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SIMPLE CONCEPTS IN LIQUID STATE PHYSICS[1]

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Simple Concepts in Liquid State Physics [2]

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Introduction:

In university physics courses dealing with applications of kinetic theory and thermodynamics, the gaseous state of matter is analyzed in great detail. Ideal gas model, Van der Waals equation of state and, sometimes, gas-liquid condensation are discussed. Quite often, attention is then turned to the study of crystals, and the properties of the solid state. Group theory is introduced and applied to crystals. Electron theory of solids and band structure calculations are developed in great detail.

The topic of liquids is seldom considered in physics courses, a possible reason could be the rather lengthy theoretical derivations employing statistical mechanics. Therefore, some important questions might remain unanswered to researchers: What is the difference between the gaseous and liquid phases at a microscopic level? Does a solid or a liquid has more symmetry elements?, etc. There are excellent books discussing liquid state physics [1]. The attempt in this article is to motivate the theoretical concepts in a physical way. It is addressed to graduate and postgraduate students; however, fresh researchers (in condensed matter physics) may find it useful as a link connecting the (seemingly) different descriptions of the three states of matter.

Currently, there is an added attraction to study liquid state physics: Its concepts are finding applications in a newly emerging inter-disciplinary topic -the colloidal domain, also known as soft condensed matter. Colloids are suspensions of particulate matter in a fluid medium: milk, inks, blood, paints, etc. are a few common examples. Milk is a suspension of fats and proteins in water; various types of inks are suspensions of carbon particles in a suitable medium. Particle sizes in colloidal solutions are typically in the range of 10 A^o to 1 μm. Their number densities are in the range of 10^{12} cm^{-3} to 10^{17} cm^{-3} depending on the specific situations. All the physical properties of a suspension crucially depend on the inter-particle interactions between colloidal particles. Other examples of soft matter are self-assembled aggregates of certain organic compounds called

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surfactants in aqueous solutions, polymers in solutions etc. The colloidal domain has important connections to several biological processes; like that across a cell membrane; flow of blood, etc. It is at the interfaces of physics, chemistry, biology and industry, and hence has tremendous applications. [2]

This article will introduce the description of liquid state through the pair-distribution function. Its usefulness in expressing all macroscopic properties will be explained, possibilities of measuring it via scattering experiments and simple methods for its calculation are also covered.

Interaction potentials:

We shall restrict the entire discussion to the equilibrium properties of simple liquids, which are made up of mono-atomic constituents. Consider N such atoms confined in a volume V, which is in thermal equilibrium with a heat bath at temperature T. Atoms can be replaced by colloidal particles for describing properties of colloidal dispersions. Thus to include normal fluids and colloidal solutions in our discussions, we can refer to the constituents as particles of the fluid. The parameters N and V specify the mean (number) density of the fluid:

$$n_0 = N/V$$

The mean inter-particle distance d, which is a characteristic length of the fluid, varies as $n_0^{-1/3}$. This is easily obtained as the volume available per particle is, approximately,

$$d^3 = V/N = n_0^{-1}.$$

Let the interaction energy between the particles be specified in terms of a potential function u(r), where r is the distance between the particles. Particles are assigned a diameter σ, which is the second characteristic length of the fluid. Then, the closest distance of approach between two particles is σ. This fact, called the hard sphere condition, is expressed in terms of the potential as

$$u(r) = \propto, r < \sigma$$

$$u(r) = 0, r \geq \sigma.$$

There are very nice examples of liquids and colloidal particles with interaction potential of the hard sphere type (figure-1). A fluid made up of such particles shall be called a hard sphere fluid. Generally, there is also a short ranged attractive interaction between atoms. For example, the Van der Waals interaction originating from induced dipole moments is of such type. This combined with the hard sphere part generates a model inter-particle potential (figure-1). The depth u_0 of the attractive potential characterizes the strength of the attractive interaction. The hard sphere diameter is marked as the distance where u(r) vanishes in figure-1.

In reality, atoms do not have a well-defined hard sphere diameter. More realistic inter-atomic potential is that specified by a soft-sphere potential like the called the Lennard-Jones potential. Here repulsion between two atoms at close distances as well as attraction between them are modeled as power law functions:

$$u(r) = u_0\ (r/\sigma)^{12} - u_1\ (r/\sigma)^{6}$$

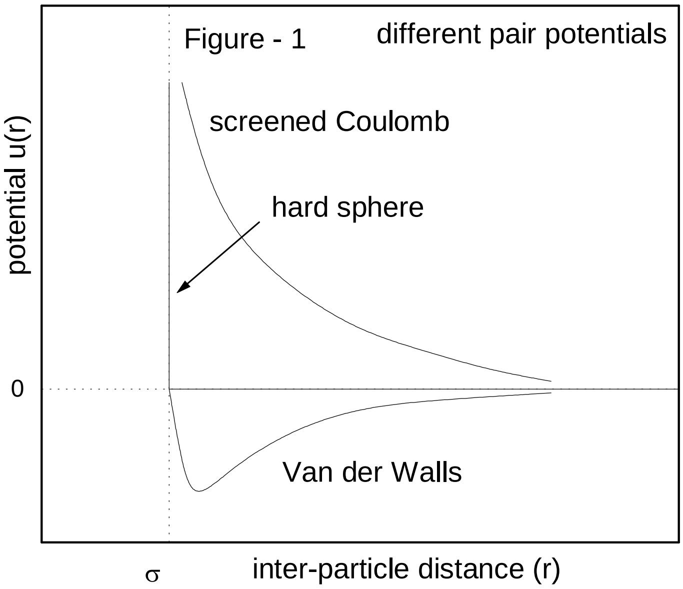


Figure-1

Charged colloidal particles experience a smooth repulsive potential in the solvent medium. A screened Coulomb potential, where screening arises due to the oppositely charged ions surrounding the colloidal particles is known as the Yukawa potential (figure-1). This is a typical model potential used in colloidal physics for describing inter-particle interaction.

$$u(r) = (u_0\ /r)\ \exp(-r/\lambda) \qquad \text{for } r \geq \sigma$$

$$u(r) = \propto \qquad \text{for } r < \sigma.$$

When the screening length λ, which scales as [ion density]$^{-1/2}$, is very large compared to the mean inter-particle distance d, u(r) reduces to the un-screened 1/r Coulomb potential. Thus a solution of charged colloids can be described by treating them as 'atoms' interacting via a suitable inter-particle potential.

