Theory of liquids and polymers

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Contents

1 Introduction

The physics of liquids and polymers comprises a very large area of physical research, which nowadays operates under the name *soft matter physics*, which also includes the investigation of colloids and liquid crystals. The aim of the present set of lectures is twofold: Firstly I want to give an introduction to the structure, thermodynmamics and dynamics of liquids binary solutions and polymers which enables an undergraduate or graduate student to read textbooks and possibly start to work in this field.

The starting point is the description of distribution functions which describe the statistical arrangements of atoms or molecule in a simple liquid[1].

The main concepts will involve *mean field theories* like the Perkus-Yevick theory and the Random Phase Approximation which relate the forces to the distribution functions.

The Random Phase Approximation (RPA) will also turn out to be the basis of the thermodynamics of *binary solutions*, which has been used by *Flory* and *Huggins* to discuss polymer melts and solutions, as we shall do in the end of part I.

We shall not give an introduction to the general statistical mechanics of an interacting many-body system but take the knowledge of these concepts for granted. In particular the fact that in a *classical* liquid the *static* and *dynamic* aspects of such a system can be discussed separately forms the basis of the two-fold structure of the present lecture series.

Before turning to the discussion of polymer melts and solutions we shall try to get acquainted to *scaling concepts* by discussing *random walks* and *fractals*. On this basis we then shall discuss the scaling concepts of polymer science.

Part II. of the lecture series will mainly be devoted to discuss the dynamics of simple and complex liquids in terms of the generalized hydrodynamics concept introduced by *Mori* and *Zwanzig*. The highlight will be the discussion of the liquid-glass transition and its discussion in terms of the *mode-coupling theory* of *W. Götze*. In the end we shall discuss the peculiarities of the dynamics of polymer melts and solutions.

2 Structure of Liquids

2.1 Molecular distribution functions

The *structure* of a liquid is governed by the statistical distribution of the centers of gravity of the atoms or molecules. Of course the latter keep moving, but we can ask about the atomic distributions if one could perform a snapshot of the atomic arrangements. This is what we call the (static) *structure* of the liquid. We now pose the question of how a collection of $N \approx 10^{23}$ atoms or molecules (or much less in a computer simulation) are distributed inside a certain volume V. We call the probability for these particles to occupy volume elements $d^3\mathbf{r}_1, d^3\mathbf{r}_2, \ldots d^3\mathbf{r}_N$ around positions $\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N$

$$P(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N)d^3\mathbf{r}_1, d^3\mathbf{r}_2, \ldots d^3\mathbf{r}_N \,. \tag{1}$$

$P(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N)$ is the *probability density* of the configuration $\{\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N\}$ and is normalized to 1:

$$\int_V \prod_{\alpha=1}^{N} d^3\mathbf{r}_\alpha P(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N) = 1 \,. \tag{2}$$

If a physical quantity A depends on the position of the particles the *configurational average* can be calculated as

$$\langle A \rangle = \int_V \prod_{\alpha=1}^{N} d^3\mathbf{r}_\alpha A(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N) P(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N) \,. \tag{3}$$

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[1]We are going to call a liquid *simple* if it can be described in terms of a set of *pairwise intermolecular forces or potentials*.

One can select $n < N$ particles in order to define the *reduced n-particle densities*

$$\rho^{(n)}(\mathbf{r}_1, \mathbf{r}_2, \dots \mathbf{r}_N) = \frac{N!}{(N-n)!} \int_V \prod_{i=n+1}^{N} \mathrm{d}^3\mathbf{r}_\alpha P(\mathbf{r}_1, \mathbf{r}_2, \dots \mathbf{r}_N), \tag{4}$$

In the case of a *complete random arrangement*, which is only realized in an ideal gas we have

$$\rho(\mathbf{r}_1, \mathbf{r}_2, \dots \mathbf{r}_N) = \left(\frac{N}{V}\right)^n \equiv \rho_0^n. \tag{5}$$

where ρ_0 is called the *homogeneous density* of the liquid. The deviation from this random distribution is given by the *n-particle correlation functions* $g^{(n)}$, which are defined as follows

$$\rho^{(n)}(\mathbf{r}_1, \mathbf{r}_2, \dots \mathbf{r}_N) = \rho_0^n g^{(n)}(\mathbf{r}_1, \mathbf{r}_2, \dots \mathbf{r}_N). \tag{6}$$

In *homogeneous* systems we have
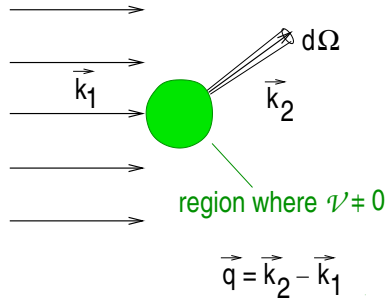
$$\rho^{(1)}(\mathbf{r}_1) = \rho_0 \tag{7}$$

$$g^{(1)}(\mathbf{r}_1) = 1. \tag{8}$$

In a *homogeneous* and *isotropic* material we have

$$g^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = g(|\mathbf{r}_1 - \mathbf{r}_2|) \tag{9}$$

$g(r)$ is called *radial pair correlation function* or *radial pair distribution function* and can, as we shall see in the nect section, be determined by neutron or x-ray diffraction.

