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INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
34100 TRIESTE (ITALY) - P.O.B. 586 - MIRAMARE - STRADA COSTIERA 11 - TELEPHONES: 224281/2/3/4/5/6
CABLE: CENTRATOM - TELEX 460392 - I

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SPRING COLLEGE ON AMORPHOUS SOLIDS
AND THE LIQUID STATE

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STRUCTURE AND FORCES IN LIQUIDS AND LIQUID MIXTURES

Summary of Lecture VIII

N.H. MARCH

Dept. of Theoretical Chemistry
University of Oxford
1 South Parks Road
Oxford OX1 3TG
UK

Introduction to statistical mechanics of inhomogeneous systems

We have assumed until now, in our fluid eqns, that the one-body density, $\rho^{(1)}(\mathbf{r})$ say, is a constant ρ. Then, the lowest order non-trivial eqn. of Born-Green-Yvon hierarchy was the one relating $\rho^{(2)}(\mathbf{r}_1\mathbf{r}_2) = \rho^2 g(|\mathbf{r}_1-\mathbf{r}_2|)$, $\rho^{(3)}(\mathbf{r}_1\mathbf{r}_2\mathbf{r}_3)$ and pair potential ϕ.

However, in a number of important areas, we need to relax the constraint that $\rho^{(1)}(\mathbf{r})$ is constant:

(i) Freezing of monatomic liquids (Kirkwood & Monroe ($\phi(r)$) and recently Ramakrishnan and Yussouff) ($c(r)$: not $\phi(r)$)

(ii) Surface phenomena in liquids (Prof Tosi will discuss this)

(iii). Transition from ionic melt to superionic phase (one sub-lattice freezes; leaving liquid in periodic potential).

Basic eqn of Born-Green-Yvon hierarchy when density $\rho^{(1)}(\mathbf{r})$ is non-uniform

The same basic eqns are useful for the application cited above.

In the pair potential approx., the definitions of $\rho^{(n)}$ can be used (as with force eqn on p. 1, eqn (3) of notes on lectures I-IV) to prove that

$$k_B T \, \nabla_1 \rho^{(1)}(\mathbf{r}_1) + \int d\mathbf{r}_2 \, \nabla_2 \phi(\mathbf{r}_1-\mathbf{r}_2) \, \rho^{(2)}(\mathbf{r}_1\mathbf{r}_2) = 0 \qquad (8.1)$$

Of course, in the presence, say, of a surface (Prof. Tosi's later lectures) the pair function $\rho^{(2)}(\mathbf{r}_1\mathbf{r}_2)$ will be changed from the bulk liquid value $\rho^{(2)}(|\mathbf{r}_1-\mathbf{r}_2|)$ by the presence of the surface. Therefore (8.1) can only be integrated to get the 'singlet density' $\rho^{(1)}(\mathbf{r}_1)$, given an approximation to $\rho^{(2)}(\mathbf{r}_1\mathbf{r}_2)$.

Freezing of liquid

Kirkwood and Monroe, in pioneering work on freezing, proposed to use eqn (8.1) in a different way.

This was to take $\rho^{(2)}(\underset{\sim}{r_1}\,\underset{\sim}{r_2})$ as the bulk liquid pair function infinitesimally above the freezing temperature (from expt. say!) and to ask whether eqn (8.1) could give rise to a periodic solution $\rho^{(1)}(\underset{\sim}{r})$ for the singlet density. Of course, knowledge of the pair potential $\phi(r)$ is required to solve (8.1).

This approach naturally will not be meaningful unless there is considerable similarity in the local coordination just above and just below the freezing temp.

Prof. Enderby's lectures made it clear that alkali halides, and some other ionic melts are GOOD CANDIDATES.

One must not consider the freezing of liquid Ge (good liquid metal: 4 cond. els/atom) in this way — tetrahedrally coordinated solid.

Quite recently, Ramakrishnan and Yussouff have reopened this approach, but with one important difference. Instead of working with $\rho^{(2)}(\underset{\sim}{r_1}\,\underset{\sim}{r_2})$ and $\phi(r)$ from bulk liquid, they use the bulk liquid direct correlation function c(r) as the major tool.

