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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

Summaries of Lectures I - IV

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Summary of 1st Lecture

If $\Phi(\underset{\sim}{r}_1 \underset{\sim}{r}_2 \cdots \underset{\sim}{r}_N) = \sum_{i<j} \phi(r_{ij})$ *

then

① Internal energy is

$$E = \frac{3}{2} N k_B T + \frac{N\rho}{2} \int_0^\infty \phi(r)\, g(r)\, 4\pi r^2 dr$$

(2) Equation of state is

$$P = \rho k_B T - \frac{\rho^2}{6} \int r \frac{\partial \phi}{\partial r}\, g(r)\, d\underset{\sim}{r}$$

and

(3) Force equation is

$$-\frac{\partial U(r_{12})}{\partial \underset{\sim}{r}_1} = -\frac{\partial \phi(r_{12})}{\partial \underset{\sim}{r}_1} - \int \frac{\rho^{(3)}(\underset{\sim}{r}_1 \underset{\sim}{r}_2 \underset{\sim}{r}_3)}{\rho^2 g(r_{12})} \frac{\partial \phi(r_{13})}{\partial \underset{\sim}{r}_1} d\underset{\sim}{r}_3$$

where $g(r_{12}) = e^{-U(r_{12})/k_B T}$.

ALL THESE EQNS are exact classically, from *.

(4) $h(r) = c(r) + \rho \int h(\underset{\sim}{r} - \underset{\sim}{r}')\, c(r')\, d\underset{\sim}{r}'$.

Thus,

Probability that a system in the grand canonical ensemble does contain N atoms is given by

$$P_N = \frac{e^{\frac{N\mu}{k_B T}} Z(N, \Omega, T)}{Z_G}$$

Let $\rho^{(n)}(\underset{\sim}{r}_1 \cdots \underset{\sim}{r}_n)\, d\underset{\sim}{r}_1 \cdots d\underset{\sim}{r}_n$ be the probability of observing molecules in $d\underset{\sim}{r}_1 \cdots d\underset{\sim}{r}_n$ at $\underset{\sim}{r}_1 \cdots \underset{\sim}{r}_n$, irrespective of N. Then evidently

$$\rho^{(n)} = \sum_{N \geq n} \rho_N^{(n)} P_N$$

where the $\rho_N^{(n)}$ are the distribution fns we defined in Lecture 1 in canonical ensemble.

Also

$$\iint \cdots \int \rho^{(n)}(\underset{\sim}{r}_1 \cdots \underset{\sim}{r}_n)\, d\underset{\sim}{r}_1 \cdots d\underset{\sim}{r}_n = \sum_{N \geq n} P_N \frac{N!}{(N-n)!}$$

Always defining averages with P_N we may write

$$\int \cdots \int \rho^{(n)}(\underset{\sim}{r}_1 \cdots \underset{\sim}{r}_n)\, d\underset{\sim}{r}_1 \cdots d\underset{\sim}{r}_n = \left\langle \frac{N!}{(N-n)!} \right\rangle$$

$n=1$ $\int \rho^{(1)}(\underset{\sim}{r}_1)\, d\underset{\sim}{r}_1 = \langle N \rangle = \bar{N}$ say

$n=2$ $\int \rho^{(2)}(\underset{\sim}{r}_1 \underset{\sim}{r}_2)\, d\underset{\sim}{r}_1\, d\underset{\sim}{r}_2 = \langle N(N-1) \rangle = \overline{N^2} - \bar{N}$

$\int \rho^{(1)}(\underset{\sim}{r}_1) d\underset{\sim}{r}_1 \int \rho^{(1)}(\underset{\sim}{r}_2) d\underset{\sim}{r}_2 = (\bar{N})^2$

Subtracting, and remembering the fluid properties $\rho^{(1)}(\underline{r}) =$ constant density ρ, $\rho^{(2)} = \rho^{(2)}(|\underline{r}_2 - \underline{r}_1|)$ we find

$$\Omega \int [\rho^{(2)}(r) - \rho^2]\, d\underline{r} = \overline{N^2} - (\bar{N})^2 - \bar{N}.$$

Thus, we can express $\int [g(r) - 1]\, d\underline{r}$ in terms of the difference between $\overline{N^2}$ and $(\bar{N})^2$.