The problem of liquid state theory is to predict the properties of liquids when the inter-particle potential is specified. *We shall assume that the total potential energy of the fluid can be expressed as a sum over distinct pairs; this assumption is usually referred to as pair-wise additive property*. This is quite satisfied in almost all conditions.

The pair distribution function

If the fluid is in equilibrium, the local density n is spatially uniform over distances large compared to d. However, over smaller length scales, the density n varies with distance from a specific atom or particle. In fact, the density fluctuates in space and time, but for considering static properties of fluids, it is appropriate to introduce a time average density distribution, which is obtained by averaging over a sufficiently large time interval. If the center of a particle is taken as the origin -of a suitable co-ordinate system - the time averaged number density varies with distance from the particle, and approaches the mean density n_0 for distances large compared to d. Thus n(r) can be expressed as

$$n(r) = g(r)\, n_0$$

The newly introduced function g(r) must satisfy some obvious physical requirements: First, as g(r) represents a time-averaged distribution, it must depend only on the distance r - and not on the vector **r -** in an isotropic fluid. Second,

$$g(r) = 0 \text{ for } r \leq \sigma$$

This is simply the hard sphere condition. As n(r) approaches n_0 for larger values of r,

$$g(r) \rightarrow 1 \text{ as } r \rightarrow \propto$$

Finally, one expects g(r) to be oscillatory, with the first peak at the mean inter-particle distance, the second peak at the next-nearest distance etc. This function g(r) is called the pair distribution function as it depicts the distribution of a pair of particles. The successive peak-heights in g(r) decrease and become almost invisible after a few inter-particle separations. This is because an atom at the origin cannot induce correlations at larger distances because of the short ranged character of molecular forces. The qualitative features of g(r) are shown in figure-2

One can imagine a similar distribution function for atoms in a crystal, but then the peaks are very sharp; the small width of these peaks arise from the thermal vibrations about the equilibrium position. Figure-2 shows schematic variations of g(r) for a crystal also. In fact, g(**r**) for a crystal is non-zero only along some specific directions. Also, it has certain translation symmetries. The rotational symmetry elements of g(**r**) and the crystal will be finite, while an isotropic fluid has arbitrary translation and rotational symmetry. To understand this fact, it is important to remember that g(r) is a time average quantity, with all temporal fluctuations averaged out. In a dilute gas, the particles are quite far apart. Thus the presence of a particle does not force the locations of other particles. Thus g(r) has the asymptotic value unity -a time averaged value- outside the hard-core diameter. Seen in this way, all the states of matter can be described in terms of the pair distribution function.

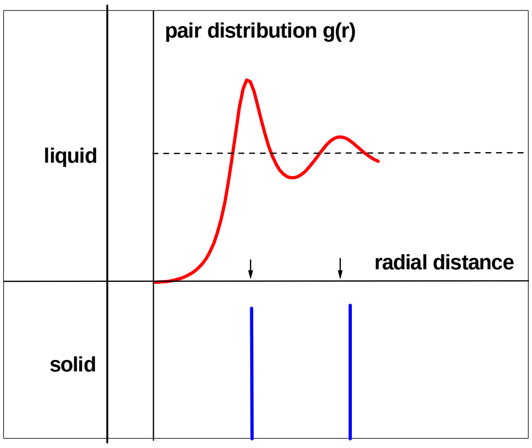
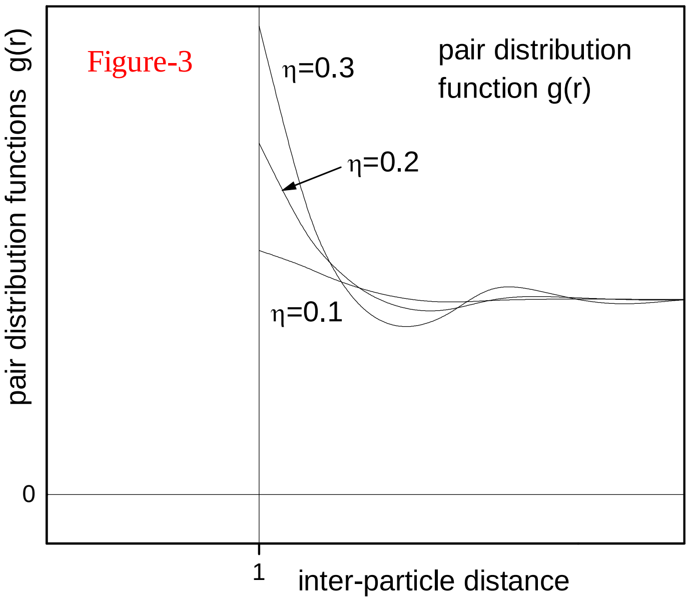


Figure-2

Qualitative Aspects:

A good deal of properties of g(r) can be brought out qualitatively. For instance, in an ideal gas, which are point particles, g(r)=1 for all r as the particles are uncorrelated. In the case of a hard sphere gas, at low number-density n_0 , g(r)=0 for r<σ, the particle diameter, and g(r)= 1 for r > σ. The first condition arises because the shortest inter-particle separation is σ. If the density is increased, the contact value of g(r), that is, g(r) at r slightly greater than σ, increases, and higher order peaks begin to appear (figure-3). Thus for denser systems, g(r) depends strongly on number density n_0=N/V. The probability of finding the nearest neighbor is largest just outside the hard-core diameter; it is as if there is an *effective attraction* between any two hard spheres.