Though they used the Abe (≡ hypernetted chain) approximation as basis, later work done independently by Oxtoby et al and by March & Tosi, gives back their results without needing to invoke the Abe approximation.

We shall outline the approach for a one-component liquid first, but in view of the emphasis on mixtures here, the main application to be discussed will be the freezing of molten $BaCl_2$ for which the liquid partial structure factors have been measured by Enderby et al (Prof. Ramakrishnan will speak in his seminar about freezing in both 3 & 2 dimensions)

Form of eqn. relating $c(\mathbf{r}_1 \mathbf{r}_2)$ to singlet density in an inhomogeneous fluid

The first appearance in the literature of this eqn relating c & $\rho^{(1)}(\mathbf{r})$ is in the surface tension calculation of Triezenberg and Zwanzig (1972), who however say the result can be traced back to Yvon.

A somewhat clearer derivation has been given by Lovett, Mou and Buff (J. Chem. Phys. 65, 570, 1976). We'll give an outline of their derivation generalized to mixtures (Bhatia, March & Tosi, 1980) below but we'll first state the one-component form, to compare with (8.1) above:

$$\frac{\nabla_1 \rho^{(1)}(\mathbf{r}_1)}{\rho^{(1)}(\mathbf{r}_1)} = \int d\mathbf{r}\; c(\mathbf{r}_1, \mathbf{r}) \nabla \rho^{(1)}(\mathbf{r}) . \qquad (8.2)$$

There is similarity to (8.1), c taking over role of $\rho^{(2)}$ plus ϕ.

Recent progress in (a) surface tension and (b) freezing has come via (8.2).

Relation to freezing of 1 component liquid

Dropping $\rho^{(1)}(\mathbf{r}) \equiv \rho(\mathbf{r})$, eqn (8.2) can be integrated to yield, with bulk $c(\mathbf{r}_1 \mathbf{r}_2)$ inserted,

$$\ln \rho(\mathbf{r}_1) = \int d\mathbf{r}_2\; c(r_{12}) \rho(\mathbf{r}_2) + \text{const} \qquad (8.3)$$

What will emerge below is that for given $c(r_{12})$, eqn (8.3) admits not only a solution for which the singlet density is uniform, with value $\rho(\mathbf{r}) = \rho_\ell$, but also a co-existing periodic solution $\rho_p(\mathbf{r})$.

Free energy difference between homogeneous and periodic phases

Apply (8.3) to both the singlet densities ρ_ℓ and $\rho_p(\mathbf{r})$ and then subtract to find:

$$\ln\left(\frac{\rho_p(\mathbf{r}_1)}{\rho_\ell}\right) - \int d\mathbf{r}_2\; c(|\mathbf{r}_1 - \mathbf{r}_2|)\left[\rho_p(\mathbf{r}_2) - \rho_\ell\right] = 0 \qquad (8.4)$$

where the constants in (8.3) are taken equal for two phases in co-existence.

Since, by assertion, ρ_p is periodic, we expand in a Fourier series using reciprocal lattice vectors $\mathbf{G}$ to obtain

$$\rho_p(\mathbf{r}) = \rho_0 + V^{-1} \sum_{\mathbf{G} \neq 0} \rho_{\mathbf{G}} \exp(i \mathbf{G} \cdot \mathbf{r}) \tag{8.5}$$

where V is the total volume. Inserting (8.5) into (8.4), integration over $\mathbf{r}_2$ can be carried out to yield

$$\ln\left(\frac{\rho_p(\mathbf{r})}{\rho_l}\right) = \frac{(\rho_0 - \rho_l)}{\rho_l} \tilde{c}(0) - (\rho_l V)^{-1} \sum_{\mathbf{G} \neq 0} \rho_{\mathbf{G}} \tilde{c}(\mathbf{G}) \exp(i \mathbf{G} \cdot \mathbf{r}) \tag{8.6}$$

where as usual $\tilde{c}(k)$ is Fourier transform of $c(r)$.

This eqn (8.6) is, for a given set of Fourier components of the liquid direct correlation function, to be solved for the Fourier components $\rho_{\mathbf{G}}$ of the singlet density.

