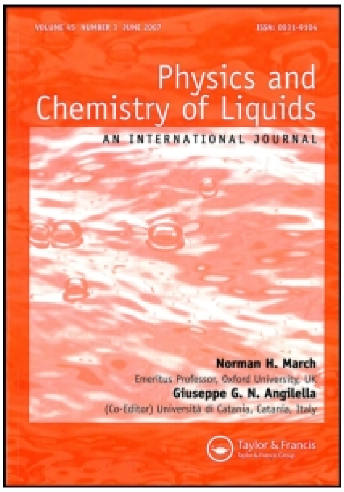

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Thermodynamic consistency within the density-wave theory of freezing is briefly discussed. The non equivalence of different routes to calculate the change in a thermodynamic quantity upon freezing is related to the approximations involved in practical calculations. In particular, a new way of calculating entropy and volume changes is proposed. It is shown that this new route avoids an unphysical feature of the entropy formula previously proposed by other authors. The freezing of hard spheres is discussed as an illustration.

The density-wave theory of freezing, first formulated in the pionering work of Kirkwood and Monroe,[1] has received renewed attention during the last few years. Ramakrishnan and Yussouff[2] reformulated the theory in terms of the direct corelation functions, avoiding the explicit presence of the interparticle interaction potential. By doing so, they shift the emphasis to the structural properties of the system and give a unifying description of the liquid solid transition in simple liquids. The density-wave theory of freezing involves the expansion of the appropriate thermodynamic potential of the ordered phase around that of the homogeneous liquid. This requires: i) the knowledge of the liquid structure; ii) a functional expansion in which direct correlation functions of any order appear; iii) a Fourier representation of the one-body density $\rho(r)$. In practical applications,[3–6] for a given description of the liquid structure, one has to truncate the expansion in both ii) and iii).

In the present note, we discuss the thermodynamic inconsistency which arises in the theory because of the approximations mentioned above. This means that different routes to calculate the same thermodynamic quantity may give different results. Such a problem is well known in the case of approximate theories for the liquid structure.[7–8]

For freezing with finite volume change, one can calculate the entropy change per particle (Δs) at least in two different ways. Even within the usual approach[2,3,9] of relating Δs to the difference in grandcanonical potential between the two phases, the formulae published hitherto are incomplete or in error. We therefore first present the correct expression within this approach. We then propose a new method of calculating Δs which, in particular, avoids an unphysical dependence of the entropy change on the mass of the particles yielded by approximate calculations carried out within the previous approach. Moreover an additional manner to calculate the volume change on freezing, through thermodynamic derivatives, is obtained. This can be used to check the degree of internal consistency of a given calculation.

The essential equations of the theory can be written, following Haymet and Oxtoby,[10] as

$$\Delta W \equiv -\frac{(P_s - P_l)}{K_B T n} = (-1 + c_0)\eta + \tfrac{1}{2}c_0\eta^2 + \sum_{\bar{G}_i} c_{\bar{G}_i}\rho^2_{\bar{G}_i} + \cdots, \tag{1}$$

$$\Delta\mu \equiv \mu_s - \mu_l = -K_B T \ln\left[\int d\bar{r}\, e^{\Delta C(\bar{r})}/(1+\eta)V\right], \tag{2}$$

$$\rho_{\bar{G}_i} = (1+\eta)\int d\bar{r}\, e^{i\bar{G}_i\cdot\bar{r} + \Delta C(\bar{r})}\bigg/\int d\bar{r}\, e^{\Delta C(\bar{r})}, \tag{3}$$

where

$$\Delta C(\bar{r}) \equiv C_s(r) - C_l = c_0\eta + \sum_{\bar{G}_i} c_{\bar{G}_i}\rho_{\bar{G}_i} e^{i\bar{G}_i\cdot\bar{r}} + \cdots, \tag{4}$$

$$C_{\bar{G}_i} = n\int d\bar{r}\, c(r)\, e^{i\bar{G}_i\cdot\bar{r}}, \tag{5}$$

and $\rho_{\bar{G}_i}$ is the Fourier component, at the reciprocal lattice vector $\bar{G}_i$, of the density in the ordered phase

$$\rho(\bar{r}) = n\left[1 + \eta + \sum_{\bar{G}_i} \rho_{\bar{G}_i} e^{i\bar{G}_i\cdot\bar{r}}\right]. \tag{6}$$

Above, $C_s(r)$ and C_l are the one body direct correlation functions of the solid and of the liquid and η is the fractional volume change on freezing.