This “attraction” is a consequence of maximizing the entropy of the particle configurations. In a time-average sense, if the spheres are close to one another, there is more volume for a particle to move around. So there is more randomness in its position, and hence (translation) entropy is also maximized.



For a general potential, and low number density, a useful approximation is

$$g(r) \approx \exp(-u/KT)$$

This follows directly from Boltzmann distribution. For a low-density hard sphere gas, the qualitative aspects of g(r), namely, g(r)=0 for r<σ, and g(r)= 1 for r > σ, are reproduced by this formula. It has the correct asymptotic behavior for large r, however cannot provide the dependence of g(r) on the mean density n_0 or the peak positions on n_0. The position of the first peak in g(r) is always the mean inter-particle separation $\sim[n_0]^{-1/3}$. What is shown in figure-3 is a schematic variation of g(r) for a Lennard-Jonnes fluid at a typical density. As density reduces to low values, the peaks will disappear and g(r) ~1 for r > σ. On increase of the density, the peaks will become sharper and sharper. The width of the peaks will be characteristic of the thermal motion of the atoms in the liquid. For still higher densities, all the peaks should reduce to delta-functions. However, this transition from liquid to solid can be seen in g(r) only in computer simulations of liquids using, say, Monte Carlo or molecular dynamics methods. In a hard sphere fluid, such a transition, to a fcc solid, will take place when the volume fraction of the atoms is around ~ 0.66. The volume fraction is given by

$$\eta = (N/V)\ (\pi/6)\ \sigma^3$$

At this density, again, particles will not be touching each other, however transition to a frozen solid-structure with thermal motion around the equilibrium positions maximizes the entropy of the system. This liquid-solid phase transition in a hard sphere fluid is purely driven by considerations of entropy, as there is no force between the hard spheres.

Probabilistic interpretation:

The pair distribution function can also be introduced in a probabilistic language. Let $p(\mathbf{r}_1)$ denote the probability distribution that an atom is in a volume element $d\mathbf{r}_1$ around $\mathbf{r}_1$. In a homogeneous fluid, this distribution is uniform, and is given by

$$p(\mathbf{r}_1)d\mathbf{r}_1=(d\mathbf{r}_1/V)$$

This follows because an atom is equally likely to be found anywhere. Let $p(\mathbf{r}_1, \mathbf{r}_2)d\mathbf{r}_1\ d\mathbf{r}_2$ be the joint distribution that one atom is in $d\mathbf{r}_1$ around $\mathbf{r}_1$ and another is in $d\mathbf{r}_2$ around $\mathbf{r}_2$. It has an important property:

$$p(\mathbf{r}_1, \mathbf{r}_2)\ d\mathbf{r}_1\ d\mathbf{r}_2 \rightarrow p(\mathbf{r}_1)\ d\mathbf{r}_1 \times p(\mathbf{r}_2)\ d\mathbf{r}_2 \text{ for } |\mathbf{r}_1\text{-}\mathbf{r}_2| >> d$$

This is because, as molecular forces are short range, a particle can induce a correlation only over a few inter-particle distances. Therefore, it is appropriate to introduce a function $g(|\mathbf{r}_1\text{-}\mathbf{r}_2|)$ defined as

$$p(\mathbf{r}_1, \mathbf{r}_2)\ d\mathbf{r}_1\ d\mathbf{r}_2 = g(|\mathbf{r}_1\text{-}\mathbf{r}_2|)\ (d\mathbf{r}_1/V)\ (d\mathbf{r}_2/V).$$

Its argument is $|\mathbf{r}_1\text{-}\mathbf{r}_2|$, rather than $\mathbf{r}_1$ and $\mathbf{r}_2$, for a homogeneous fluid. Thus

$$g(|\mathbf{r}_1\text{-}\mathbf{r}_2|) \rightarrow 1 \text{ for } |\mathbf{r}_1\text{-}\mathbf{r}_2| >> d$$

To repeat, this condition is due to the lack of interdependence between atoms, when large distances separate them. Now, $g(|\mathbf{r}_1\text{-}\mathbf{r}_2|)\ d\mathbf{r}_2/V$ can be interpreted as the conditional probability that there is a particle in $d\mathbf{r}_2$ around $\mathbf{r}_2$ when there is one at $\mathbf{r}_1$. This interpretation is the unambiguous meaning of the pair correlation function $g(r) = g(|\mathbf{r}_1\text{-}\mathbf{r}_2|)$. The density distribution n(r) around the particle is obtained on multiplying g(r) with the mean particle density N/V:

$$n(r)\ d\mathbf{r} = (N/V)\ g(r)\ d\mathbf{r}.$$

The two reduced distributions $p(\mathbf{r_1})$ and $g(r)$ are adequate to represent all static properties of fluids if the total potential energy is pair wise additive.

Macroscopic properties of fluids:

The total inter-particle potential energy of N particles in V is denoted as $U(\mathbf{r}_1, \mathbf{r}_2,..,\mathbf{r}_N)$. Hereafter, the notation $\{\mathbf{r}_i\}$ will denote the set of co-ordinates of the N particles. The principal quantity used in describing equilibrium structure of fluids (at temperature T) is the Gibbs-Boltzmann distribution for the particle positions $\{\mathbf{r}_i\}$:

$$P(\{\mathbf{r}_i\}) = Z^{-1} \exp[- U(\{\mathbf{r}_i\})/ kT]$$

Here Z is the partition function and k is Boltzmann constant. All the physical quantities can be computed as averages (denoted with angular brackets <···>) with P. Total energy is

$$< E > = < U > + (3/2) N k T$$

The free energy of N particles is

$$F = -kT \ln[Z]$$

Finally, entropy of the system is

$$S = (kT)^{-1} (<E> - F)$$

The calculation of these averages is in fact the problem of statistical mechanics, and is feasible only for simple systems. We shall not discuss this direct method any more, what follows is a different approach.