$$\therefore S(0) = 1 + \rho \int [g(r) - 1]\, d\underline{r}$$

$$= 1 + \frac{\overline{N^2} - (\bar{N})^2 - \bar{N}}{\rho \Omega}$$

$$= \frac{\overline{N^2} - (\bar{N})^2}{\rho \Omega}.$$

Final step is to relate $\overline{N^2} - (\bar{N})^2$ to the isothermal compressibility. We can do this by noting that

$$\bar{N}\, \Xi_G = \sum_N N\, e^{\frac{N\mu}{k_B T}}\, \Xi(N, \Omega, T).$$

Now differentiate w.r.t. the chemical potential μ, at constant Ω and T. We get

$$\left(\frac{\partial \bar{N}}{\partial \mu}\right)_{\Omega T} \Xi_G + \bar{N} \sum_N \frac{N}{k_B T}\, e^{\frac{N\mu}{k_B T}}\, \Xi(N, \Omega, T)$$

$$= \sum_N N \cdot \frac{N}{k_B T}\, e^{\frac{N\mu}{k_B T}}\, \Xi(N, \Omega, T)$$

$$\text{or } \left(\frac{\partial \bar{N}}{\partial \mu}\right)_{\Omega T} = \frac{1}{k_B T} \left[\overline{N^2} - (\bar{N})^2\right]$$

Hence

$$S(0) = \frac{k_B T}{\rho \Omega} \left(\frac{\partial \bar{N}}{\partial \mu}\right)_{\Omega, T}. \qquad *$$

All that remains is to relate $\left(\frac{\partial \bar{N}}{\partial \mu}\right)_{\Omega, T}$ to $\left(\frac{\partial p}{\partial \Omega}\right)_{N, T}$ remembering that in thermodynamics $\bar{N} \leftrightarrow N$.

We use Gibbs-Duhem relation

$$S\, dT - \Omega\, dp + N\, d\mu = 0,$$

S being the entropy. This expresses the fact that μ is determined by p and T, and we cannot vary the 3 quantities independently. In a system at const T we have $\therefore$

$$d\mu = \frac{-\Omega}{N}\, dp$$

$$\text{or } \left(\frac{\partial \mu}{\partial \rho}\right)_T = \frac{1}{\rho} \left(\frac{\partial p}{\partial \rho}\right)_T$$

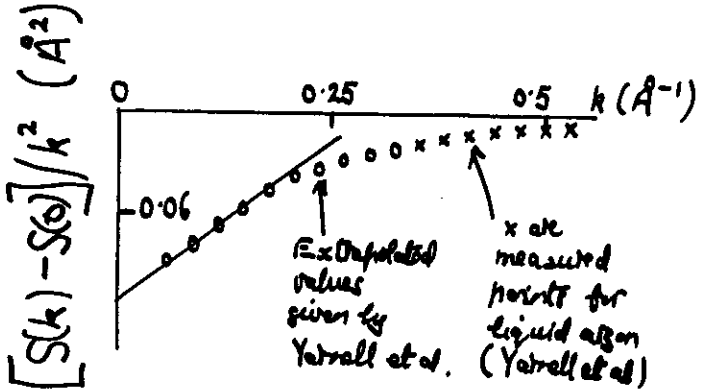
$$\text{But } \left(\frac{\partial N}{\partial \mu}\right)_{\Omega, T} = \Omega \left(\frac{\partial \rho}{\partial \mu}\right)_T$$

$$= -\Omega \rho \left(\frac{\partial \rho}{\partial p}\right)_T$$

$$\frac{1}{K_T} = -\Omega \left(\frac{\partial p}{\partial \Omega}\right)_T = \rho \left(\frac{\partial p}{\partial \rho}\right)_T$$

$$\text{or finally } \underline{S(0) = \rho\, k_B T\, K_T}$$

'Test' of $c(r) = -\frac{\phi(r)}{k_B T}$ for small angle scattering from liquid argon.