We next proceed to set up a minimum free energy principle, of which (8.4) is the Euler equation.

Of course, the thermodynamic requirement for the two phases to be in equilibrium is that this free energy difference be zero.

We'll work with the thermodynamic potential Ω_p say, related to the Helmholtz free energy F and chemical potential μ by

$$\Omega_p = F - N\mu . \tag{8.7}$$

The Helmholtz free energy can be conveniently divided into:

(i) Free particle piece

and (ii) Piece taking account of interparticle interactions via the direct correlation function $c(r)$.

It is readily verified that if we thereby construct $\Delta\Omega_p$ in units of k_BT as

$$\frac{\Delta\Omega_p}{k_BT} = \int d\mathbf{r} \left[\rho_p(\mathbf{r}) \ln\left(\frac{\rho_p(\mathbf{r})}{\rho_l}\right) - (\rho_p(\mathbf{r}) - \rho_l)\right] - \frac{1}{2} \iint d\mathbf{r}_1 \, d\mathbf{r}_2 \left[\rho_p(\mathbf{r}_1) - \rho_l\right] c(|\mathbf{r}_1 - \mathbf{r}_2|) \left[\rho_p(\mathbf{r}_2) - \rho_l\right] \tag{8.8}$$

then performing the variation of $\Delta\Omega_p$ w.r. to $\rho_p(\mathbf{r})$ leads back to eqn (8.4) as Euler equation.

At this stage, we insert the Fourier expansions (8.5) and (8.6) into (8.8) to find, with $N = \rho_\ell V$,

$$\frac{\Delta\Omega_p}{k_B T} = \frac{1}{2N}\sum_{\underset{\sim}{G}} \tilde{c}(\underset{\sim}{G})\,|\rho_{\underset{\sim}{G}}|^2 - \frac{N(\rho_0-\rho_\ell)}{\rho_\ell} + \frac{1}{2}N\,\tilde{c}(0)\,\frac{(\rho_0^2-\rho_\ell^2)}{\rho_\ell^2}. \qquad (8.9)$$

This is the desired expression for the free energy difference in terms of the Fourier components $\rho_{\underset{\sim}{G}}$ of the periodic density, and the volume change reflected in the difference between liquid and solid densities, $(\rho_\ell - \rho_0)$.

The possibility of coexistence of homogeneous liquid and periodic phases is clear from (8.9), because of the balance between positive contributions from the first and third terms on the right-hand-side, and the negative term from the volume change, provided solid phase has higher density

The actual coexistence point is evidently determined by the properties of $\tilde{c}(\underset{\sim}{G})$, including $\underset{\sim}{G} = 0$, linking liquid structure intimately with the appearance of the periodic phase.

The work of Ramakrishnan and Yussouff shows how an explicit periodic solution, for given liquid $c(r)$, can be calculated from eqn (8.6).

We'll turn instead to two-component treatment, with $BaCl_2$ in mind. We must clearly generalize first the Triezenberg – Zwanzig equation to apply to mixtures (Bhatia, March and Tosi, 1980).

Derivation of singlet density equations in a mixture

Consider a multicomponent mixture in which $u_i(\mathbf{r})$ denotes the dimensionless one-body potential for species i:

$$u_i(\mathbf{r}) = \beta\left(\mu_i - U_i(\mathbf{r})\right) : \quad \beta = (k_B T)^{-1}.$$

Here $U_i(\mathbf{r})$ is the external potential for species i, with μ_i its chemical potential. The system is considered at volume V and temperature T.

Given all the $u_i(\mathbf{r})$, the various singlet densities $\rho_j(\mathbf{r})$ are uniquely determined and vice-versa, at given V and T. Hence the quantities $u_i(\mathbf{r})$ can be regarded as functionals of the various $\rho_j(\mathbf{r})$. One has then

$$\frac{\delta u_i(\mathbf{r})}{\delta \rho_j(\mathbf{r}')} = \delta_{ij}\,\frac{\delta(\mathbf{r}-\mathbf{r}')}{\rho_i(\mathbf{r})} - c_{ij}(\mathbf{r},\mathbf{r}')$$

$$\equiv K_{ij}(\mathbf{r},\mathbf{r}'),$$

which is an alternative (and quite equivalent) definition of partial direct c_{ij}'s, to one in terms of g_{ij}'s.