For systems where interactions are pair wise pair wise additive, the total potential energy is

$$U(\{\mathbf{r}_i\}) = (1/2) \Sigma_{i,j}\ u(|\mathbf{r_i}-\mathbf{r_j}|)$$

Here u(r) is the pair potential that depends only on $r = |\mathbf{r}|$ for spherical particles. The average potential energy is then given by

$$< U > = [N(N-1)/2] \int u(r)\, g(r)\, d\mathbf{r/V}$$

The integral gives the interaction energy of a pair; one particle at the origin and another at a distance r, and the factor N(N-1)/2 is the number of distinct pairs of particles.

Similarly, a formula for pressure can be derived. The total time derivative of the quantity $\sum_i \mathbf{r_i}\, \mathbf{p}_i$, where $\mathbf{p}_i$ is the momentum of the i^{th} particle, is

$$(d/dt) \sum_i \mathbf{r_i}\, \mathbf{p}_i = \sum_i (d\mathbf{r_i} /dt)\, \mathbf{p}_i + \sum_i \mathbf{r_i}\, (d\mathbf{p}_i /dt)$$

The time average of the left hand side over a (sufficiently) large time interval is zero if particles are confined to a finite volume V and velocities are not unbounded. The average of the first term on the RHS is twice the kinetic energy, which is 3NkT. The average of the second term, which is the sum of terms like $\mathbf{r}_i\bullet\mathbf{F}_i$, where $\mathbf{F}_i$ is the force on i^{th} particle, can be expressed as

$$\sum_i < \mathbf{r_i} \, (d\mathbf{p}_i /dt) > = - \int_{surface} P \, \mathbf{r} \, \mathbf{ds} - [N(N-1)/2] < \mathbf{r} \, \nabla \, u>$$

While the first integral term arises from the average pressure P acting on the surface of volume V, the second part accounts for the contribution from inter-particle forces of all distinct pairs; the force between any pair being replaced by the negative gradient of the potential. The surface integral is easily evaluated as

$$3V = \int_{surface} \mathbf{r} \, \mathbf{ds} = \int (\nabla \, \mathbf{r}) \, \mathbf{dr}$$

Then, pressure is given by

$$P = (NkT/V) – [N(N-1)/2V] \int \mathbf{r} \, \nabla \, u \, g(r) \, d\mathbf{r/V}$$

In this, the averaging is expressed in terms of the pair distribution function. This expression is known as the virial pressure as it is derived using the term $\sum_i \mathbf{r_i} \, \mathbf{p}_i$, called ‘virial’ in classical mechanics. Once pressure P is known, it can be related to free energy as:

$$P = -(\partial F/\partial V)_T$$

Thereafter all other thermodynamic quantities can be derived using free energy. Thus the pair distribution function g(r) contains all the necessary information about the fluid, whose potential energy is pair-wise additive. This route to thermodynamics of fluid is known as the ‘virial’ route.

Structure factor:

The pair distribution function is directly measurable by scattering experiments, which are invariably used to probe the structure of condensed phases like solids and liquids. In a scattering experiment, one measures the scattering intensity I(q) with respect to the scattering vector defined as $\mathbf{q} = \mathbf{q}_i-\mathbf{q}_f$ where $\mathbf{q}_i$ and $\mathbf{q}_f$ are wave vectors of the incident and scattered radiation. Magnitude of the incident wave vector is

$$|\mathbf{q_i}| = 2\pi/\lambda$$

If the scattering angle is θ, then for elastic scattering,

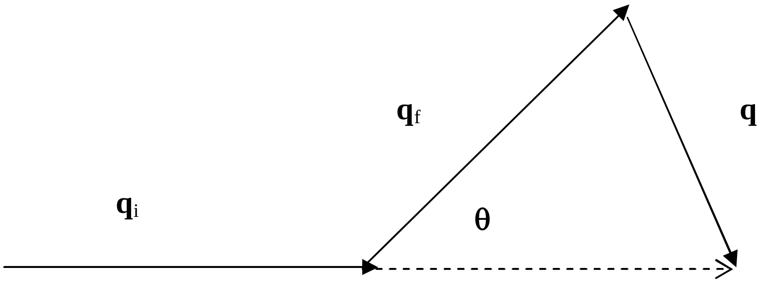
$$q = |\mathbf{q}| = (4\pi/\lambda) \sin(\theta/2)$$

Here λ is the wavelength of the radiation. If a(q) is the scattering amplitude of a single atom - which is decided by the electronic structure of the atom and its interaction with the radiation - the scattering intensity from a single particle is

$$I_0(q) = |a(q)|^2.$$

The radiation scattered by two atoms separated by a distance r has a phase difference exp(i $\mathbf{q}\cdot\mathbf{r}$).

