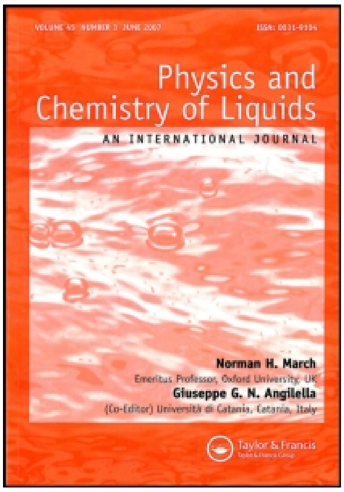

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Liquid Direct Correlation Function, Singlet Densities and the Theory of Freezing

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We have examined the solutions for the singlet density $\rho(\mathbf{r})$ in the hierarchical equation connecting $\rho(\mathbf{r})$ with the liquid direct correlation function $c(r)$. In addition to the homogeneous solution $\rho(\mathbf{r}) = \rho_{\text{liquid}}$, we exhibit a periodic solution which can coexist with the liquid solution. If the defining equation for this is linearized, we recover the bifurcation condition of Lovett and Buff. We stress the difference between the two treatments as that betweeen first- and second-order transitions.

It turns out that the treatment presented here leads to the same periodic density as that derived, using the hypernetted chain approximation, by Ramakrishnan and Yussouff in their theory of freezing. Invoking that approximation is shown thereby to be inessential.

1 INTRODUCTION

Lovett and Buff[1] have recently revived interest in the question as to whether classical statistical mechanical equations, such as the first member of the Born-Green-Yvon hierarchy which connects the singlet density $\rho(\mathbf{r})$ and the liquid pair correlation function $g(r)$, can admit more than one solution for ρ for a given g. Actually, these workers focused on the equation relating ρ and the Ornstein-Zernike direct correlation function $c(r)$ of a liquid. This latter equation has been derived by a number of workers[2,3] and has the advantage over the equation relating $g(r)$ and $\rho(\mathbf{r})$ that no assumption of pairwise interactions need be invoked.

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This equation relating $\rho(\mathbf{r})$ and $c(r)$, namely

$$\ln \rho(\mathbf{r}_1) = \int \mathrm{d}\tau_2 c(r_{12})\rho(\mathbf{r}_2) + \text{constant} \tag{1.1}$$

is the central tool employed in the present work. The integrated form (1.1) has been discussed, for example, by Lovett.[4] We shall demonstrate below, by direct solution of this equation, that for a given liquid direct correlation function, Eq. (1.1) admits not only a solution for which the singlet density is uniform, with value $\rho(\mathbf{r}) = \rho_l$, but also a co-existing periodic solution $\rho_p(\mathbf{r})$. If we then linearize our equation determining $\rho_p(\mathbf{r})$, we regain the bifurcation condition of Lovett and Buff.[1]

We then go on to set up the free energy difference corresponding to the two types of singlet density. Somewhat surprisingly, by using the equation for $\rho_p(\mathbf{r})$ in this free energy, we find a result obtained earlier in a theory of freezing by Ramakrishnan and Yussouff,[5] which was derived by making use of the hypernetted chain approximation. The present work thereby shows that this approximation is inessential in their theory of freezing.

2 FREE ENERGY DIFFERENCE BETWEEN HOMOGENEOUS AND PERIODIC PHASES

Evidently there is for a given liquid direct correlation function $c(r)$ a solution of Eq. (1.1) for which $\rho(\mathbf{r})$ is constant with a value ρ_l say. What is more important for our present purposes is to prove that a periodic solution $\rho_p(\mathbf{r})$ for the singlet density, for a given liquid $c(r)$, also exists.

To do this, we apply Eq. (1.1) to both the singlet densities ρ_l and $\rho_p(\mathbf{r})$ and then subtract to find

$$\ln\left(\frac{\rho_p(r_1)}{\rho_l}\right) - \int \mathrm{d}\tau_2 c(|\mathbf{r}_1 - \mathbf{r}_2|)[\rho_p(\mathbf{r}_2) - \rho_l] = 0 \tag{2.1}$$

where it is assumed that the constants in Eq. (1.1) are equal for the two phases in coexistence. Since, by assertion, ρ_p is periodic, we expand in a Fourier series using the reciprocal lattice vectors $\mathbf{G}$ to obtain

$$\rho_p(\mathbf{r}) = \rho_0 + V^{-1} \sum_{G \neq 0} \rho_{\mathbf{G}} \exp(i\mathbf{G} \cdot \mathbf{r}) \tag{2.2}$$

where V is the total volume. Inserting Eq. (2.2) into (2.1) and integrating over $\mathbf{r}_2$ yields

$$\ln\left(\frac{\rho_p(\mathbf{r})}{\rho_l}\right) = \frac{(\rho_0 - \rho_l)}{\rho_l} \tilde{c}(0) + (\rho_l V)^{-1} \sum_{G \neq 0} \rho_{\mathbf{G}} \tilde{c}(\mathbf{G}) \exp(i\mathbf{G} \cdot \mathbf{r}) \tag{2.3}$$

where $\tilde{c}(k)$ is the Fourier transform of $c(r)$. This Eq. (2.3) 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.