2.2 Scattering theory

$$\vec{q} = \vec{k}_2 - \vec{k}_1$$

We want to describe the scattering of X-rays or neutrons from a simple liquid sample. We study an ingoing plane wave (1st term) and an outgoing scattered spherical wave (2nd term) of the following asymptotic form

$$\psi(\mathbf{r}) \overset{|\mathbf{r}| \to \infty}{=} e^{i\mathbf{k}_1 \cdot \mathbf{r}} + f(\theta)\frac{1}{r}e^{ik_2 r} \tag{10}$$

The scattering cross-section into the solid angle element $\mathrm{d}\Omega$ in the direction of $\mathbf{k}_2$ is then given by the modulus-square of the scattering amplitude

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = |f(\theta)|^2 \tag{11}$$

If the scattering potential (the potential between the scattered rays and the particles) can be decomposed as

$$\mathcal{V}(\mathbf{r}) = \sum_{\alpha=1}^{N} v(\mathbf{r} - \mathbf{r}_\alpha) \tag{12}$$

the scattering amplitude is given in 2nd approximation (*Born approximation*)

$$f(\theta) = -\frac{m}{2\pi\hbar^2}\langle \mathbf{k}_2|\mathcal{V}|\mathbf{k}_1\rangle = -\frac{m}{2\pi\hbar^2}\mathcal{V}(\mathbf{q}) = -\frac{m}{2\pi\hbar^2}\sum_{\alpha=1}^{N} e^{i\mathbf{q}\cdot\mathbf{r}_\alpha}v(\mathbf{q}) \equiv \sum_{\alpha=1}^{N} e^{i\mathbf{q}\cdot\mathbf{r}_\alpha}f(\mathbf{q}), \tag{13}$$

$f(\mathbf{q})$ is called *form factor* and has the unit of length. In the case of *energy unresolved* neutron or X-ray diffraction there is no net energy exchange with the sample, i.e. $|\mathbf{k}_1| = |\mathbf{k}_2|$. In an isotropic material the form factor depends only on the modulus of the exchanged momentum, which is given by

$$q = |\mathbf{k}_1 - \mathbf{k}_2| = k_1\sqrt{2[1-\cos(\theta)]} = \frac{4\pi}{\lambda}\sin\left(\frac{\theta}{2}\right), \tag{14}$$

where θ is the angle between $\mathbf{k}_1$ and $\mathbf{k}_2$ and $\lambda = \frac{2\pi}{|k_1|}$ is the wavelength.

In the case of neutrons, which scatter from the nuclei, whose potential $v(\mathbf{r})$ is extremely short-ranged, $f(q)$ does not depend on q (in the range of interest $q < 20$ Å^{-1}) and is called *scattering length* and is denoted by the letter b.

Inserting (13) into (11) and averaging over an ensemble of different configurations we obtain

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = |f(q)|^2 \left\langle \sum_{\alpha,\beta=1}^{N} e^{i\mathbf{q}\cdot[\mathbf{r}_\alpha - \mathbf{r}_\beta]} \right\rangle \equiv |f(q)|^2 N S(q), \tag{15}$$
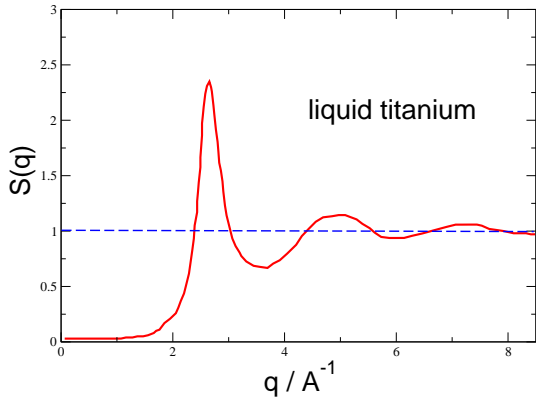
where $S(q)$ is the *static structure factor*

$$S(q) = \frac{1}{N} \left\langle \sum_{\alpha,\beta=1}^{N} e^{i\mathbf{q}\cdot[\mathbf{r}_\alpha - \mathbf{r}_\beta]} \right\rangle \tag{16}$$

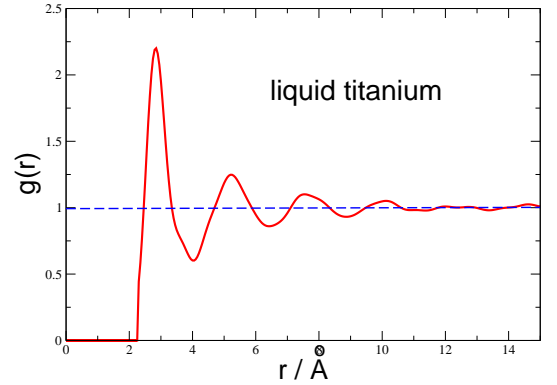It can be shown that $S(q)$ is related to the pair correlation function by a simple Fourier transform

$$S(q) = 1 + \rho_0 \int_{-\infty}^{\infty} \mathrm{d}^3\mathbf{r}\, e^{i\mathbf{q}\mathbf{r}}[g(r) - 1] \tag{17}$$

which can - because g and S depend only on the moduli of their arguments - be simplified as

$$S(q) = 1 + \frac{4\pi\rho_0}{q} \int_0^{\infty} \mathrm{d}r\, r\sin(qr)[g(r) - 1] \tag{18}$$

Structure factor of liquid titanium, measured by *Lee et al*

Corresponding pair distribution function calculated via Fourier-back transform from (18) with $\rho_0 = 0.05$

2.3 Thermodynamic relations

We are now assuming that the liquid under consideration can be described by a classical Hamiltonian

$$\mathcal{H} = \sum_{\alpha=1}^{N} \frac{1}{2}m\dot{\mathbf{r}}_\alpha^2 + \frac{1}{2}\sum_{\alpha\neq\beta} \phi(|\mathbf{r}_\alpha - \mathbf{r}_\beta|). \tag{19}$$