Figure-4



Therefore, for coherent elastic scattering, the total scattering amplitude from all the N particles which are at positions $\{\mathbf{r}_i\}$ is

$$A(q) = \sum_j a(q) \exp[i\, \mathbf{q}\cdot\mathbf{r}_j]$$

The total scattered intensity is then given by

$$I'(q) = |A(q)|^2$$

However, we do not know the position of the atoms explicitly. What is known is only the Gibbs-Boltzmann probability distribution $P(\{\mathbf{r}_i\})$ of the particle positions. Hence I′(q), which depends on all $\mathbf{r}_\mathbf{j}$ values implicitly, has to be averaged over this distribution:

$$I(q) = < |A(q)|^2 >$$

The angular brackets denote average over the (statistical) distribution of particle positions. Thus one gets

$$I(q) = |a(q)|^2 N [1+ (1/N) \sum_{j\neq k} < \exp(i\, \mathbf{q}\cdot. (\mathbf{r}_\mathbf{j} - \mathbf{r}_\mathbf{k}) >]$$

The average in this expression can be expressed in terms of the pair distribution function:

$$< \exp(i\, \mathbf{q}\cdot. (\mathbf{r}_\mathbf{j} - \mathbf{r}_\mathbf{k}) > = \iint \exp[i\, \mathbf{q}\cdot. (\mathbf{r}_\mathbf{j} - \mathbf{r}_\mathbf{k})]\, g(|\mathbf{r}_\mathbf{j} - \mathbf{r}_\mathbf{k}|)\, (d\mathbf{r}_k /V)\, (d\mathbf{r}_j /V)$$
$$= \int \exp[i\, \mathbf{q}\cdot. \mathbf{r}]\, [g(r) -1]\, (d\mathbf{r} /V) + \int \exp[i\, \mathbf{q}\cdot. \mathbf{r}]\, (d\mathbf{r} /V)$$

The double integral has been reduced to a single integral in the relative co-ordinate r. Further the last term -which is the delta function $\delta(\mathbf{q})$ - is separated out so that the Fourier transform is properly defined as [g(r)-1] goes to zero for large r. Since there are a total of $N(N-1) \cong N^2$ exponential terms in I(q), it can now be written as

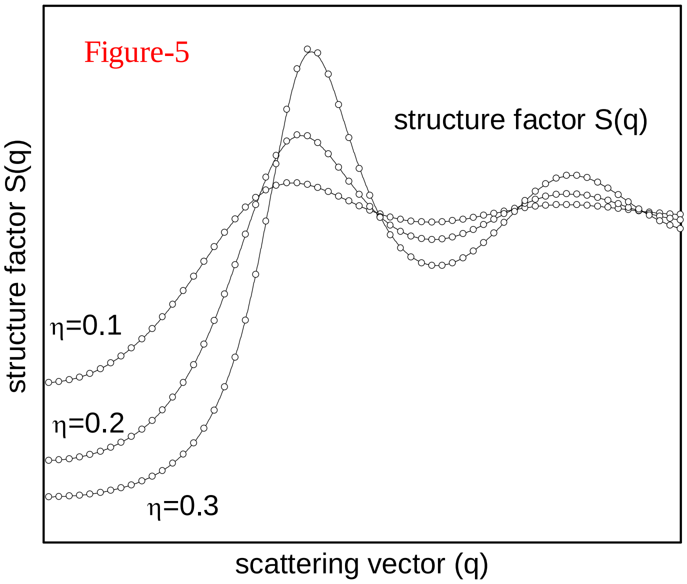
$$I(q) = I_0(q)\, N\, [1 + (N/V) \int \exp(i\, \mathbf{q}\cdot\mathbf{r})\, \{g(r) - 1\}\, d\mathbf{r}\,],\ q \neq 0$$

The delta function term is omitted as this formula for I(q) is to be used only for $q \neq 0$. The terms inside the square bracket are called the structure factor S(q). Then, I(q) becomes

$$I(q) = N\, I(q)_0\, S(q)$$

Statistical average of the spatial distribution of atomic positions, is implicitly contained in the structure factor S(q); which is given by

$$S(q) = 1 + (N/V) \int \exp(i\, \mathbf{q}\cdot\mathbf{r})\, \{g(r) - 1\}\, d\mathbf{r}$$



The first term $N\, I_0(q)$ in I(q) results from addition of intensity from N particles. Hence it is the incoherent scattering intensity. The second term - proportional to N^2 - denotes inter-particle interference effects. The intensity I(q) is the coherent intensity.

Thus the Fourier transform of [g(r)-1] is directly measured by scattering experiments. This function denoted by h(r) is called the pair correlation function:

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

This function describes the correlation between two particles.

Figure-5 shows the structure factors corresponding to g(r) functions (of increasing density) for hard sphere fluid. Note that the peak positions shift to lower q-values on increasing density. This is due to the corresponding decrease of mean inter-particle separation d, where the interference of scattering from two particles has maximum effects. The peak positions, q_m and d satisfy the well known relation:

$$2\pi q_m d = 1.$$

This is a statement Bragg's law in terms of q, rather than θ

Relation to compressibility:

If we take V as a sub-volume of the system, the number of particles N in it will vary in time, and the mean single particle density is <N> / V. Similarly, the number of pairs N(N-1) also will vary in time, and its average value in V is <N(N-1)>. This can be expressed in terms of $g(|\mathbf{r}_1-\mathbf{r}_2|)$:

$$< N(N-1) > = \iint <N> (d\mathbf{r}_1 /V)\, g(|\mathbf{r}_1 - \mathbf{r}_2|) <N-1> (d\mathbf{r}_2 /V)$$

This follows easily as $(d\mathbf{r}_1 /V)$ is the probability of finding one particle in $d\mathbf{r}_1$ at $\mathbf{r}_1$. The integrand is then is the probability of finding one particle (out of N) at $\mathbf{r}_1$ and another (out of N-1) at $\mathbf{r}_2$. Note that $<N> (d\mathbf{r}_1/V)$ is the probability of finding any one of the particles in $d\mathbf{r}_1$. Using the approximation $<N-1> \cong <N>$ on the RHS, one gets

$$<N^2 > - <N> = <N/V>^2\, V \int g(r)\, d\mathbf{r}$$

$$= <N>^2 + <N/V>^2\, V \int [g(r)-1]\, d\mathbf{r}$$

This shows that the relative number fluctuation in V is given by

$$[<N^2> - <N>^2] / N = 1 + <N/V> \int [g(r)-1]\, d\mathbf{r}$$

The right hand side is simply the limit of S(q) as $q \to 0$

$$S(q \to 0) = 1 + <N/V> \int [g(r)-1]\, d\mathbf{r}$$

The LHS is the ratio of the isothermal compressibility of the fluid to that of an ideal gas.