If $u_i(\mathbf{r})$ is written as

$$u_i(\mathbf{r}) = \ln\left(\rho_i(\mathbf{r})\Lambda_i^3\right) - C_i(\mathbf{r}),$$

where $\Lambda_i = h\,(2\pi m_i k_B T)^{-\frac{1}{2}}$ then

$$c_{ij}(\mathbf{r}\,\mathbf{r}') = \frac{\delta C_i(\mathbf{r})}{\delta \rho_j(\mathbf{r}')}.$$

Now we exhibit the functional dependence of u_i by

$$u_i\big(\mathbf{r}_1, \underbrace{[\rho_1(\mathbf{r}), \rho_2(\mathbf{r}) \cdots \rho_\nu(\mathbf{r})]}_{\nu \text{ components}}\big) \equiv u_i(\mathbf{r}_1) \text{ say},$$

then we can translate by δ to write

$$u_i\left(\mathbf{r}_1, [\rho_1(\mathbf{r}+\boldsymbol{\delta}) \cdots \rho_\nu(\mathbf{r}+\boldsymbol{\delta})]\right) \equiv u_i(\mathbf{r}_1+\boldsymbol{\delta}) \text{ say}$$

Hence we find

$$u_i(\mathbf{r}_1+\boldsymbol{\delta}) - u_i(\mathbf{r}_1)$$

$$= \sum_{j=1}^{\nu} \int d\mathbf{r}\, \frac{\delta u_i(\mathbf{r}_1)}{\delta \rho_j(\mathbf{r})} \left[\rho_j(\mathbf{r}+\boldsymbol{\delta}) - \rho_j(\mathbf{r})\right] + \cdots$$

Taking $\delta \to 0$ yields

$$\nabla u_i(\mathbf{r}_1) = \sum_{j=1}^{\nu} \int d\mathbf{r}\, \frac{\delta u_i(\mathbf{r}_1)}{\delta \rho_j(\mathbf{r})} \nabla \rho_j(\mathbf{r})$$

$$= \sum_{j=1}^{\nu} \int d\mathbf{r}\, K_{ij}(\mathbf{r}_1, \mathbf{r}) \nabla \rho_j(\mathbf{r}).$$

The final step in the argument is now to reduce the external potential u_i to zero, when of course $\nabla u_i(\underset{\sim}{r}) = 0$. Thus we find

$$\sum_{j=1}^{\nu} \int d\underset{\sim}{r}\, K_{ij}(\underset{\sim}{r_1}, \underset{\sim}{r}) \nabla\rho_j(\underset{\sim}{r}) = 0$$

and, using the definition of K in terms of c, the desired equations follow as

$$\frac{\nabla\rho_i(\underset{\sim}{r_1})}{\rho_i(\underset{\sim}{r_1})} = \sum_{j=1}^{\nu} \int d\underset{\sim}{r}\, c_{ij}(\underset{\sim}{r_1}, \underset{\sim}{r}) \nabla\rho_j(\underset{\sim}{r}).$$

In applying these equations to the singlet densities in the presence of a surface, one must use, as in the monatomic case, the direct correlation functions in the presence of the surface. Not much is known about these presently.

But in the application below to the freezing of $BaCl_2$, we can input, as we did for the monatomic freezing problem, the direct correlation functions of the bulk liquid from experiment.

Freezing of ionic melts into superionic phase

The Ba – Ba correlation fn in molten $BaCl_2$ is highly structured, and can be thought of as 'driving' the freezing of the Ba cations on to their sub-lattice. One can usefully have the picture then of the anion 'liquid' moving in a periodic potential, which evidently modulates the singlet density of this anionic 'liquid'. March and Tosi (1981) have used the above eqns to describe this 'freezing' transition into a superionic phase, with specific reference to $BaCl_2$.