Equations (1) and (2) give, respectively, the difference in pressure and in chemical potential between the solid and the liquid phase, at given temperature T. They are expressed in terms of properties of the liquid phase, namely its density n and its direct correlation functions. We stress that in Eqs (1) and (4) direct correlation functions of any order appear, starting from the two body one $c(r)$. The set of order parameters $\{\rho_{\bar{G}_i}\}$ and η, at coexistence, must satisfy the equilibrium Eqs (3) under the condition that the pressure and the chemical potential differences should vanish, $\Delta W = \Delta\mu = 0$. This fixes the freezing line (n_f, T_f) once the liquid structure is known as function of n and T, and gives the fractional volume change η and the Fourier components $\{\rho_{\bar{G}_i}\}$ of the density in the coexistent solid.

The change on freezing of a thermodynamic property such as the entropy per particle s can be calculated from the slopes of $\Delta W(\Delta\mu)$ near the freezing point. These can be obtained, in turn, by solving Eqs (3) under the only condition $\Delta\mu = 0$ $(\Delta W = 0)$. In terms of ΔW the entropy change per particle can be written as

$$\Delta s \equiv s_s - s_l = -\frac{1}{1+\eta}\left[K_B T \frac{\partial \Delta W}{\partial T}\bigg|_\mu + \eta s_l\right]_{n_f,T_f} \tag{7}$$

$$= -\frac{1}{1+\eta}\left[K_B T \frac{\partial \Delta W}{\partial n}\bigg|_T \frac{\partial n}{\partial T}\bigg|_\mu + K_B T \frac{\partial \Delta W}{\partial T}\bigg|_n + \eta s_l\right]_{n_f,T_f},$$

where to obtain the expression in the second row we have used the fact that from Eq. (1) ΔW is a function of the temperature T and of the density n of the liquid. The contribution $-\eta s_l/(1+\eta)$ to the entropy change in Eq. (7) originates from the fact that, in the grandcanonical ensemble, the number of particles in the volume V for the crystalline phase, N_S, is different from that for the liquid phase, N_l, $(N_s - N_l)/N_l = \eta$. Such a term, which has been neglected in previous formulae[2,3,9] for Δs, has the unpleasant feature that it contains the mass of the particles. This appears in the ideal part of s_l. However, there is another term in Δs which is proportional to s_l. By utilizing thermodynamic identities, in fact, Eq. (7) can be modified to read

$$\Delta s = \left[(1-\alpha)n\Delta v s_l + \alpha \frac{\partial S_l}{\partial V}\bigg|_T \Delta v - \frac{K_B T}{1+\eta}\frac{\partial \Delta W}{\partial T}\bigg|_n\right]_{n_f,T_f} \tag{8}$$

with $\Delta v = v_s - v_l$, the volume change per particle and

$$\alpha = \left[-\frac{K_B T}{\eta}\frac{\partial \Delta W}{\partial n}\bigg|_T n\frac{\partial \eta}{\partial P}\bigg|_T\right]_{n_f,T_f}. \tag{9}$$

The entropy per particle is now decomposed, in Eq. (8), into three terms. The first one contains all the dependence on the mass m of the particles. Since Δs cannot depend on m, an exact calculation must yield $\alpha = 1$. (We notice that, if the first term vanishes due to $\alpha = 1$, one recovers the partitioning of the entropy change into a volume term[11] plus a remainder as proposed by Tallon.[12]) Nevertheless, this will not happen in general for approximate calculations, as we have checked in one case. In his model study on the freezing of hard spheres Haymet[3] gives $\Delta W(n)$ around n_f so that α can be easily evaluated to be 2.3. We conclude that Eq. (7) or (8) does not provide a convenient way of evaluating the entropy change.