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There are the following thermodynamic relationships (*equations of state*):

Potential Energy

$$\frac{1}{N} \langle E_{\text{pot}} \rangle = 2\pi \rho_0 \int_0^\infty \mathrm{d}r \ r^2 \phi(r) g(r) \tag{20}$$

Pressure

$$\langle P \rangle \frac{V}{N k_B T} = \langle P \rangle \frac{1}{\rho_0 k_B T} = 1 - \frac{2\pi \rho_0}{3 k_B T} \int_0^\infty \mathrm{d}r \ r^3 \phi'(r) g(r) \tag{21}$$

Number fluctuations and isothermal compressibility κ_T

$$\frac{\langle N \rangle^2 - \langle N^2 \rangle}{N} = \rho_0 k_B T \left(-\frac{1}{V} \frac{\partial V}{\partial P} \right)_T = \rho_0 k_B T \kappa_T \tag{22}$$

$$= S(q = 0) = 1 + 4\pi \rho_0 \int_0^\infty \mathrm{d}r \ r^2 [g(r) - 1] \tag{23}$$

2.4 Direct correlation function

The static structure factor can be split in an obvious way into a *self* and *distinct* part by separating the $\alpha \neq \beta$ term in the summation over the particles:

$$S(q) = \frac{1}{N} \left\langle \sum_{\alpha,\beta=1}^N e^{i\mathbf{q}\cdot[\mathbf{r}_\alpha - \mathbf{r}_\beta]} \right\rangle = 1 + \frac{1}{N} \left\langle \sum_{\alpha \neq \beta}^N e^{i\mathbf{q}\cdot[\mathbf{r}_\alpha - \mathbf{r}_\beta]} \right\rangle \equiv 1 + \rho_0 h(q) \tag{24}$$

The self part is just equal to unity, and the distinct part is ρ_0 times the Fourier transform of the *deviation of $g(r)$ from unity*, i.e.

$$h(r) = g(r) - 1 . \tag{25}$$

We now sub-divide the correlation function $h(r)$ into a part which involves only a particular pair of atoms, say $\mathbf{r}_1$ and $\mathbf{r}_2$ and a part which involves more than two atoms. Following Ornstein and Zernike, the first term is called *direct correlation function*. The second part can be generated by combining several direct functions in the following way:

$$h(r_{12}) = c(r_{12}) + \rho_0 \int \mathrm{d}^3\mathbf{r}_3 c(r_{13}) c(r_{32}) + \rho_0^2 \int \mathrm{d}^3\mathbf{r}_3 \int \mathrm{d}^3\mathbf{r}_4 c(r_{13}) c(r_{34}) c(r_{42}) + \ldots \tag{26}$$

The terms under the $\mathbf{r}_3$ integral can be summed again to give the function $h(r_{32})$:

$$h(r_{12}) = c(r_{12}) + \rho_0 \int \mathrm{d}^3\mathbf{r}_3 c(r_{13}) h(r_{32}) \tag{27}$$

This is the so-called *Ornstein-Zernike equation*. It is the starting point for some *integral equation theories* for $g(r)$ (See section 2.7).

If we introduce the Fourier transform $c(q)$ of $c(r)$ and use the convolution theorem we obtain

$$h(q) = \frac{c(q)}{1 - \rho_0 c(q)} \tag{28}$$

which finally leads to

$$S(q) = \frac{1}{1 - \rho_0 c(q)} \tag{29}$$

2.5 Density response function

We can be interested in the density change due to the presence of an external potential

$$\mathcal{V}_{\text{ext}}(\mathbf{r}) = \sum_\alpha \phi_{\text{ext}}(\mathbf{r} - \mathbf{r}_\alpha) \,. \tag{30}$$

The average density in the presence of $\mathcal{V}_{\text{ext}}(\mathbf{r})$ is given by[2]

$$\langle \rho(\mathbf{r}) \rangle_{\mathcal{V}_{\text{ext}}} = \frac{1}{Z_{\mathcal{V}_{\text{ext}}}} \int \frac{\mathrm{d}^3 \mathbf{r}'}{V} \prod_\alpha \mathrm{d}^3 \mathbf{r}_\alpha \underbrace{\sum_\alpha \delta(\mathbf{r} - \mathbf{r}_\alpha)}_{\rho(\mathbf{r})} e^{-\beta V\{\mathbf{r}_\alpha\}} e^{-\beta \mathcal{V}_{\text{ext}}(\mathbf{r}')} \tag{31}$$

with

$$Z_{\mathcal{V}_{\text{ext}}} = \int \frac{\mathrm{d}^3 \mathbf{r}'}{V} \prod_\alpha \mathrm{d}^3 \mathbf{r}_\alpha e^{-\beta V\{\mathbf{r}_\alpha\}} e^{-\beta \mathcal{V}_{\text{ext}}(\mathbf{r}')} \tag{32}$$

and

$$V\{\mathbf{r}_\alpha\} = \frac{1}{2} \sum_{\alpha \neq \alpha'} \phi(|\mathbf{r}_\alpha - \mathbf{r}_{\alpha'}|) \tag{33}$$

Defining $\langle \rho \rangle_0$ to be the density average with $\mathcal{V}_{\text{ext}} = 0$ and going over to Fourier Transforms we obtain to lowest order in $\mathcal{V}_{\text{ext}} = 0$ (*linear response*)

$$\delta\rho(\mathbf{q}) = \langle \rho(\mathbf{q}) \rangle_{\mathcal{V}_{\text{ext}}} - \langle \rho \rangle_0 = -\frac{\beta}{V} \langle \rho^*(\mathbf{q})\rho(\mathbf{q}) \rangle \phi_{\text{ext}}(\mathbf{q}) \equiv \chi(q)\phi_{\text{ext}}(\mathbf{q}) \tag{34}$$

the (static) *response function* or *susceptibility* is therefore given by

$$\chi(q) = -\beta \rho_0 S(q) \tag{35}$$

This is a version of the famous *fluctuation-dissipation theorem*.