Denoting the singlet densities in liquid and in superionic phases by $\rho_{i\ell}$ and ρ_{is} respectively, we have, in close similarity to 1 component case, equations connecting these with the liquid c_{ij}'s, namely

$$\ln\left(\frac{\rho_{is}(\underset{\sim}{r_1})}{\rho_{il}}\right) = \sum_{j=1}^{2}\int d\underset{\sim}{r_2}\, c_{ij}(|\underset{\sim}{r_2}-\underset{\sim}{r}|)\,[\rho_{js}(\underset{\sim}{r})-\rho_{jl}] : \quad i=1,2.$$

The two phases must be taken at the coexistence point, the condition of equilibrium of the two phases being that the difference $\Delta\Omega_p$ of the thermodynamic potential is zero.

As before we set up the Euler equations above from a minimum free energy principle, namely

$$\frac{\Delta\Omega_p}{k_BT} = -(\rho_0-\rho_e)V + \frac{1}{2}\sum_{i,j=1}^{2}\iint d\underset{\sim}{r_1}\,d\underset{\sim}{r_2}\,[\rho_{is}(\underset{\sim}{r_1})+\rho_{il}]\times c_{ij}(|\underset{\sim}{r_1}-\underset{\sim}{r_2}|)\,[\rho_{js}(\underset{\sim}{r_2})-\rho_{jl}]$$

where ρ_0 and ρ_l are the mean number densities in solid and liquid phases and V as usual is the volume.

Paralleling the one-component argument, we Fourier analyze the singlet densities in the superionic phase, by writing

$$\rho_{is}(\underset{\sim}{r}) = \rho_0 + \frac{1}{V}\sum_{\underset{\sim}{G}}{}' \rho_{i\underset{\sim}{G}}\, e^{i\underset{\sim}{G}\cdot\underset{\sim}{r}} \; ; \; i=1,2$$

where $\rho_0 = \rho_{10}+\rho_{20}$ and the $\underset{\sim}{G}$'s are reciprocal lattice vectors. The prime means $\underset{\sim}{G}\neq 0$. We also Fourier analyze the direct correlation functions by writing

$$c_{ij}(\underset{\sim}{r}) = \frac{1}{V\sqrt{\rho_{il}\rho_{jl}}}\sum_{\underset{\sim}{k}}\tilde{c}_{ij}(\underset{\sim}{k})\, e^{i\underset{\sim}{k}\cdot\underset{\sim}{r}}.$$

Substituting in the Euler equations, we then obtain for the $\underset{\sim}{k}=0$ component

$$\ln\left(\frac{\rho_{i0}}{\rho_{il}}\right) + \frac{1}{V}\int d\underset{\sim}{r}\,\ln\left[1+\frac{1}{\rho_{i0}V}\sum_{\underset{\sim}{G}}{}'\rho_{i\underset{\sim}{G}}\,e^{i\underset{\sim}{G}\cdot\underset{\sim}{r}}\right] = \sum_{j=1}^{2}\left(\frac{\rho_{j0}-\rho_{jl}}{\{\rho_{il}\rho_{jl}\}^{\frac{1}{2}}}\right)\tilde{c}_{ij}(0).$$

-divergent Coulomb terms in the $\tilde{c}_{ij}(k)$ r $k\to 0$ cancel in the above equation on account of the electrical neutrality condition

$$\frac{\rho_{10}}{\rho_{1l}} = \frac{\rho_{20}}{\rho_{2l}}.$$

After the divergent terms in $\tilde{c}_{ij}(k)$ at small k are accounted for as above, there is a finite limit as $k \to 0$, with value $\tilde{c}^{0}_{ij}(0)$ say.

Then we find

$$\ln\left(\frac{\rho_{i0}}{\rho_{i\ell}}\right) + \frac{1}{V}\int d\underset{\sim}{r}\, \ln\left[1 + \frac{1}{\rho_{i0}V}\sum_{\underset{\sim}{G}}{}' \rho_{i\underset{\sim}{G}}\, e^{i\underset{\sim}{G}\cdot\underset{\sim}{r}}\right] = \frac{(\rho_0 - \rho_\ell)}{\rho_\ell}\sum_{j=1}^{2}\sqrt{\rho_{j\ell}/\rho_{i\ell}}\;\tilde{c}^{0}_{ij}(0).$$

The combination of $\tilde{c}^{0}_{ij}(0)$ entering the above eqn. involves (compare discussion of number-concentration structure factors at $\underset{\sim}{k} = 0$) the compressibility, and the difference in partial molar volumes for the 2 components of the liquid.

