave plus the superposition of scattered spherical wavelets. We assume that the Born approximation is adequate so that each scattered wavelet is proportional to the incident amplitude with a common constant of proportionality. The total wave function then becomes

$$\psi[\vec{r}] \approx \text{Exp}[i\,\vec{k}\cdot\vec{r}] + \sum_{j=1}^{N} A_j\,\text{Exp}[i\,\vec{k}\cdot\vec{r}_j]\,\frac{\text{Exp}[i\,k'\,|\,\vec{r}-\vec{r}_j\,|]}{|\,\vec{r}-\vec{r}_j\,|}$$

where k' is the final wave number, $\vec{r}_j$ is the position of a scattering source, and A_j is its scattering amplitude. In the far-field limit

$$r \gg r_j \implies |\vec{r} - \vec{r}_j| \approx r - \vec{r}_j \cdot \hat{r}$$

where $\hat{r}$ is the unit vector pointing from the origin to the detector. Although there is no need to retain the dependence of the magnitude $|\vec{r} - \vec{r}_j|$ on r_j, the phase varies extremely rapidly with $k' r_j$ and its dependence on r_j must be retained, so that

$$\psi[\vec{r}] \approx \text{Exp}\left[i\,\vec{k}\cdot\vec{r}\right] + \frac{\text{Exp}[i\,k'\,r]}{r} \sum_{j=1}^{N} A_j\,\text{Exp}[i\,\vec{q}\cdot\vec{r}_j]$$

where $\vec{q} = \vec{k} - \vec{k}'$ is the momentum transfer. Identifying the coefficient of the spherical wave as the scattering amplitude, the differential cross section becomes

$$\frac{d\sigma}{d\Omega} = \left\langle \left| \sum_{j=1}^{N} A_j\,\text{Exp}[i\,\vec{q}\cdot\vec{r}_j] \right|^2 \right\rangle$$

The ensemble average is taken because any practical experiment requires a time interval that is long enough for the temporal average to be equivalent to the ensemble (thermodynamic) average. Although the atomic scattering amplitude A_j may depend upon momentum transfer, we assume for simplicity that it is the same for all atoms in the sample, such that $A_j = A[\vec{q}]$. More detailed analyses must account for variations with respect to species or other effects.

The differential cross section

$$\left\langle \left| \sum_{j=1}^{N} A_j\,\text{Exp}[i\,\vec{q}\cdot\vec{r}_j] \right|^2 \right\rangle = |A[\vec{q}]|^2 \left\langle N + \sum_{i,j\neq i} \text{Exp}[i\,\vec{q}\cdot(\vec{r}_i - \vec{r}_j)] \right\rangle$$

may now be separated into N independent single-atom contributions and an interference term. Using

$$\int d^3r\,\text{Exp}[i\,\vec{q}\cdot\vec{r}] \left\langle \sum_{i,j\neq i} \delta[\vec{r} + \vec{r}_j - \vec{r}_i] \right\rangle = \left\langle \sum_{i,j\neq i} \text{Exp}[i\,\vec{q}\cdot(\vec{r}_i - \vec{r}_j)] \right\rangle$$

we recognize the interference term as the Fourier transform of the pair distribution function, whereby

$$\frac{d\sigma}{d\Omega} = N\,|A[\vec{q}]|^2 \left(1 + \rho \int d^3r\,e^{i\,\vec{q}\cdot\vec{r}}\,g[\vec{r}]\right)$$

Finally, recall that a uniform medium, homogeneous and isotropic, does not produce real scattering. The coherent superposition of scattered wavelets in a uniform medium is responsible for the index of refraction which alters the propagation speed without deflecting the wave. Since we are interested in spatial correlations ($g \neq 1$) and not in forward scattering, which requires a somewhat different analysis, we subtract off the uncorrelated part

$$g[\vec{r}] = 1 + h[\vec{r}] \implies \frac{d\sigma}{d\Omega} = N\,|A[\vec{q}]|^2 \left(1 + (2\pi)^3\,\delta[\vec{q}]\,\rho + \rho \int d^3r\,e^{i\,\vec{q}\cdot\vec{r}}\,h[\vec{r}]\right)$$

to obtain

$$\vec{q} \neq \vec{0} \implies \frac{d\sigma}{d\Omega} = N\,|A[\vec{q}]|^2\,S[\vec{q}]$$

