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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 VII

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Effect of scaling pair potential in monatomic fluid

$$\phi(r) \rightarrow \phi_m(r) \equiv A\,\phi(\lambda r).$$

Scaling of thermodynamics

1. Chemical potential μ.

$$\mu_m(\beta, \Omega) = A\mu(A\beta, \lambda^3\Omega) + \frac{3}{\beta}\ln\lambda \; : \; \beta = \frac{1}{k_BT}$$

so that fugacity becomes:

2. $z_m(\beta, \Omega) = \lambda^3 A^{3/2} z(A\beta, \lambda$ [illegible]

Scaling of pair function g(r)

Using grand canonical ensemble,

3. $g_m(r, \beta, \Omega) = g(\lambda r, A\beta, \lambda^3\Omega, A^{3/2}z)$

These results lead to useful insight into two-component mixtures.

In particular, density-density correlation in mixture, $g_{NN}(r)$, can be set by re-interpreting A and λ.

Mo et al (1974, Molecular Physics, 27, 1173) have directly applied perturbation theory (next transparency: very complicated; we'll not attempt to derive it therefore in these lectures), (argon-krypton mixture) choosing the reference liquid as the one-component liquid whose pair fn. g(r) coincides, at each concentration, with $g_{NN}(r)$ and adopting Kirkwood approx. for higher order correlation fns.

Computer calcs. have shown that while small size differences affect the thermodynamic properties in an unimportant way, the conformal soln theory, to first order in $\lambda_{\alpha\beta} - 1$ gives rather too little structure in $S_{cc}(k)$.

Summary of theory of partial structure factors at finite wavelength in conformal solns

Assumptions (i). Pair potentials $\phi_{\alpha\beta}(r)$ between the different atoms in the mixture related to the pair potential $\phi(r)$ in the reference liquid by

$$\phi_{\alpha\beta}(r) = A_{\alpha\beta}\,\phi(\lambda_{\alpha\beta} r).$$

(ii) In lowest order theory (we'll stick to that), it is further assumed that the A's and λ's deviate only slightly from unity and that $\lambda_{12} = \frac{1}{2}(\lambda_{11}+\lambda_{22})$.

Outcome Thermodynamic properties of binary mixture can be expressed in terms of product of parameter $d_{12} = 2A_{12} - A_{11} - A_{22}$ and of quantity

$$E_0 = \frac{1}{2}\rho\int d\mathbf{r}\;\phi(r)\,g(r)$$ of ref liquid

(char. energy $w = d_{12}E_0$).

Perturbative technique needed (a bit compl.!)

$$\begin{aligned} g_{\alpha\beta}(r) - g(r) = \sum_\gamma \frac{\Delta z_\gamma}{z}\Big\{ &(\delta_{\alpha\gamma}+\delta_{\beta\gamma})\,g(r) \\ &+ \rho_\gamma\int d\mathbf{s}\,\big[g_3(\mathbf{r},\mathbf{s}) - g(r)\big]\Big\} \\ -\frac{1}{k_BT}\Big\{ &\Delta\phi_{\alpha\beta}(r)\,g(r) + \sum_\gamma \rho_\gamma\int d\mathbf{s}\,\big[\Delta\phi_{\alpha\gamma}(s) + \Delta\phi_{\beta\gamma}(s)\big]\,g_3(\mathbf{r},\mathbf{s}) \\ &+ \frac{1}{2}\sum_{\gamma\gamma'}\rho_\gamma\rho_{\gamma'}\int d\mathbf{s}\,d\mathbf{s}'\,\Delta\phi_{\gamma\gamma'}(s')\big[g_4(\mathbf{r},\mathbf{s},\mathbf{s}') - g(r)g(s')\big]\Big\}. \end{aligned}$$

Δz_γ is change in fugacity of the γth component in mixture from the reference liquid.

Simplest classical mixture with non-trivial dynamics

This is mixture of isotopes! Here the forces between the components are all the same, as are the static structure factors.

Being an 'ideal' solution, the static concentration fluctuations are independent of k and given by

$$S_{cc}(k) = c_1 c_2 .$$

Dynamical properties of such mixtures discussed, independently by Parrinello, Tosi and March (1974), via simple analytical models and by Ebbsjo (present at this College), Schofield, Sköld and Waller (1974) by computer simulation in Lennard-Jones isotopic mixtures. These workers discuss mass transport: we can compare analytical (perturbative) studies with their computer experiment.