Turning to the $\underset{\sim}{G} \neq 0$ terms, we find

$$\int d\underset{\sim}{r}\, \ln\left[1 + \frac{1}{V\rho_{i0}}\sum_{\underset{\sim}{G}'}{}' \rho_{i\underset{\sim}{G}'}\, e^{i\underset{\sim}{G}'\cdot\underset{\sim}{r}}\right] e^{-i\underset{\sim}{G}\cdot\underset{\sim}{r}} = \sum_{j=1}^{2}(\rho_{i\ell}\rho_{j\ell})^{-\frac{1}{2}}\rho_{j\underset{\sim}{G}}\;\tilde{c}_{ij}(\underset{\sim}{G}).$$

As for the 1 component case, the expression for $\Delta\Omega_p$ can be obtained; namely

$$\frac{\Delta\Omega_p}{k_BT} = -(\rho_0 - \rho_\ell)V + \frac{V}{2}\left(\frac{\rho_0^2}{\rho_\ell^2} - 1\right)\sum_{i,j=1}^{2}\sqrt{\rho_{i\ell}\rho_{j\ell}}\;\tilde{c}^{0}_{ij}(0) + \frac{1}{2V}\sum_{i,j=1}^{2}\sum_{\underset{\sim}{G}}{}' \tilde{c}_{ij}(\underset{\sim}{G})\,\frac{\rho_{i\underset{\sim}{G}}\,\rho_{j\underset{\sim}{G}}}{\sqrt{\rho_{i\ell}\rho_{j\ell}}}.$$

This form of $\Delta\Omega_p$ makes quantitative the fact that the phase transition occurs as a balance between a favourable term from the volume contraction and an increase in Ω_p from the Fourier component modulation of the singlet densities.

So far, development of idea of using bulk c_{ij}'s to generate periodic singlet densities has been carried out without further approximation.

We now turn to see how, with $BaCl_2$ in mind, the anion density modulation described by the Fourier components $\rho_{2\underset{\sim}{G}}$ say, can be related to the cation sub-lattice Fourier components $\rho_{1\underset{\sim}{G}}$.

For the special case $\underset{\sim}{G}=0$, it is important to stress that ρ_{20} is already determined exactly by ρ_{10} using the charge neutrality condition given above.

Recalling the experimental result that the Ba cations are highly ordered in the liquid phase, it is a reasonable starting point to argue that the freezing into a cation sub-lattice can be treated as a perturbation on the anion singlet density, which is homogeneous, with density $\rho_{2\ell}$, in the liquid phase. We shall return below to discuss the validity of this approximation for $BaCl_2$.

We therefore linearize the theory in the $\rho'_{2\underset{\sim}{G}}$'s, which allows the remaining integration to be performed, to yield

$$\rho_{2\underset{\sim}{G}} = \frac{(\rho_{2\ell}/\rho_{1\ell})^{1/2}\,\tilde{c}_{12}(\underset{\sim}{G})\,\rho_{1\underset{\sim}{G}}}{(\rho_{2\ell}/\rho_{20}) - \tilde{c}_{22}(\underset{\sim}{G})}$$

The coupling of the sub-lattice 1 to the modulated liquid density, described by $\rho_{2\underset{\sim}{G}}$, is determined by the cross-correlation function $\tilde{c}_{12}(\underset{\sim}{G})$. The denominator represents, in essence, the response function of the system 2, ie the anions in $BaCl_2$.

One is still left with the coupled non-linear eqns for $i=1$, to determine (i) the volume change ρ_0/ρ_ℓ and (ii) the Fourier components $\rho_{1\underset{\sim}{G}}$.