$$[<N^2> - <N>^2] / N = - (1/V)\, (\partial V/\partial P)\, [<N> kT / V]$$

Thus we arrive at an important relation, called the compressibility equation:

$$1 + <N/V> \int [g(r)-1]\, d\mathbf{r} = - (1/V)\, (\partial V/\partial P)\, [<N> kT / V]$$

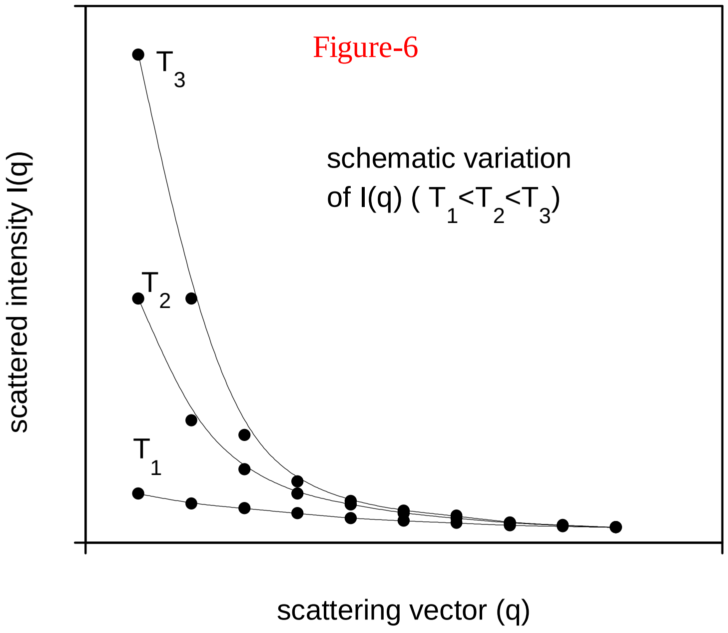
This relates two measurable macroscopic quantities; one is a thermodynamic quantity and the other is related to the structure of the fluid. Thus from g(r) it is possible to calculate the compressibility, and, hence, from integration, pressure P as a function of V. Finally, the free energy and all the other thermodynamic quantities can be obtained. This is called the 'compressibility' route.

Note that in the case of an ideal gas g=1 and the above equation gives the ideal gas law

$$P = \langle N \rangle KT/V$$

Using the low density expression $g = \exp[-u/KT]$ in the compressibility equation, it is also possible to derive the Van der Waals equation.

Equilibrium structure of matter - at a given temperature T, and volume V -is determined by the principle of minimum free energy: F=E-TS. The principles of minimum energy for mechanical equilibrium and maximum entropy for isolated thermodynamic equilibrium are combined together in terms of free energy when T and V are fixed externally. Phase changes occurring in various systems are understood in terms of this principle. A common example of such a phase transition is condensation of gases. The gaseous phase prevails above the critical temperature T_c. Below T_c, there may be a gaseous phase, liquid phase or co-existence of both depending on number density.



Light scattering experiments on a system at critical density and close to T_c (from above) show very predominant scattering of light in the forward direction, i.e., $q \rightarrow 0$ as shown schematically in figure–6. This phenomenon, called critical opalescence, is modeled in terms of the Ornstein-Zernike formula for scattered intensity:

$$I(q)/I_0 = S_0 / (1+q^2 \xi^2)$$

Here S_0 is the isothermal compressibility factor, explained earlier, and ξ is a characteristic length - called correlation length - over which strong correlations between atomic positions persist in the system. These quantities diverge as power laws as $T \rightarrow T_c$: Thus one finds

$$S_0 \sim t^{-\gamma}$$

$$\xi \sim t^{-\nu}$$

The parameter $t = (T-T_c)/T_c$ is called the reduced temperature. For all mono-atomic fluids, it is found that two critical exponents have universal values $\gamma \sim 1.23$ and $\nu \sim 0.63$.

The divergence of isothermal compressibility near the critical point means that $h(r) = g(r)-1$ becomes non-zero over the entire volume of the system. This indicates the development of strong correlations between all the atoms near critical points. Development of such long ranged correlations is the most important feature of critical phenomena.

Ornstein - Zernike equation:

Theories of pair correlation function h(r) invariably employ the Ornstein-Zernike equation (OZE). The principal idea in setting up this equation is to separate h(r) into two parts: a direct part denoted by c(r) and the remaining indirect part h(r) - c(r). As molecular forces are short range, it is appropriate to assume that the direct part is also short ranged. More explicitly, the direct correlation $c(\left|\mathbf{r}-\mathbf{r}'\right|)$ denotes the correlation that a particle at $\mathbf{r}$ induces directly, and not through a third particle, on another at $\mathbf{r}'$. So h(r), which is the total correlation between a particle at the origin and another at $\mathbf{r}'$, is postulated to satisfy an integral equation:

$$h(r) = c(r) + [<N> /V] \int c(|\mathbf{r} - \mathbf{r}'|)\, h(\mathbf{r}')\, d\, \mathbf{r}'$$

A Neumann series solution of this equation can be obtained by writing h(r) as a series:

$$h(r) = \sum_{0 \le n \le \infty} [<N>/V]^n h_n(r)$$

Then it is easily found that

$$h_0(r) = c(r)$$

For larger values of n, $h_n(r)$ satisfy the recurrence relation

$$h(r)_n = \int c(|\mathbf{r} - \mathbf{r}'|)\, h(\mathbf{r}')_{n-1}\, d\,\mathbf{r}', \quad n \geq 0$$