2.6 Mean field potential and random phase approximation

In order to to formulate an approximate theory for $S(q)$ it is useful to represent the interatomic interactions in terms of a *mean field potential $U(q)$* which acts on the individual atoms as an *effective external polarization potential*

$$\phi_{\text{pol}}(\mathbf{q}) \equiv U(q)\delta\rho(\mathbf{q}) \,. \tag{36}$$

One then can use the *non-interacting Curie response function $\chi_0 = -\beta\rho_0$* to write down the density change in terms of the real and the effective external potential:

$$\begin{aligned} \delta\rho(q) &= \chi_0 \left[\phi_{\text{pol}}(\mathbf{q}) + \phi_{\text{ext}}(\mathbf{q}) \right] \\ &= \chi_0 \left[U(q)\delta\rho(\mathbf{q}) + \phi_{\text{ext}}(\mathbf{q}) \right] \\ &= \chi(\mathbf{q})\phi_{\text{ext}}(\mathbf{q}) \end{aligned} \tag{37}$$

from which follows

$$\chi(q) = \frac{\chi_0}{1 - \chi_0 U(q)} \tag{38}$$

If we compare this with (29) we find

$$c(q) = -\beta U(q) \tag{39}$$

We conclude that $-k_B T c(r)$ has the meaning of a *mean-field* potential. Identifying $U(r)$ with the true pairwise potential $\phi(r)$ is called the *Random-Phase approximation*. It gained its name from the theory of interacting electrons (or nucleons). There the RPA involves the decoupling of electronic correlation functions, which is only possible if the wave functions are assumed to have "random phases".

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[2]$\beta = 1/k_B T$.

2.7 Integral equation theories for $g(r)$

We recall again the Ornstein-Zernike (OZ) relation between $g(r) = 1 + h(r)$ and the direct correlation function $c(r)$ (in a slightly modified form):

$$h(r) = c(r) + \rho_0 \int \mathrm{d}^3\mathbf{r}' h(|\mathbf{r} - \mathbf{r}'|)c(r') \tag{40}$$

The function $c(r)$ can, on the other hand, be calculated by functional integral and functional derivative techniques. Using such techniques and an appropriate diagram formalism one can come up with a second relation between $c(r)$ and $g(r)$ which is called the *closure relation* and constitutes a specific *integral equation theory* for $g(r)$ The most popular closure relations are

Percus-Yevick (PY):

$$c(r) = g(r)\left[1 - e^{\beta\phi(r)}\right] \tag{41}$$

Hypernetted-Chain (HNC):

$$c(r) = -\beta\phi(r) + h(r) - \ln g(r) \tag{42}$$

These closures together with the OZ relation constitute a self-consistent set of integral equations for $h(r)$ or $g(r)$.

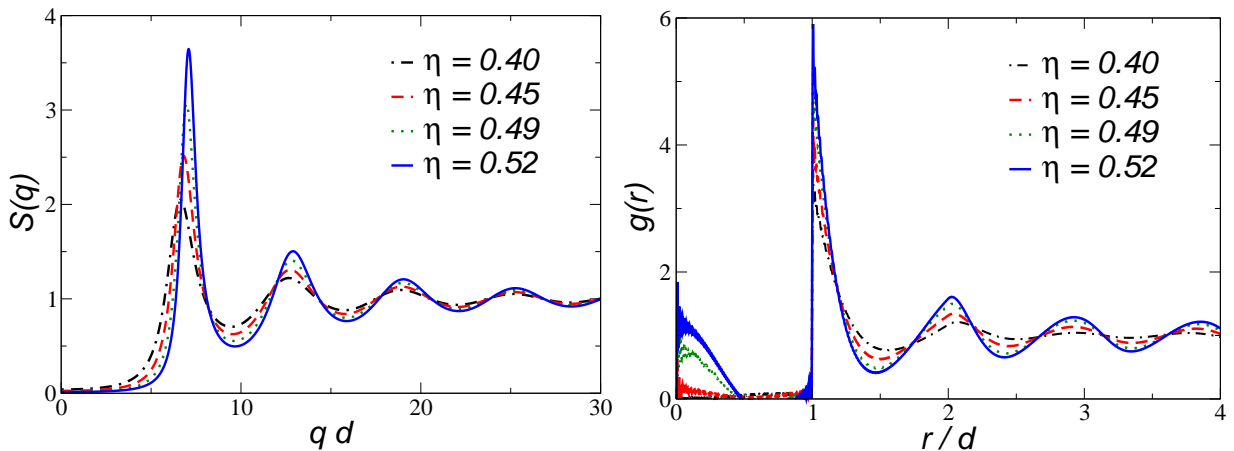## 2.8 PY solution for hard spheres

Fig. 4a and Fig. 4b: Hard-sphere PY structure factors $S(q)$ and pair correlation functions $g(r)$