In the absence (to date) of a numerical solution of these equations, we can relate these two quantities (i) and (ii) above in the approximation in which we single out the principle Fourier components $\rho_{1\underset{\sim}{G}_1}$ say. For $BaCl_2$, it is evident that the pronounced main peak in S_{Ba-Ba} corresponds to the first reciprocal lattice vector of the Ba sub-lattice, which thereby fixes $\underset{\sim}{G}_1$, except for the contraction implied by the volume change.

Order of magnitude estimates for $BaCl_2$

Presently there seems to be suitable data only on the molten state structure of one superionic conductor, $BaCl_2$. We shall therefore concern ourselves exclusively with making estimates for this material.

Using the data of Edwards, Enderby et al, we can use the relation between ρ_{2G}, ρ_{1G} and the measured c's to get, for the first reciprocal lattice vector $\underset{\sim}{G}_1$:

$$\rho_{2\underset{\sim}{G}_1} \simeq 0.4\, \rho_{1\underset{\sim}{G}_1} .$$

Though this ratio is somewhat large for linear response theory to be fully quantitative, of course, it is possible that other materials, eg AgI, may be better described than $BaCl_2$.

However, using the above ratio of 0.4, we can now relate volume change and $\rho_{1\underset{\sim}{G}_1}$. Since the observed volume change on freezing into the Ba sub-lattice is small, about 3.5%, we [illegible] linearised in the volume change, to find

$$\frac{\rho_0-\rho_\ell}{\rho_\ell}\left[1-\sum_{i,j=1}^{2}\frac{\sqrt{\rho_{i\ell}\rho_{j\ell}}}{\rho_\ell}\,\tilde{c}^{\,0}_{ij}(0)\right]$$

$$= \frac{4}{V^2\rho_{1\ell}\rho_\ell}\left|\rho_{1\underset{\sim}{G}_1}\right|^2\left\{\tilde{c}_{11}(\underset{\sim}{G}_1)+\frac{2\tilde{c}_{12}^{\,2}(\underset{\sim}{G}_1)}{(\rho_\ell/\rho_0)-\tilde{c}_{22}(\underset{\sim}{G}_1)}\right.$$

$$\left.+\frac{\tilde{c}_{12}^{\,2}(\underset{\sim}{G}_1)\,\tilde{c}_{22}(\underset{\sim}{G}_1)}{(\{\rho_\ell/\rho_0\}-\tilde{c}_{22}(\underset{\sim}{G}_1))^2}\right\},$$

where we have used the fact that there are 8 equivalent vectors of length $\underset{\sim}{G}_1$.

We obtain $|\rho_{1\underset{\sim}{G}_1}|$ in terms of observable quantities as

$$|\rho_{1\underset{\sim}{G}_1}|/V\rho_{1\ell} \sim 0.6,$$

assuming quantity in [ ] on LHS of above equation, which is the inverse of the number-number structure factor $S_{NN}(k)$ at $k=0$, is ~ 10 as in molten alkali halides.

Experiment should be able to test the above predictions. From the theoretical angle, there is obviously need to examine the influence of longer reciprocal lattice vectors.

Some concluding comments

1. For monatomic liquids, every effort should be made to establish more quantitative information on the three-atom correlation function $\rho^{(3)}$, which is at the heart of the theory relating structure and forces.

This can be done by:

(a) Always, in molecular dynamics studies, extracting the function $f(r)$, involving the p term of $\rho^{(3)}$, as well as $\phi(r)$, given by

$$\frac{\partial g(r)}{\partial r} + \frac{g(r)}{k_B T}\frac{\partial \phi(r)}{\partial r} = f(r)$$

(b) Studying further experimentally the pressure and temperature dependences of $g(r)$, related to $\rho^{(3)}$ and $\rho^{(4)}$ (specific heat theory is also of interest, here, involving as it does $\rho^{(3)}$ & $\rho^{(4)}$)

2. In metallic mixtures, though concentration-dependent pair interactions no doubt offer the most fundamental description, simpler descriptions are strongly suggested by (a) some successes of conformal solution theory & its generalizations; (b) Miedema's work on metallic alloys. More work on relating (a) & (b) fundamentally. Reference system;