This yields for n=1 and 2

$$h_1(r) = \int c(|\mathbf{r} - \mathbf{r}_1|)\, h_0(\mathbf{r}_1)\, d\,\mathbf{r}_1 = \int c(|\mathbf{r} - \mathbf{r}_1|)\, c(\mathbf{r}_1)\, d\,\mathbf{r}_1$$

$$h_2(r) = \int c(|\mathbf{r} - \mathbf{r}_1|)\, h_1(\mathbf{r}_1)\, d\,\mathbf{r}_1 = \int c(|\mathbf{r} - \mathbf{r}_1|)\, d\,\mathbf{r}_1 \int c(|\mathbf{r}_1 - \mathbf{r}_2|)\, c(\mathbf{r}_2)\, d\,\mathbf{r}_2$$

Hence the solution can be written as

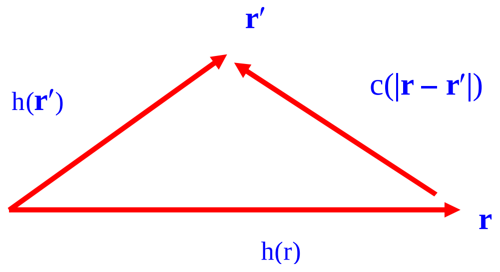
$$h(r) = c(r) + [\langle N\rangle /V)] \int c(|\mathbf{r} - \mathbf{r}_1|)\, c(\mathbf{r}_1)\, d\,\mathbf{r}_1 + $$

$$+ [\langle N\rangle /V)]^2 \int c(|\mathbf{r} - \mathbf{r}_1|)\, d\,\mathbf{r}_1 \int c(|\mathbf{r}_1 - \mathbf{r}_2|)\, c(\mathbf{r}_2)\, d\,\mathbf{r}_2$$

+ higher order terms.

The first term gives the direct correlation between a particle at origin and at **r**, the second involves an intermediate particle at $\mathbf{r}_1$, which may be any where in the volume. The third term involves two intermediate particles, one at $\mathbf{r}_1$ and the other at $\mathbf{r}_2$, again situated anywhere in the volume. Higher order terms will involve more and more intermediate particles.

Figure-7



The integral equation for h(r) was originally motivated by writing an expansion for h(r) as in the above relation, and then summing up all the terms together. The first term on the RHS of the integral equation is the direct part. Now, $d\mathbf{r}'/V$ is the probability of finding a particle in $d\mathbf{r}'$ and $\langle N\rangle\, d\mathbf{r}'/V$ times $c(|\mathbf{r}-\mathbf{r}'|)$ expresses the direct correlation between the particle at **r** and another at **r**'. This term multiplied by h(r'), then, yields the correlation between one particle at **r** and another at the origin. Since **r**' can be anywhere, it is integrated over the volume V. Seen in this way, the OZE expresses a relation between the two parts of the correlation function. This is only one equation for two unknowns: c(r) and h(r). In fact both are the same in the limit of low density, $<N>/V \rightarrow 0$,wherein c(r) = h(r). But, as discussed earlier, in this limit

$$h(r) \approx \exp(-u/KT) - 1.$$

As a minor improvement on this approximation, we may introduce an effective potential $u_{eff}(r)$ between two particles, which includes the effects of other particles. For example, $u_{eff}(r)$ would contain effects arising from the requirement of maximizing entropy of the system. The pair potential u(r) is between two bare atoms. Now we may write

$$h(r) \approx \exp(-u_{eff}/kT) - 1$$

Thus the difference between h(r) and c(r) is similar to that between u_{eff} (r) and u(r).

Closure Relations:

Closure relations can now be introduced between the two correlation functions, h(r) and c(r), and the pair potential u(r) so as to get a closed system of equations. We discuss the most commonly used closures below:

(i) *Mean Spherical Approximation (MSA)*

This is the simplest of all closure approximations, and is specified by

$c(r) = -u/kT$ for $r > \sigma$ (particle diameter)

$g(r) = 0$ for $r < \sigma$.

$h(r) = -1$ for $r < \sigma$.

The first is obtained by assuming a weak potential (compared to kT) in the low-density approximation. The second condition, which is same as the third, is simply the hard sphere condition. For a given pair-potential, the OZE is then solved using these two conditions. The solution would provide h(r) for $r > \sigma$ and c(r) for $r < \sigma$. Analytical solution of OZE is possible with MSA for Coulomb and screened Coulomb potentials, and hence has found applications in colloidal physics.

(ii) Percus-Yevic Closure (PYC)

This is a better approximation and is obtained as follows. The low-density approximation yields,

$$\begin{aligned} c(r) &\approx g(r) - 1 \\ &= \exp(-u/kT) - 1 \\ &= [1-\exp(u/kT)] \exp(-u/kT). \end{aligned}$$

Now we may replace the last term exp(-u/kT) by g(r) itself so as to correct for the low density approximation. Thus the PY closure relation is:

$c(r) = [1-\exp(u/kT)]\, g(r)$

Now the OZE is solved with this relation between c(r) and g(r) or h(r). Substitution in to the OZE will produce a non-linear equation for h(r). The mean spherical approximation (MSA) can also be obtained if the exponential in the PYC is approximated to first order and g(r) is approximated to unity for values of r outside the hard core. Hard sphere fluid systems are amenable to analytical solution using the PY closure.

(iii) Hyper-netted Chain Closure (HNC)

To motivate yet another closure relation, called the (H NC) closure, note that the right hand side of OZE, which is same as h - c, accounts for the correlation between two particles due to the presence of others. Now h - c= 0 in the limit of low density. Using $u_{eff}(r)$ introduced earlier we may write

$h - c \approx [\exp(-u_{eff}/kT)-1] - [\exp(-u/kT)-1] \approx (u - u_{eff}) / kT$

The last relation follows from the assumption that interaction energy is weaker than thermal energy, and approximating the exponential functions. We may now write

$g(r) \approx \exp(-u_{eff}/kT) = \exp[- u/kT + (u-u_{eff})/kT]$

Finally, $(u - u_{eff})/kT$ is eliminated in terms (h - c) to obtain the HNC closure:

$g(r) = \exp[- u/kT + h(r)-c(r)]$

The OZE together with this closure reduces to a highly non-linear. Its numerical solution produces all the correlation functions.