Models of partial dynamical structure factors

For the ideal solution which an isotopic mixture constitutes, the dynamical structure factors $S_{NN}(k,\omega)$ and $S_{NC}(k,\omega)$ have zero-order moments given by:

$$\int \frac{d\omega}{2\pi} S_{NC}(k,\omega) = S_{NC}(k) = 0$$

$$\int \frac{d\omega}{2\pi} S_{NN}(k,\omega) = S(k).$$

Simplest model is to use Feynman idea of well defined excitations, with dispersion relns ω_k, and to find ω_k (as in collective mode in liquid metals) from second moment;

These are: $$\int_{-\infty}^{\infty} \frac{d\omega}{2\pi}\,\omega^2 S_{\alpha\beta}(k\omega) = \delta_{\alpha\beta}\frac{k_BTk^2}{M_\alpha}$$

which yields for S_{NN} etc the following moment relns:

$$\int_{-\infty}^{\infty} \frac{d\omega}{2\pi}\,\omega^2 S_{Nc}(k\omega) = c_1c_2k_BTk^2\left(\frac{1}{M_1}-\frac{1}{M_2}\right)$$

$$\int_{-\infty}^{\infty} \frac{d\omega}{2\pi}\,\omega^2 S_{NN}(k\omega) = k_BTk^2\left(\frac{c_1}{M_1}+\frac{c_2}{M_2}\right)$$

and

$$\int_{-\infty}^{\infty} \frac{d\omega}{2\pi}\,\omega^2 S_{cc}(k\omega) = \frac{c_1c_2Mk_BTk^2}{M_1M_2}$$

where $M = c_1M_1 + c_2M_2$.

Now, except for lightest isotopes, mass differences small and 1st of these moments → 0 with $M_1 - M_2$, other 2nd moments remaining finite.

Thus, there is no link between number density $\rho(\underline{k}\,t)$ and conc. $c(\underline{k}\,t)$ in the limit $M_1 - M_2 \to 0$ and they oscillate independently, with frequencies $\omega_{10}(k)$ and $\omega_{20}(k)$, say, respectively.

To satisfy zeroth and second moments in this limit of small $(M_1 - M_2)$, we therefore adopt the forms

$$S_{NN}(k\,\omega) \doteq \tfrac{1}{2} S(k)\Big[\delta(\omega-\omega_{10}(k)) + \delta(\omega+\omega_{10}(k))\Big]$$

and

$$S_{cc}(k\,\omega) \simeq \tfrac{1}{2} c_1 c_2 \Big[\delta(\omega-\omega_{20}(k)) + \delta(\omega+\omega_{20}(k))\Big]$$

with $S_{Nc}(k,\omega) \doteq 0$. Then we find

$$\omega_{10}^2(k) = \frac{k_B T k^2}{S(k)}\left[\frac{c_1}{M_1} + \frac{c_2}{M_2}\right]$$

and

$$\omega_{20}^2(k) = M k_B T k^2 / M_1 M_2 .$$

Two limitations must be noted:

(i) Velocity of sound in isotopic mixture will only be correct if ratio of specific heats γ is near to unity. (OK for simple liquid metals just above freezing point: $\gamma \sim 1{\cdot}1 - 1{\cdot}3$; but for argon at triple point with $\gamma = 2{\cdot}2$, error is severe.

(ii) Treatment valid only for $M_1 - M_2$ small.

Case of arbitrary mass difference

Then $S_{Nc}(k,\omega)$ is non-zero and the pure modes ω_{10} and ω_{20} interact and mix. Can be formulated in terms of response functions: we'll simply summarize main results here:

(i) New squared frequencies are:

$$\omega^2(k) = \tfrac{1}{2}\left\{ \omega_{10}^2 + \omega_{20}^2 \pm \left[(\omega_{10}^2 + \omega_{20}^2)^2 - \frac{4k^4}{M_1 M_2 \beta^2 S(k)}\right]^{\frac{1}{2}} \right\}$$

When mass difference is small,

$$\frac{4k^2}{M_1 M_2 \beta^2 S(k)} \simeq 4\omega_{10}^2 \omega_{20}^2$$

giving back pure mode frequencies.