Without seeking a specific solution of Eq. (2.3), a matter which we shall refer to again below, it will be useful at this point to regard Eq. (2.1) as the Euler equation of a minimum free energy principle. Of course, the thermodynamic requirement for the two phases to be in equilibrium is that this free energy difference shall be zero. Actually, we shall work with the thermodynamic potential Ω, related to the Helmholtz free energy F and chemical potential μ by

$$\Omega = F - N\mu. \tag{2.4}$$

The Helmholtz free energy can be conveniently divided into two parts, one corresponding to free particles and the other taking account of the interparticle interactions via the direct correlation function $c(r)$. The first part is well known for uniform density[6] and we merely take the free energy density over into the local density $\rho(\mathbf{r})$. The second part is also available in essence, for example in Ref. 2, and thus we can write

$$\frac{\Delta\Omega}{k_B T} = \int d\tau \left[\rho_p(\mathbf{r}) \ln\left(\frac{\rho_p(\mathbf{r})}{\rho_l}\right) - (\rho_p(\mathbf{r}) - \rho_l)\right] - \frac{1}{2}\iint d\tau_1\, d\tau_2 [\rho_p(\mathbf{r}_1) - \rho_l] c(|\mathbf{r}_1 - \mathbf{r}_2|)[\rho_p(\mathbf{r}_2) - \rho_l]. \tag{2.5}$$

Performing the variation of $\Delta\Omega$ with respect to $\rho_p(\mathbf{r})$ is readily verified to lead back to Eq. (2.1).

At this stage, we insert the Fourier expansions (2.2) and (2.3) into (2.5) to find, with $N = \rho_l V$,

$$\frac{\Delta\Omega}{k_B T} = \frac{1}{2N}\sum_{\mathbf{G}} \tilde{c}(\mathbf{G})|\rho_{\mathbf{G}}|^2 - \frac{N(\rho_0 - \rho_l)}{\rho_l} + \tfrac{1}{2}N\tilde{c}(0)\frac{(\rho_0^2 - \rho_l^2)}{\rho_l^2} \tag{2.6}$$

This is the desired expression for the free energy difference in terms of the Fourier components $\rho_{\mathbf{G}}$ of the periodic density, and the volume change reflected in the difference between ρ_l and ρ_0.

The possibility of coexistence of homogeneous liquid and periodic phases is clear from Eq. (2.6) 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 the periodic phase has the higher density. That these terms are strongly coupled is clear from the highly non-linear nature of the Euler equation (2.3). The actual coexistence point is evidently determined by the properties of $\tilde{c}(\mathbf{G})$, including $\mathbf{G} = 0$, linking the liquid structure intimately with the appearance of the periodic phase.

3 DISCUSSION AND SUMMARY

The above discussion of Eqs. (2.6) and (2.3) has, of course, been focussed on what is, in principle, possible from the structure of these two equations. It is remarkable that the work of Ramakrishnan and Yussouff[5] using as it does the hypernetted chain (HNC) approximation nevertheless leads to the same Euler Eq. (2.3). Our work, based directly on Eq. (2.1), shows clearly that this use of HNC is inessential to their theory of freezing. However, a significant difference between their treatment and ours resides in the variational principle from which the Euler equation derives. Our basic variation is of $\Delta\Omega$ in Eq. (2.5). Their variation is on an equation resembling, but not identical to, Eq. (2.6). This latter equation, in our treatment, already embodies the result for the periodic density determined by the non-linear Euler Eq. (2.3). The specific difference between our Eq. (2.6) and their form for $\Delta\Omega$ is that they have an additional term of order $(\rho_0 - \rho_l)$ giving their result as

$$\frac{\Delta\Omega}{k_B T} = \frac{1}{2N} \sum_{\mathbf{G}} \tilde{c}(\mathbf{G}) |\rho_G|^2 - \tfrac{1}{2} N [1 - \tilde{c}(0)] \frac{(\rho_0^2 - \rho_l^2)}{\rho_l^2} \tag{3.1}$$

This form is appealing because $[1 - \tilde{c}(0)]$ is essentially the inverse compressibility of the liquid. Their work[5] in fact shows how an explicit periodic solution, for a given liquid direct correlation function $c(r)$, can be derived from Eq. (2.3).

Our final comment concerns the relation of the non-linear Eq. (2.3) to the work of Lovett and Buff[1,4] on bifurcation. Whereas the above treatment is evidently describing a first-order transition, with a volume change and finite Fourier components $\rho_{\mathbf{G}}$ actually at the freezing point, their work explores the condition under which the $\rho_{\mathbf{G}}$ develop continuously from the homogeneous phase. The procedure they use corresponds to linearizing Eq. (2.3) which then has a solution of periodic form provided the condition $(1 - \rho_l \tilde{c}(\mathbf{G})) = 0$ is satisfied. This corresponds in fact to the structure factor $S(\mathbf{G}) = 1/(1 - \rho_l \tilde{c}(\mathbf{G}))$ becoming infinite. This is an instability of the liquid phase.

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Note added in proof

Since our work was completed, the closely related investigation of Haymet and Oxtoby (*J. Chem. Phys.*, **74**, 2559, 1981) has appeared.

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