Rigorous derivations of these relations are available in the literature [1]. However, it is clear that once the pair potential u(r) is known, the OZE can be solved together with an appropriate closure to obtain h(r). Then the structure factor can be evaluated and results of scattering experiments interpreted. Parameters in the potential u(r) may then be modified to get quantitative information on the inter-particle interaction. Thermodynamics can then be derived via one of the two routes – virial or compressibility - mentioned earlier.

HNC for long ranged potentials and PYC for short ranged potentials are found to give good results when compared with results of Monte Carlo and molecular simulations of fluids. The pair distribution functions g(r) shown in figure-5 for hard sphere system are obtained using PYC. The corresponding S(q) are given in figure-6. Note that as the number density increases, i.e. as the mean separation between particles decreases, the peak position q_m in S(q) shifts to lower q values.

(iv) Rogers - Young Closure (RYC)

Though more accurate than MSA, the PYC and HNC approximations these closures also do not yield thermodynamic consistency. That is, the thermodynamic properties computed via two equivalent routes – virial and compressibility - are different. More specifically, the normalized isothermal compressibility:

$$\chi = \langle N \rangle kT\, K_T$$

where K_T isothermal compressibility, obtained from the compressibility equation and the virial equation of state have different numerical values. This arises due to the approximate nature of the closure relations. To impose thermodynamic consistency, Rogers and Young [3] proposed a closure relation by interpolating between the HNC and PY approximations. This is given by:

$$g(r) = \exp(-u/kT)\ [\ 1+ \exp\{\ f(r)\ \ (h-c)\} - 1]\ /\ f(r)$$

The mixing function f(r) is chosen as:

$$f(r) = 1 - \exp(-\alpha\ r)$$

where α is a parameter to be adjusted to impose thermodynamic consistency. The limit $\alpha \to 0$ (with r fixed) yields the PY closure: $c=[1-\exp(u/kT)]g$. The HNC closure: $g = \exp(-u/kT + h - c)$ follows from the opposite limit $\alpha \to \infty$ (with r fixed). Further, for a specific value of α, the choice of f(r) assures that RY closure reduces to the HNC closure for $r >> 1/\alpha$ and to the PY closure for $r << 1/\alpha$. The RY α is fixed using the condition that χ calculated by the two routes are same. However, this procedure restores thermodynamic consistency only partially since properties computed via the third route of energy equation may not agree with those obtained by the other two routes. Nevertheless, RY closure results are in good agreement with simulation data on systems with repulsive interactions. The main drawback of RY closure, and also HNC and PY, is that the OZE has to be solved using numerical techniques. An efficient approach is to use the Newton - Ralphson method and conjugate gradient iterations, which can be implemented easily by using the fast Fourier transform algorithms [4]. The basic idea used in the numerical approach is discussed below.

Numerical Solution of OZE:

All the numerical approaches make use Fourier transforms, h(k) and c(k), of h(r) and c(r): Fourier transform of OZE, which has a displacement kernel, yields the relation:

$$h(k) = c(k) / [\ 1 - \langle N \rangle\ c(k) / V\ ]$$

The general closure can be written as:

$$c(r) = f\ [g(r), h(r), u(r)]$$

where f is a non-linear function of the arguments. The calculation procedure is summarized below:

- Start with initial guess values for all functions, g(r) and h(r). The low-density approximation may be a good approximation.
- Calculate $c(i\ \Delta r)$ for $1 \le i \le I_{MAX}$, where Δr is a suitable mesh size. Typical values of I_{MAX} and Δr should be such that about 50 units of d are covered with enough points to resolve the variation of g(r). About 100 points in one σ may give good resolution.
- Use a FFT program to calculate $c(j\ \Delta k)$ and hence $h(j\ \Delta k)$ for $1 \le j \le I_{MAX}$, where $\Delta k\ \Delta r = \pi$.
- Use inverse-FFT to determine $h(i\ \Delta r)$ for $1 \le i \le I_{MAX}$.
- Use closure relation to calculate $c(i\ \Delta r)$ for $1 \le i \le I_{MAX}$
- Repeat the steps until point wise convergence to required accuracy is obtained in g(r).

•Conclusion:

The concept of pair distribution function is a useful concept in fluid physics. It also allows us to visualize all the different states of matter – gaseous, liquid, solid, etc., in a unified manner. All the thermodynamic quantities can be calculated in terms of the pair distribution function via two routes – virial and compressibility. A third route also may be added using the energy equation, where in the free energy can be computed using the relation

$$E = \partial\ (F/T) / \partial\ (1/T)$$

Structure factor and scattering intensity can be interpreted using the pair distribution function. Integral equation theories using the OZE and various closure relations can be used to get good results for the pair distribution function.

The concept of pair distribution can be extended for mixtures: For a two-component mixture we may introduce three distributions, $g_{11}(r)$, $g_{12}(r)$ and $g_{22}(r)$. However, three coupled OZEs will have to be solved for this case. An-isotropic systems, e.g., molecular fluids, can also be studied with this concept, but by including relative orientation co-ordinates (θ, φ) of two molecules in the pair distribution function $g = g(r, \theta, \varphi)$.

References:

1. J. P. Hansen and I. R. Mc Donald, *Theory of Simple Fluids* (Academic Press, 1985)
2. J. Israelachvilli, *Intermolecular and Surface Forces* (Academic Press, 1992)
3. F.J.Rogers and D.A.Young, *Physical Review*, A30, 999 (1984).
4. G.Zerah, *Journal of Computational Physics*, 61, 280 (1985).

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