In $S(k) = S(0) + a_2 k^2 + a_3 k^3$

$$a_3 = \pi^2 \rho \{S(0)\}^2 C_6 / 12 k_B T$$

C_6 — Van der Waals const.

using $c(r) \doteq -\frac{\phi(r)}{k_B T}$: large r

$$= -\frac{C_6}{r^6 k_B T}$$

	a_2 (Å²)	a_3 (Å³)
Ar (calc)	−0·08	0·375
Ar (exptl)	−0·12	0·35.

Summary of 2nd Lecture

1. $S(0) = \rho k_B T \chi_T$

χ_T — isothermal compressibility

$$\left(\frac{\partial p}{\partial \rho}\right)_T = \frac{k_B T}{S(0)} = k_B T \left(1 - \tilde{c}(0)\right)$$

gives alternative route (to that of pair potential and $g(r)$) to eqn of state.

2. Thermodynamic consistency (with pair pot. result) gives

$$-k_B T \rho \int c(r)\, d\underset{\sim}{r} = -\frac{\partial}{\partial \rho}\left[\int d\underset{\sim}{r} + g \frac{\partial \phi}{\partial r} \frac{g(r)}{6} \rho^2\right]$$

which implies

3. $$-\rho k_B T\, c(r)\, r^2 = \phi(r) \frac{\partial^2}{\partial \rho \partial r}\left[\frac{g r^3 \rho^2}{6 k_B T}\right] + F$$

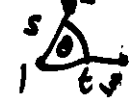
where $\int_0^\infty F\, dr = 0$

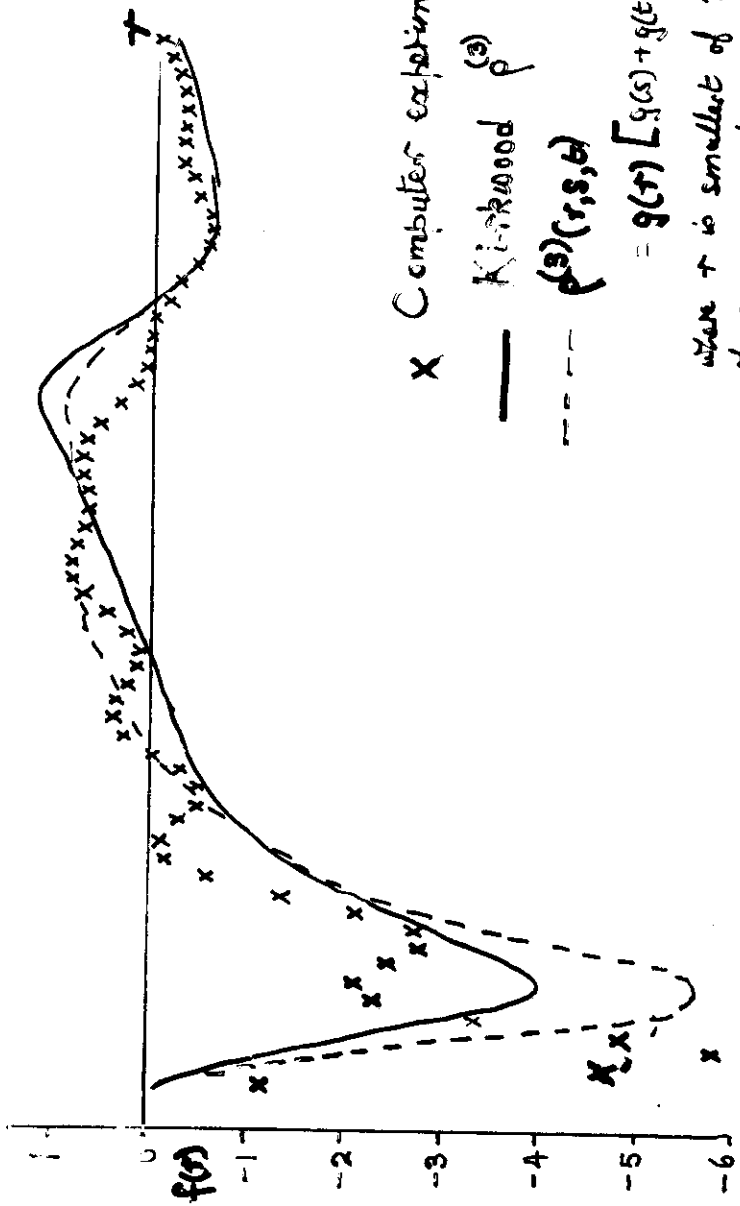
Assumption that F falls off more rapidly that ϕ for from critical point and to large r form : $c(r) = -\phi(r)/k_B T$.