where the structure factor is given by

$$S[\vec{q}] = 1 + \rho \int d^3r\,e^{i\,\vec{q}\cdot\vec{r}}\,h[\vec{r}]$$

The function $h[\vec{r}]$ is usually called the *total correlation function* (although the motivation for the adjective "total" is not obvious). The constant term represents the incoherent contribution of uncorrelated, randomly positioned, scatterers whereas the second term is a measure of spatial correlations. Therefore, the Fourier transform of the pair correlation function is extracted from the measured angular distribution using

$$\frac{d\sigma}{d\Omega} = N \, |A[\vec{q}]|^2 \, S[\vec{q}]$$

$$\int d^3r \, e^{i\vec{q}\cdot\vec{r}} \, (g[\vec{r}] - 1) = \frac{S[\vec{q}] - 1}{\rho} \implies g[s] = 1 + \frac{1}{2\pi^2\rho} \int_0^\infty dq \, q^2 \, j_0[q\,s] \, (S[q] - 1)$$

where in the final step we assumed that $g[s]$ is isotropic.

One of the first measurements of neutron scattering by liquids sufficiently precise to investigate the sensitivity of the pair correlation function to details of the interatomic potential was performed by Yarnell *et al.* for argon at 85 kelvin, which is near its triple point. The figure below shows a fit to the data for $S[q]$ measured with $k = 6.42 \, \text{Å}^{-1}$; the data were sufficiently precise that deviations from the fitted curve would be difficult to perceive on this plot. The pair correlation function shown in the bottom panel was obtained by numerical Fourier transform using a very simple *Mathematica* code and reproduces their figure nicely. We see that $g[s] \approx 0$ within a hard core radius $r_c \approx 3 \, \text{Å}$, with small wiggles arising from numerical truncation errors. The correlation function rises very quickly, showing a strong enhancement of the density just outside the hard core. The authors compared their results with several theoretical calculations which are not reproduced here. They found that calculations for the Lennard-Jones potential with parameters fitted to thermodynamic data agree very well with the measured correlation function. However, one must also recognize that calculations for a pure hard-sphere model, with radius 1.025 times the Lennard-Jones radius, also reproduce the data fairly well. The discrepancies are subtle and require great precision to recognize. Therefore, one concludes that the nature of pair correlations in liquids is largely dictated by the repulsive core. The longer-ranged attraction establishes a mean field that is responsible for the average density but has relatively little other effect upon the correlation function.

Structure factor for ^{36}Ar at 85 kelvin

Correlation Function for ^{36}Ar at 85 kelvin
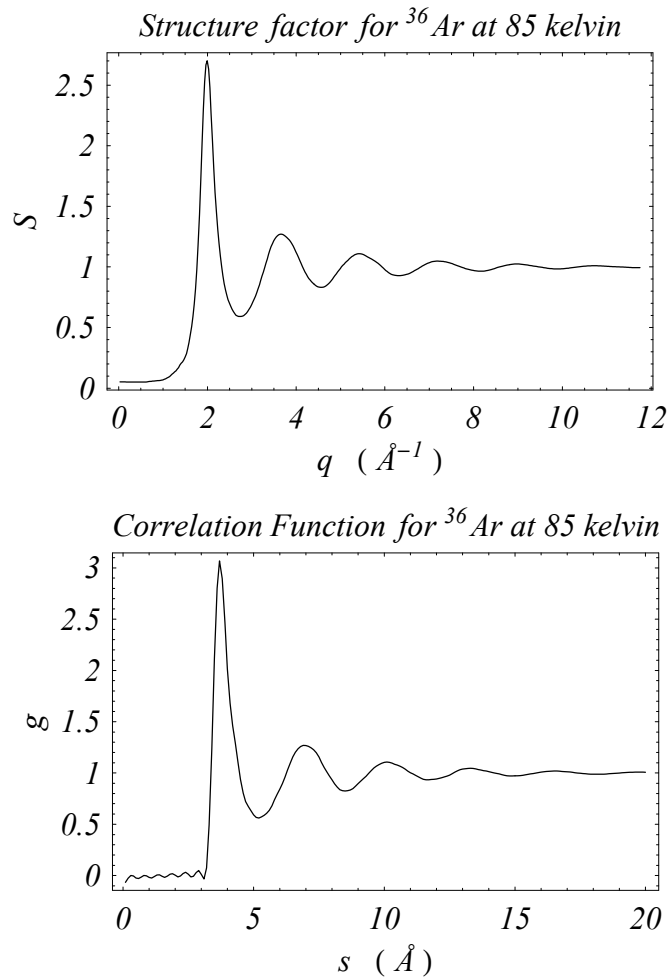
The data for $S[q]$ are from J.L. Yarnell *et al*., Phys. Rev. A7, 2130 (1973).