We now consider the hard-sphere potential

$$\phi_{HS}(r) = \begin{cases} \infty & r < d \\ 0 & r > d \, , \end{cases} \tag{43}$$

where d is the *hard-sphere diameter*. In this case the PY integral equation can be solved *exactly*. The solution is given in terms of the *packing fraction*

$$\eta = \frac{\text{volume filled with spheres}}{\text{total volume}} = \frac{\pi}{6}d^3\rho_0 \tag{44}$$

and the dimensionless variable $x = r/d$

$$c(r) = \begin{cases} \lambda_1 - 6\eta\lambda_2 x + \frac{1}{2}\eta\lambda_1 x^3 & x < 1 \\ \\ 0 & x > 1 \, , \end{cases} \tag{45}$$

with

$$\lambda_1 = (1 + 2\eta)^2/(1 - \eta)^4 \tag{46a}$$

$$\lambda_2 = (1 + \frac{1}{2}\eta)^2/(1 - \eta)^4 \tag{46b}$$
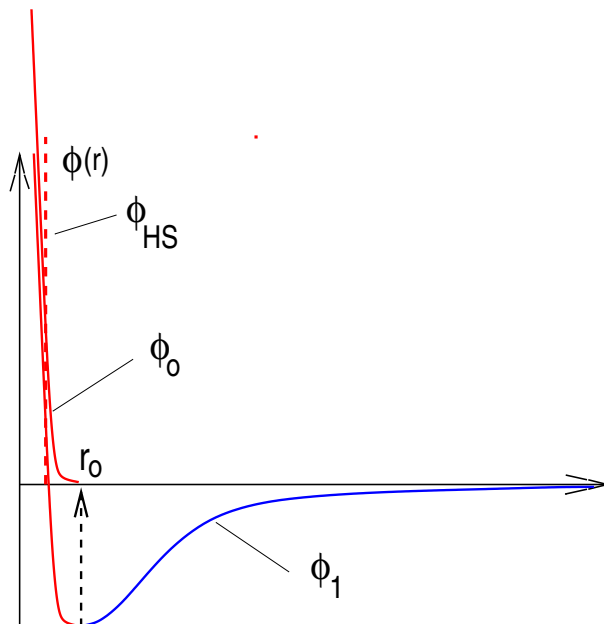
2.9 Hard-sphere reference sytem

Fig. 5:
Breakdown of a potential $\phi(r)$ into a hard-sphere-like part $\phi_0(r)$ and a long-range (LR) part $\phi_1(r)$.

We now want to relate the structure of a simple liquid, which is described by a pairwise potential $\phi(r)$, in terms of the structure of hard spheres. For doing so we adopt the following procedure (due to *Weeks, Chandler and Andersen* 1971). Denoting the separation at the minimum r_0 we define

$$\phi_0(r) = \begin{cases} \phi(r) - \phi(r_0) & r < r_0 \\ 0 & r > r_0 \, , \end{cases} \tag{47}$$

$$\phi_1(r) = \begin{cases} \phi(r_0) & r < r_0 \\ \phi(r) & r > r_0 \, , \end{cases} \tag{48}$$

We then relate a HS potential to ϕ_0. This can be done *"by hand"*, but a more systematical procedure is to require that some physical property of the hypothetical fluid described by $\phi_0(r)$ should coincide with a HS fluid with HS diameter d. One can demand that the spatial integral over $g_0(r)$ should coincide with that over $g_{HS}(r)$. This requirement is equivalent to demanding that the isothermal compressibilities of the two fluids should co-incide.

2.10 Mean-spherical approximation

A quite successful integral equation theory for the structure of simple liquids is the *mean-spherical approximation* (MSA), which works with the procedure introduced in the last section and introduces the two constraints

$$g(r) = 0 \qquad\qquad r < d \tag{49a}$$

$$c(r) = -\frac{1}{k_B T}\phi_1(r) \qquad r > d \tag{49b}$$

i.e. we use a *random-phase approximation* for the *long-range* (LR) part of the direct correlation function and use the short-range part for just demanding that $g(r)$ should be 0 for $r < d$. Together with the Ornstein-Zernike relation this constitutes an integral-equation theory for $g(r)$ which in many cases is even more successful as the PY or HNC theory. Of course it reduces to the PY theory for $\phi_1 = 0$.

2.11 Perturbative RPA for the compressibility of liquids

The main features of the structure factors of simple liquids can be roughly accounted for by a HS structure. This means that the repulsive part of the potential $\phi_0(r)$ essentially acts as a HS potential, and that the LR part $\phi_1(r)$ does not really play a major role for $S(q)$. This is, in fact, the reason for the success of the MSA. Studying the structure of simple liquids -especially liquid metals- it has turned out that, if their structure factors were fitted with the HS-PY model in a state just above their melting points, the packing fraction was always in the range between $0.42 < \eta < 0.45$. The reason for this lies in the fact that there exists a *maximum* packing fraction $\eta_c \approx 0.5$ for the particles to be able to pass each other in order to maintain liquid fluidity. If η exceeds η_c the *glass transition* occurs, and the liquid turns into an amorphous solids - if (and this is an important *if*) there was given no chance to nucleate towards a crystalline solid. A crystalline solid has always a lower (free) energy than the amorphous one of the same chemical composition but is separated from the liquid state by the nucleation barrier.