[Consistent with Yarnell results on liquid argon].

4. In force eqn, only p term in Legendre polyn. expansion enters :

$$\rho^{(3)}(s, t, \cos\theta) = \sum_{l=0}^{\infty} \varphi^l(s,t) P_l(\cos\theta)$$





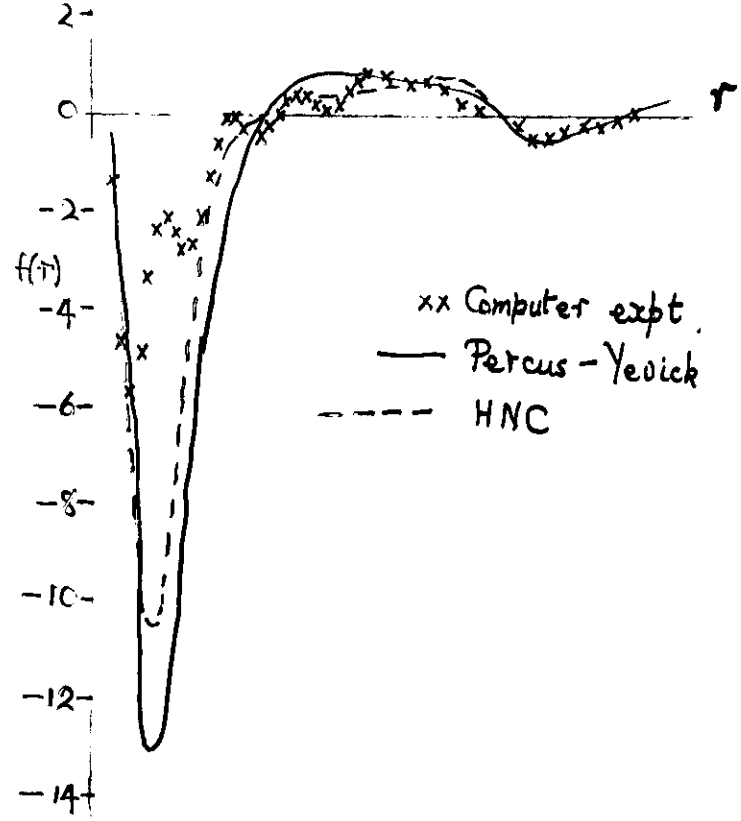
× Computer experiment

—— Kirkwood $\rho^{(3)}$

- - - - $\rho^{(3)}(r,s,t) = g(r)\,[g(s)+g(t)-1]$

when r is smallest of 3 values r, s, t

fig 7



Specific heat difference in terms of $\rho^{(3)}$

Can be shown also that C_p & C_V involve separately 3 and 4 particle correlation functions (Schofield).

Method can be developed for $C_p - C_V$ (Brathby, Gaskell & March 1970) with result:

$$\frac{C_p - C_V}{S(0)} = 1 - \frac{2\pi\rho}{3k_BT}\int dr\, r^3 g(r)\frac{d\phi}{dr} - \frac{\rho}{2k_BTS(0)} \times \left[\int d\underset{\sim}{r}\, g(r)\phi(r) + \rho\int d\underset{\sim}{r}\, d\underset{\sim}{s} \left\{ \frac{\rho_3^{(3)}(\underset{\sim}{r},\underset{\sim}{s})}{\rho^3} - g(r)g(s) \right\}\phi(r) \right]$$

3 body fn

Again, only 's' term enters ($\ell = 0$).

Kirkwood again inadequate for this.

$$g_3(\underset{\sim}{r}\,\underset{\sim}{s}) - g(r)g(s) \simeq g(r)\,h(|\underset{\sim}{s}-\underset{\sim}{r}|)$$

inside integral gives $C_p - C_V \sim 3k_B$ at triple pt of argon (measured value $2{\cdot}8\,k_B$).