Density fluctuations

Consider a small but macroscopic subvolume in equilibrium with the remainder the system. The subsystem is in thermal and diffusive contact with the remainder, which serves as a reservoir of heat and particles. The fluctuation in particle number within the subsystem is measured by the variance

$$\sigma_N{}^2 = \left\langle (N - \overline{N})^2 \right\rangle = \langle N^2 \rangle - \langle N \rangle^2$$

where the ensemble averages are computed by integrating the associated density operators over the volume of the subsystem. The mean particle number is simply $\langle N \rangle = \rho\, V$ while the mean square particle number is

$$\langle N^2 \rangle = \int d^3 r \, d^3 r' \left\langle \sum_{i,j} \delta[\vec{r} - \vec{r}_i] \, \delta[\vec{r}' - \vec{r}_j] \right\rangle = \int d^3 r \, d^3 r' \left\langle \sum_{i} \delta[\vec{r} - \vec{r}_i] \, \delta[\vec{r}' - \vec{r}_i] \right\rangle + \int d^3 r \, d^3 r' \left\langle \sum_{i, j \neq i} \delta[\vec{r} - \vec{r}_i] \, \delta[\vec{r}' - \vec{r}_j] \right\rangle$$

Performing the integrals sequentially, the first term reduces to

$$\int d^3 r \, d^3 r' \left\langle \sum_{i} \delta[\vec{r} - \vec{r}_i] \, \delta[\vec{r}' - \vec{r}_i] \right\rangle = \int d^3 r \left\langle \sum_{i} \delta[\vec{r} - \vec{r}_i] \right\rangle = \rho \, V$$

while the second is

$$\int d^3 r \, d^3 r' \left\langle \sum_{i, j \neq i} \delta[\vec{r} - \vec{r}_i] \, \delta[\vec{r}' - \vec{r}_j] \right\rangle = \int d^3 r \, d^3 r' \, \rho_2[\vec{r}, \vec{r}'] = \rho^2 \, V \int d^3 s \, g[\vec{s}]$$

so that

$$\frac{\sigma_N^2}{N} = 1 + \rho \int d^3 s \, (g[\vec{s}] - 1) = 1 + \rho \int d^3 s \, h[\vec{s}]$$

where $h = g - 1$ vanishes in the absence of interactions.

Next we relate the density fluctuation to thermodynamic response functions using the grand canonical ensemble, which is appropriate for a subsystem with fixed volume but variable particle number in equilibrium with a reservoir at temperature T and chemical potential μ. The mean particle number is obtained from the grand partition function

$$\mathcal{Z} = \sum_{\alpha} \text{Exp}[-\beta (E_\alpha - \mu N_\alpha)] \implies \langle N \rangle = \frac{k_B T}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial \mu} \qquad \langle N^2 \rangle = \frac{(k_B T)^2}{\mathcal{Z}} \frac{\partial^2 \mathcal{Z}}{\partial \mu^2}$$

such that

$$\langle N^2 \rangle - \langle N \rangle^2 = k_B T \left(\frac{\partial N}{\partial \mu} \right)_{T,V}$$

Recognizing that $\mu = \mu[T, p]$ is a function of only temperature and pressure, we can determine the derivative using

$$\left(\frac{\partial \mu}{\partial N} \right)_{T,V} = \left(\frac{\partial \mu}{\partial p} \right)_{T} \left(\frac{\partial p}{\partial N} \right)_{T,V}$$

and the Gibbs-Duhem relation

$$d\mu = \frac{V}{N} dp - \frac{S}{N} dT \implies \left(\frac{\partial \mu}{\partial p} \right)_T = \frac{V}{N}$$

A cyclic relation gives

$$\left(\frac{\partial N}{\partial p} \right)_{T,V} = -\left(\frac{\partial N}{\partial V} \right)_{T,p} \left(\frac{\partial V}{\partial p} \right)_{T,N} = N \kappa_T$$

where

$$\kappa_T \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_{T,N}$$

is the isothermal compressibility and

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

by the extensivity postulate. Combining these factors, we obtain

$$\left(\frac{\partial N}{\partial \mu}\right)_{T,V} = \frac{N^2}{V}\,\kappa_T \quad\Longrightarrow\quad \frac{\langle N^2\rangle - \langle N\rangle^2}{N} = \frac{N\,k_B\,T}{V}\,\kappa_T$$

Finally, comparing the two expressions for the density fluctuation, we obtain results

$$\frac{\sigma_N{}^2}{N} = \rho\,k_B\,T\,\kappa_T = 1 + \rho\int d^3 s\,h[\vec{s}]$$

known as the *compressibility equation* or the *fluctuation equation of state*.