Returning to the discussion of the role of the LR part of the interatomic potential there *is* a regime where it is quite important. This is the *long-wavelength* regime $q \ll q_0$, where q_0 marks the maximum of $S(q)$.
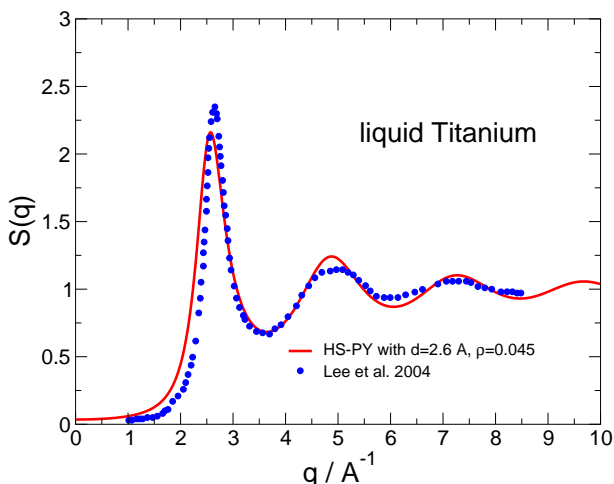

Fig 5 Structure factor of liquid Ti, compared with a HS-PY model calculation

We have noted above, that in this limit we have

$$\lim_{q \to 0} S(q) = \rho_0 k_B T \kappa_T \tag{50}$$

So our statement involves the *thermodynamic limit* of $S(q)$, namely its *compressibility* limit. In this limit we can try the validity of the RPA - but not for the *entire* direct correlation function, but rather for the LR part of the potential. So we write

$$
\begin{align}
c(r) &= c_0(r) + c_1(r) \tag{51a} \\
c_0(r) &= c_{HS}(r) \tag{51b} \\
&\tag{51c}
\end{align}
$$

with d chosen such that the ϕ_0 system has the same $S(q=0)$ as the ϕ_{HS} system. For $c_1(r)$ we write

$$c_1(r) = -\frac{1}{k_B T} U_1(r) \tag{52}$$

For the mean-field potential $U_1(r)$ we may apply the *plain* RPA or the *extended* RPA (ERPA)

$$
\begin{align}
U_1(r) &= \phi_1(r) \qquad \text{RPA} \tag{53a} \\
U_1(r) &= g(r)\phi_1(r) \qquad \text{ERPA} \tag{53b}
\end{align}
$$

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Both versions can be derived and motivated by a density functional formalism (*Evans and Schirmacher 1978.*

Inserting either of (53a) into (29) leads to

$$S(q = 0) = \frac{S_{HS}(0)}{1 + S_{HS}(0)\frac{\rho_0}{k_B T}U_1(0)} \tag{54}$$

with

$$U_1(0) = \begin{cases} 4\pi \int_0^\infty \mathrm{d}r r^2 \phi(r) & \text{RPA} \\ \\ 4\pi \int_0^\infty \mathrm{d}r r^2 g(r)\phi(r) & \text{ERPA} \end{cases} \tag{55}$$

We noted previously that simple liquids - predominantly liquid metals - could be described near its melting point in terms of a HS fluid with packing fraction $\eta \approx 0.43$. In HS-PY approximation such a packing fraction leads to a value of $S(0)$ of ≈ 0.03. From (55) we expect that materials with a predominantly *attractive* LR interaction $S(0)$ is *larger* than the HS value, and for the other case that it is *smaller*.

Fig. 6:

Potentials $\phi(r)$ for metals and insulators

Let us take a closer look at the interatomic potentials $\phi(r)$ wich characterize insulating liquids and metals. The interatomic potentials $\phi(r)$ of *Insulating* simple liquids such as liquid rare gases or CH_4 are well described by the *Lennard-Jones* potential

$$\phi(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right]. \tag{56}$$

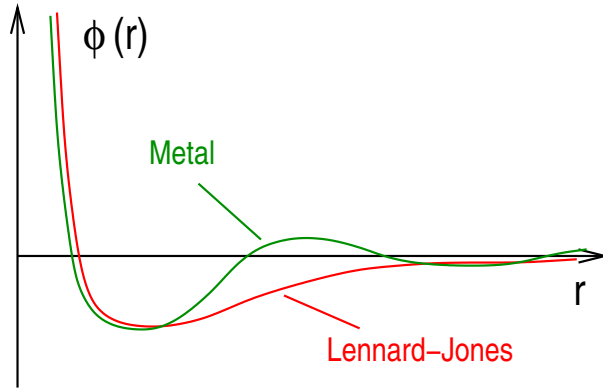If we subdivide this potential in the way described above into a hard-core (hard-sphere) part ϕ_0 and a long-range part ϕ_1 we realize that the latter is attractive in the whole r range, from which follows that both in the RPA ad ERPA the correction $U_1(0)$ is negative definite. This leads to an *increase* of $S(0)$ as compared to the hard-sphere value $S_{HS}(0)$ as can be verified from Table 1.

Table 1. The long wavelength limit of the structure factor in insulating liquids at their triple points. ρ is the number density, T the absolute temperature, and η is the calculated packing fraction. For the meaning of the other symbols see text.

	ρ (Å^{-3})	T (K)	$\epsilon_i k_B$ (K)	σ (Å)	η	$a_{hs}(q = 0)$	$a_{RPA}(q = 0)$	$a_{ERPA}(q = 0)$	$a(q = 0)$ experiment
Ne	0·0373	25	35·5[a]	2·75	0·438	0·028	0·056	0·055	0·052[g]
Ar	0·0210	85	116·4[b]	3·37	0·453	0·025	0·044	0·044	0·050[e]
			119·8[c]	3·4	0·465	0·022	0·037	0·037	
Kr	0·0175	116	163·1[d]	3·63	0·472	0·021	0·033	0·034	0·049[f]
CH$_4$	0·0171	90	147·4[b]	3·7	0·487	0·017	0·026	0·027	0·030[e]

Table 2. The long wavelength limit of the structure factor in liquid metals at their melting points. ρ is the number density, T the absolute temperature and R_c is the calculated value of the pseudopotential parameter. The various structure factors are explained in the text.