Pressure dependence of $g(r)$ and three-atom correlation function

In Ξ_G, convenient to introduce

$$z = \left(\frac{M k_B T}{2\pi\hbar^2}\right)^{3/2} \exp(\mu/k_BT)$$

which is a thermodynamic property called FUGACITY

In grand ensemble, the dependence of $g(r)$ on density at const T is then only in FUGACITY and we can write

$$\left[\frac{\partial}{\partial\rho}[\rho^2 g(r)]\right]_T = V\left(\frac{\partial[\rho^2 g(r)]}{\partial\langle N\rangle}\right)_T = V\left(\frac{\partial[\rho^2 g(r)]}{\partial z}\right)_T \Big/ \left(\frac{\partial\langle N\rangle}{\partial z}\right)_T$$

Now use Ξ_G in same way we got χ_T & $S(0)$ to get

$$z\left(\frac{\partial[\rho^2 g(r)]}{\partial z}\right)_T = \langle N\rho^{(2)}(r_1 r_2)\rangle - \langle N\rangle\langle\rho^{(2)}(r_1 r_2)\rangle$$

which evidently represents fluctuation in product $N\rho^{(2)}$

Some tedious, but straightforward manipulation allows this to be written in terms of 3 atom correlation to yield

$$z\left(\frac{\partial[\rho^2 g(r)]}{\partial z}\right)_T = 2\rho^2 g(r) + \rho^3\int d\underset{\sim}{r}_3\left[\rho^{(3)}(r_1 r_2 \underset{\sim}{r}_3) - \rho^3 g(r)g(|\underset{\sim}{r}_3 - \underset{\sim}{r}|)\right]$$

NB. Only 's' term of $\rho^{(3)}$ enters here.
Deviations from Kirkwood IMPORTANT.

Exact soln. of Retcus-Yevick (P-Y) eqn for hard spheres

Virial expansion results for the fluid of hard spheres (Nijboer and van Hove, 1952; Ashcroft & March, 1967) show that in the P-Y approx,

$c(r)$ inside hard core diameter σ ($r<\sigma$) is a simple third order polynomial in r/σ.

This form is preserved in exact soln. of P-Y (Wertheim: 1963; Thiele, 1963) which reads:

$$c(r) = A_0 + A_1(r/\sigma) + A_3(r/\sigma)^3 : r<\sigma$$

If $\eta = (\pi/6)\rho\sigma^3$ (packing fraction) then

$$A_0 = -(1+2\eta)^2/(1-\eta)^4$$
$$A_1 = 6\eta(1+\tfrac{1}{2}\eta)^2/(1-\eta)^4$$
$$A_3 = -\tfrac{1}{2}\eta(1+2\eta)^2/(1-\eta)^4.$$

Corresponding eqn of state (Reiss, Frisch & Lebowitz) is

$$P_{hs} = \rho k_B T \frac{1+\eta+\eta^2}{(1-\eta)^3}.$$ Use for liquid argon.

Simple liquid metals and independent density fluctuations

Theory of independent phonons in crystals leads to the standard results for the frequencies of longitudinal phonons as (see Pines 1963)

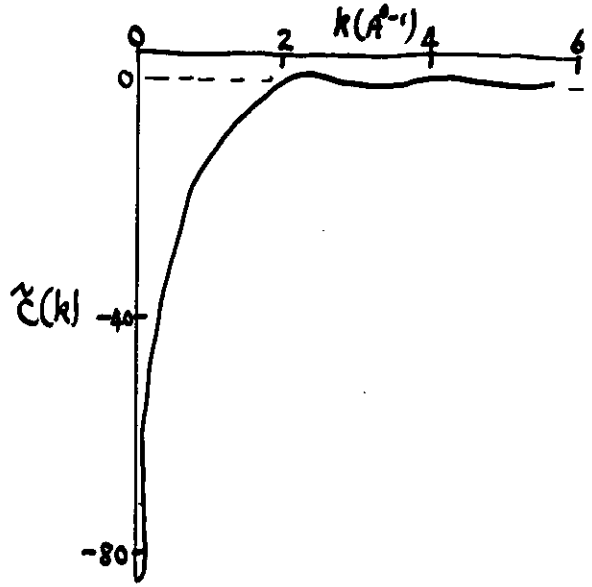
$$\omega_k^2 = \frac{\rho}{m}\sum_{\underset{\sim}{K}}\left[\left\{\frac{\underset{\sim}{k}}{k}\cdot(\underset{\sim}{k}+\underset{\sim}{K})\right\}^2\tilde{\phi}(\underset{\sim}{k}+\underset{\sim}{K}) - \left(\frac{\underset{\sim}{k}\cdot\underset{\sim}{K}}{k}\right)^2\tilde{\phi}(k)\right]$$

$\underset{\sim}{K}$ denoting reciprocal lattice vector.