Notice that the correlation integral is closely related to the structure factor

$$q \to 0 \quad\Longrightarrow\quad S[0] = \rho\,k_B\,T\,\kappa_T = \frac{\sigma_N{}^2}{N}$$

Thus, density fluctuations scatter light passing through a fluid. A more detailed analysis shows that the attenuation coefficient for light passing through an isotropic medium takes the form

$$-\frac{d\mathcal{I}}{dx} = \frac{1}{6\pi}\left(\frac{\omega}{c}\right)^4\left|\frac{(\epsilon - 1)(\epsilon + 2)}{3}\right|^2 k_B\,T\,\kappa_T$$

where ω is the frequency and ϵ is the dielectric permittivity. Thus, one finds the classic ω^4 dependence of Rayleigh scattering with an amplitude that depends upon compressibility. Scattering by atmospheric density fluctuations preferentially removes blue sunlight from the direct line of sight, producing blue sky and red sunsets.

For an ideal gas,

$$h \to 0 \quad\Longrightarrow\quad \sigma_N = \sqrt{N}$$

as expected for Poisson statistics. For a relatively dilute hard-sphere gas, on the other hand,

$$h[s] \to -\Theta[r_c - s] \quad\Longrightarrow\quad \frac{\sigma_N{}^2}{N} = 1 - \frac{4\pi r_c{}^3}{3}\,\rho$$

we find that density fluctuations are reduced by the correlations between particles that tend to reduce the compressibility of the system. However, as the temperature decreases and density increases, the positive correlations outside the core radius tend to dominate, increasing the compressibility and the relative size of the density fluctuations. As a dense gas approaches the vapor-liquid phase transition, density fluctuations represent the tendency of molecules to form droplets of increased density under the influence of attractive interactions. In fact, at the phase transition

$$\text{coexistence} \implies \left(\frac{\partial p}{\partial V}\right)_T = 0 \implies \kappa_T \to \infty$$

density fluctuations tend to become extremely strong because the compressibility diverges and any small parcel of fluid has difficulty deciding whether it should be in the liquid or vapor phase. Because density fluctuations scatter light, a transparent vapor tends to become opaque as it approaches the phase transition, a phenomenon known as *critical opalescence*. An especially dramatic example of this phenomenon is provided by the superfluid phase transition in liquid helium. As one cools liquid helium by pumping away vapor, the normal liquid boils under reduced pressure and is easily visible in an unsilvered glass dewar. As the phase transition approaches, the boiling becomes so violent that the liquid is essentially opaque and fluctuations are so strong that it appears that the liquid might escape the dewar altogether. However, after that

brief excursion, the superfluid helium is utterly calm, so calm that it is difficult to see that any liquid is actually present and very careful observation is needed to recognize the liquid surface and to determine that most of the liquid actually does remain.

Problems

▼ Boyle temperature

The Boyle temperature T_B for a gas is defined as the temperature for which the ideal gas is exact even though interactions are present. Assuming that the density is low enough to truncate the virial expansion at second order, determine the Boyle temperature for the core+square-well model.

▼ Structure factor for dilute hard-sphere gas

Compute the structure factor $S[q]$ for a dilute hard-sphere gas as a function of ρ / ρ_c where $\rho_c = 3/4 \pi r_c^3$ is the close-packed density. Plot $S[q]$ using $r_c = 3.4 \, \text{Å}$ and $\rho = 0.1 \, \rho_c$.

▼ Two-dimensional gas

Suppose that classical nonrelativistic particles are confined to two spatial dimensions and interact with each other through a pair potential $v[s]$.

a) Write a general expression for the configurational partition function and identify the second virial coefficient.

b) Evaluate the mechanical and thermal equations of state for a dilute two-dimensional gas using the core+square-well model.