	ρ (Å^{-3})	T (K)	R_c (au)	$a_{RPA}(q=0)$	$a_{ERPA}(q=0)$	$a(q=0)$ experiment
Li	0·0445	453	1·28	0·021	0·021	0·026[b]
Na	0·0243	371	1·70	0·024	0·024	0·023[a]
K	0·0127	337	2·25	0·026	0·027	0·024[a]
Rb	0·0104	312	2·45	0·027	0·028	0·022[a]
Cs	0·0083	302	2·67	0·028	0·028	0·024[a]
Cu	0·0757	1356	1·10	0·021	0·021	0·021[a]
Ag	0·0521	1234	1·32	0·022	0·022	0·019[a]
Au	0·0529	1336	1·33	0·022	0·022	0·012[c]
Mg	0·0394	923	1·31	0·019	0·020	0·025[d]
Zn	0·0605	693	0·98	0·015	0·015	0·015[a]
Cd	0·0430	594	1·20	0·017	0·017	0·011[a]
Hg	0·0411	238	1·17	0·012	0·013	0·005[a]
Al	0·0531	933	1·04	0·014	0·014	0·017[a]
Ga	0·0526	303	0·92	0·007	0·007	0·005[a]
In	0·0369	429	1·27	0·012	0·012	0·006[a]
Tl	0·0333	577	1·37	0·015	0·015	0·010[a]
Sn	0·0354	505	1·36	0·010	0·009	0·007[a]
Pb	0·0310	600	1·48	0·012	0·012	0·009[a]
Sb	0·0321	904	1·54	0·010	0·010	0·020[a]
Bi	0·0290	542	1·60	0·008	0·008	0·009[a]

The experimental results for the isothermal compressibility were taken from [a]Webber and Stephens (1968), [b]Ruppersberg and Speicher (1976), [c]Bek and Steeb (1977), [d]McAlister et al (1974).

Let us now turn our attention to the interatomic potential of a metal which does not have unfilled d orbitals (i.e. *not* transition metals which have a complicated interatomic potential). In such *simple* metals the interatomic potential is a sum of a Coulomb repulsion of the ion cores of charge Ze (Z is the number of conduction electrons per atom or *valence*) and a contribution which describes the screening of the

conduction electrons, featuring the electron-ion potential $v_i(q)$ and the electronic response function $\chi_e(q)$:

$$\phi(r) = \frac{Z^2 e^2}{4\pi\epsilon_0 r} + \frac{1}{(2\pi)^3} \int d^3\mathbf{q} e^{i\mathbf{q}\mathbf{r}} |v_i(q)|^2 \chi_e(q) \tag{57}$$

For most simple liquid metals at their melting points the electron gas has a Fermi distribution like that at $T = 0$, which has a sharp cutoff at the Fermi energy $E_F = \hbar^2 k_F / 2m$, where $k_F = [3\pi^2 n]^{1/3}$ is the Fermi wavenumber, m is the electron mass and $n = Z\rho_0$ is the electron density. This is so, because the corresponding temperature (Fermi temperature $T_F = E_F/k_B$ is of the order of 12000 K. This leads to a sharp drop-off of $\chi_e(q)$ near $q = 2k_F$, which, in turn leads – in the r dependence of $\phi(r)$ to oscillations (*Friedel oscillations*) as depicted in the figure. If $\phi(r)$ is now divided into the hard-core and long-range parts it turns out that the r integral of $r^2\phi_1(r)$ takes a *positive* value, which is small for $Z = 1$ (alkali metals) but becomes large for $Z > 1$ (polyvalent metals). This leads to a *decrease* of the compressibility of the liquid metals as compared to the hard-sphere fluid, which can be checked in Table 2.

2.12   Relation to the van-der-Waals equation of state

There exists a relation between the phenomenological equation of state of van der Waals for the liquid-vapor phase separation and the perturbative RPA treated in the previous subsection. The van-der-Waals equation of state for the pressure reads

$$\left(p + \frac{A}{V^2}\right)(V - B) = Nk_BT \tag{58a}$$

or
$$p = -\frac{A}{V^2} + \frac{Nk_BT}{V - B} \tag{58b}$$

where A and B are phenomenological parameters called internal pressure and covolume. This equation of state describes the quantities of state of expanded liquids near their critical point very well, especially the liquid-vapor phase separation.

The perturbative RPA formula (**??**) can be written as

$$\frac{1}{S(0)} = -\frac{1}{k_BT}\frac{V^2}{N}\frac{\partial p}{\partial V} = \frac{1}{S_{HS}(0)} + \frac{U_1(0)}{k_BT} \tag{59}$$

We take the derivative of the van-der-Waals pressure with respect to the volume

$$\frac{\partial p}{\partial V} = \frac{2A}{V^3} - \frac{Nk_BT}{(V - B)^2} \tag{60}$$

and insert it into the definition of $1/S(0)$ displayed in the first part of (59):

$$\frac{1}{S(0)} = -\frac{1}{k_BT}\frac{V^2}{N}\frac{\partial p}{\partial V} = \frac{V^2}{(V - B)^2} - \frac{1}{k_BT}\frac{2A}{VN} \tag{61}$$

We see that this equation has a similar structure as the perturbative RPA: If we identify the first term with a hard-core repulsion (as done, in fact, by van-der Waals), the second one is the interaction term with interaction parameter $U(0) = -2A/VN$. Therefore we expect that the perturbative RPA with negative (attractive) interaction parameter $U(0)$ also describes a liquid-vapor phase separation.