Evidently, given $S(k)$, this formula determines the frequencies for arbitrary concentration and masses. Therefore, only will discuss briefly limiting case when M_1/M_2 gets large

Then we have

$$\omega_1^2 \doteq \frac{c_1}{M_1} \frac{k_B T k^2}{S(k)}$$

and $$\omega_2^2 \doteq \frac{c_2}{M_1} k_B T k^2 .$$

When c_1 becomes small, that is a light impurity in the host liquid, the two modes are well separated, ω_1^2 becoming very small, although still reflecting the oscillations in $S(k)$ at large k.

Some discussion of damping of such modes has been given by Parrinello, Tosi and March (Proc. Roy Soc A 341, 91) but we'll not go into detail here.

Rather we'll turn to atomic transport when mass difference is small.

Atomic transport for mass difference $(M_1 - M_2)$ small

Having dealt with models for arbitrary mass differences, let us mention that the dynamics of isotopic mixtures can be discussed carefully by perturbation theory, the perturbation being the deviations of M_1 and M_2 from some suitably chosen mass M.

The theory can be posed precisely as follows. We take a reference liquid, with the same force law as the mixture, composed of $N = N_1 + N_2$ identical atoms of mass M. Then the difference H' between the Hamiltonian of the mixture and that of the reference liquid is

$$H' = -\left[\Delta_1 \sum_{i=1}^{N_1} p_i^2 + \Delta_2 \sum_{i=1}^{N_2} p_i^2 \right] \Big/ 2M$$

with $\Delta_i = (M_i - M)/M_i$. With the assumption that H' can be treated as a perturbation some simple results follow:

(1) The interdiffusion constant D is given by

$$D = c_2 D_1 + c_1 D_2 ,$$

where D_1 and D_2 are self-diffusion coefficients for the 2 isotopes in the mixture. This relation is correct to 1st order in $m_1 - m_2$.

(2) By choosing the 'reference mass' m as

$$m = \left(\frac{c_1}{m_1} + \frac{c_2}{m_2} \right)^{-1},$$

the additional relations follow:

$$c_1 D_1 + c_2 D_2 = D_1^0 \left(c_1 + c_2 \frac{m_1}{m_2} \right)^{\frac{1}{2}}$$

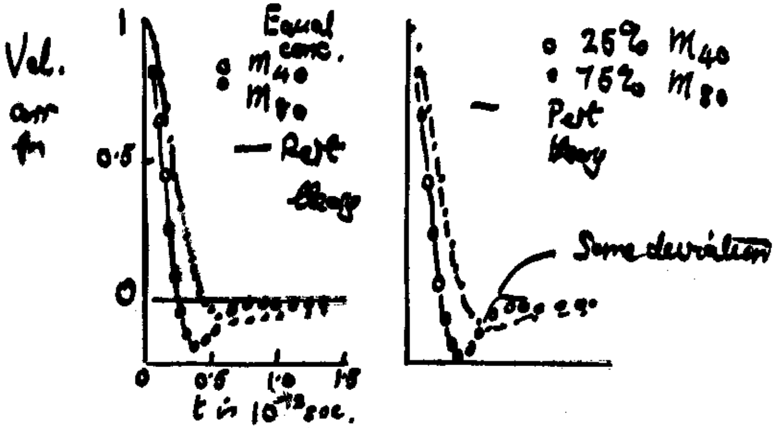
$$= D_2^0 \left(c_2 + c_1 \frac{m_2}{m_1} \right)^{\frac{1}{2}}$$

where D_i^0 are the self-diffusion efficients in the pure isotopes.

Velocity autocorrelation functions $\langle v(0)\, v(t) \rangle / \langle v(0)^2 \rangle$

Perturbation theory for small mass differences allows one to exhibit explicitly the dependence of $S_{\alpha\beta}(k\omega)$ and $S^s_{\alpha\alpha}(k\omega)$ on concentration and masses.

Molecular dynamics calcs. done on vel. autocorrelation fn (Ebbsjo et al) can be compared (related to $S^s_{\alpha\alpha}(k\omega)$).



Curves are calculated by scaling through perturbation theory for small mass differences. Significant violation from pert theory observed only for very large mass differences [m_{40} and m_{200}!]