In fluid, work with density fluctuations $\rho_{\underset{\sim}{k}}$ and canonically conjugate momenta $P_{\underset{\sim}{k}}$. In terms of $P_{\underset{\sim}{k}}$, we can find a Hamiltonian representing uncoupled harmonic oscillators, this time with frequencies given by

$$\omega_k^2 = \left(\frac{\hbar k^2}{2m}\right)^2 + \frac{k^2\rho}{m}\tilde{\phi}(k).$$

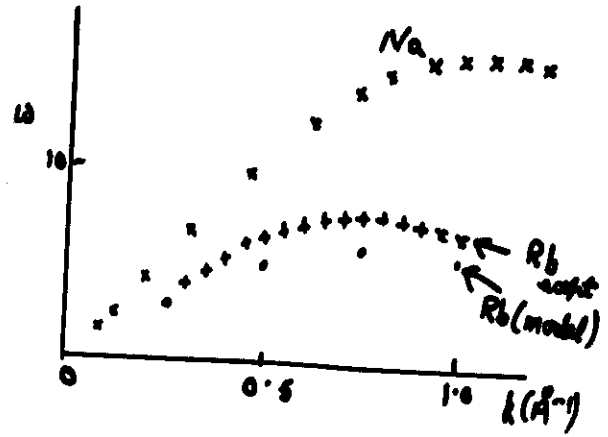
We shall <u>not</u> give detail, but only give an elementary model showing the origin of the 2nd term on the RHS of above eqn.



Ornstein-Zernike direct correlation fn. c(k) for liquid thallium at 600K (neutron data).

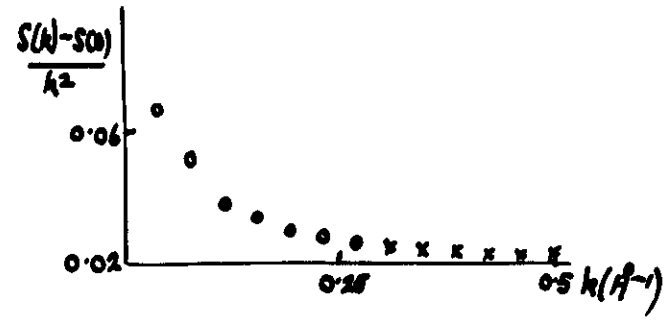
Note 'short range' in k space. Expect c(r) (and hence $\phi(r)$) to be long range.

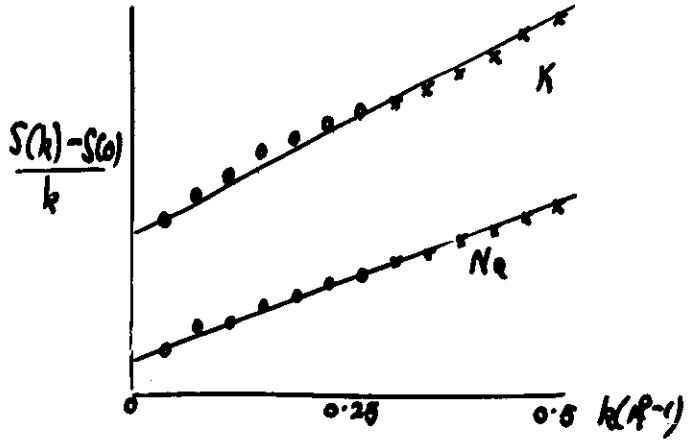
Collective mode dispersion in simple liquid metals



+ Data on Rb from Copley and Rowe (PRev Letts. 32, 49, 1974)

Small k exp of S(k) is found by analyzing Greenfield et al data on Na to be QUALITATIVELY different from ason.





No evidence for k^3 term here.