It is in fact well known that a hard-sphere fluid does not show any liquid-vapor phase separation. Therefore it is called a "fluid". These considerations will become quite of importance in the next section which deals with binary solutions.

You might be asking how the liquid-vapor phase separation is to be described if there is no negative interaction parameter. The answer is that the equation of state of fluid metals near the critical point is

much more complicated as that of insulating liquids. It does, in fact, *not* obey the law of corresponding states which can be described in terms of the van-der-Waals equation. Between the condensed liquid state and the vapor state there is a *metal-nonmetal transition*, which is until today not completely understood. The main feature of this transition is the breakdown of the screening of the conduction electrons due to the fact that at low densities the electron-electron repulsion becomes dominant and leads to a localization of the electrons near the ionic cores. Furthermore, in fluid alkali metals there is a tendency for forming diatomic molecules on the vapor side of the liquid-vapor transition.

2.13 The resistivity of liquid metals

We wish to evaluate the resistivity of liquid metals in the Drude model of nearly free electrons. The resistivity is given in terms of the *relaxation time τ* or *relaxation rate $1/\tau$* as follows

$$\rho = \frac{m}{ne^2}\frac{1}{\tau}. \tag{62}$$

τ is the mean time between collisions of electrons with ion cores, i.e. the relaxation rate is also the *collision rate* with the ion cores, which can be calculated from the transition probability $W_{\mathbf{k}\mathbf{k}_0}$ from states $|\mathbf{k}_0 >$ to states $|\mathbf{k} >$ as follows:

$$\frac{1}{\tau} = \frac{1}{(2\pi)^3}\int_{|\mathbf{k}|=k_F} d^3\mathbf{k}\, W_{\mathbf{k}\mathbf{k}_0}(1-\cos\theta) \tag{63}$$

where $\cos\theta$ is the angle between $\mathbf{k}_0$ and $\mathbf{k}$. Note that in the transport and scattering processes only electrons at the Fermi level are involved for which $|\mathbf{k}| = |\mathbf{k}_0| = k_F$ holds.
$W_{\mathbf{k}\mathbf{k}_0}$ can be evaluated in Born approximation in a similar way as the neutron or X-ray scattering cross section. Denoting, again, $\mathbf{q} = \mathbf{k} - \mathbf{k}_0$ we have

$$W_{\mathbf{k}\mathbf{k}_0} = \frac{2\pi}{\hbar}|<\mathbf{k}|\mathcal{V}_i|\mathbf{k}_0>|^2 = \frac{2\pi}{\hbar}n^2 S(q)\,|v_i(q)|^2 \tag{64}$$

from which follows (taking in mind $|\mathbf{k}| = |\mathbf{k}_0| = k_F$)

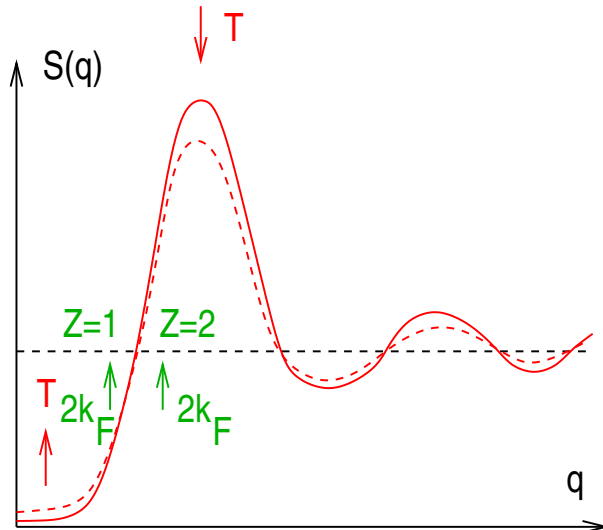$$\frac{1}{\tau} = \frac{1}{(2\pi)^3}\int_0^\pi d\theta \sin\theta\, W(q(\theta))[1-cos\theta] \tag{65}$$

Going over to the integration variable

$$\begin{aligned} q(\theta) &= \sqrt{k^2 + k_0^2 - 2kk_0\cos\theta} \\ &= \sqrt{2}k_F[1-\cos\theta]^{1/2} \\ \Rightarrow \quad dq &= \sqrt{2}k_F\frac{1}{[1-\cos\theta]^{1/2}}\sin\theta d\theta \end{aligned}$$

we have

$$\frac{1}{\tau} = \frac{1}{8\pi\hbar}\frac{n^2}{k_F^4}\int_0^{2k_F} dq\, q^3 S(q)|v_i(q)|^2 \tag{66}$$

This formula is due to Edwards, Faber and Ziman (in different publications). The important implication is that the *temperature dependence* is solely given by that of the static structure factor. Moreover, the integral is strongly peaked at its maximum value $q = 2k_F$, so we can expekt that the temperature dependence of the resistivity of liquid metals is essentially given by that of $S(q = 2k_F)$.

Fig. 7: Temperature dependence of $S(q)$ and the positions of $2k_F$ for $Z = 1$ and $Z = 2$.

From Fig. 4a we see, how $S(q)$ depends on density, which decreases with temperature. This temperature dependence is sketched also in Fig. 6. So for small q $S(q)$ *increases*, for $q \approx q_0$ (peak position) it *decreases* with temperature. From this it follows that for liquid *alkali* metals the resistivity increases with temperature as it does usually also for solid metals. In solids this is due to the increased scattering from phonons. For liquid *earth alkaline* metals and for *liquid alloys with $Z = 2$* k_F turns out to approximately coincide with q_0. This is, in fact, observed in the experimental data.