Let us turn now to the other route to evaluate Δs. By exploiting the dependence of $\Delta\mu$ on n and T one immediately gets

$$\Delta s = -\left[\left.\frac{\partial \Delta\mu}{\partial T}\right|_p\right]_{n_f, T_f} = -\left[\left.\frac{\partial \Delta\mu}{\partial n}\right|_T \left.\frac{\partial n}{\partial T}\right|_p + \left.\frac{\partial \Delta\mu}{\partial T}\right|_n\right]_{n_f, T_f} \cdot \tag{10}$$

This new formula does not contain any dependence on the mass of the particles. Moreover from the slope of $\Delta\mu$ around the freezing point it is possible to obtain an alternative thermodynamic equation for the fractional volume change

$$n_f \Delta v = -\frac{\eta}{1+\eta} = n_f\left[\left.\frac{\partial \Delta\mu}{\partial P}\right|_T\right]_{n_f, T_f} = n_f\left[\left.\frac{\partial \Delta\mu}{\partial n}\right|_T \left.\frac{\partial n}{\partial P}\right|_T\right]_{n_f, T_f} . \tag{11}$$

We stress that the comparison between η from Eq. (11) and η from the coexistence conditions (Eqs (1)–(3) with $\Delta\mu = \Delta W = 0$) provides a simple check on the internal consistency of an approximate calculation. Of course, in an exact calculation they would coincide. Finally, by combining Eq. (10) and (11) the entropy change can be written as

$$\Delta s = \Delta v\left[\left.\frac{\partial S_l}{\partial V}\right|_T\right]_{n_f, T_f} - \left[\left.\frac{\partial \Delta\mu}{\partial T}\right|_n\right]_{n_f, T_f} . \tag{12}$$

From inspection of the equation above it appears clear that, by using $\Delta\mu$, the entropy change is naturally decomposed into a volume term plus a remainder, as it was previously suggested.[12] We have already noticed that η and hence Δv can be calculated in two different ways which will be not equivalent in approximate calculations. The same will happen for Δs from Eq. (12) depending on how Δv has been calculated.

To illustrate the foregoing discussion we reconsider below the freezing of hard spheres. We have carefully repeated Haymet's calculations.[3] Having reproduced his results, we have then calculated $\beta\Delta\mu(n)$ about n_f. (We recall that for hard spheres $\beta\Delta\mu$ does not depend on the temperature T and hence $\partial\Delta\mu/\partial_T|_{n_f} = 0$.) In terms of $\partial\Delta\mu/\partial n|_{n_f}$, we have calculated the entropy change and the fractional volume change from Eq. (10) and Eq. (11), respectively. We find $\Delta s = -1.9K_B$ and $\eta = 0.15$, whereas from the coexistence condition one obtains $\eta = 0.06$. These values compare favourably with the computer simulation results $\Delta s = -1.2K_B$ and $\eta = 0.10$. The agreement, however, is still only semiquantitative. Though the two alternative values obtained for η bracket the one yielded by computer experiments, the discrepancy between them is still appreciable. In this respect we should also comment about the presence of a third value of η on such calculation a la Haymet. In fact, for a given crystalline structure, the reciprocal lattice vectors of the solid phase are fixed by the location of the first peak in the structure factor of the liquid phase. In principle, they should be calculated in a consistent manner with the fractional volume change η from the coexistence condition. However, we have found it impossible to force such a consistency without losing the physical solution to the freezing problem.

In summary, we have discussed above the problem of the internal thermodynamic consistency within the density wave theory of freezing. We have argued that inconsistency arises because of the approximations that one has to make in practical calculations. Among these, one should also mention the approximate character of the theory chosen for the liquid structure, in particular its possible thermodynamic inconsistency. We have examined in detail the cases of the entropy change and of the volume change on freezing. We have shown that the alternative way we propose to calculate the entropy change avoids an unphysical dependence on the mass of the particles yielded by the route previously considered. We also suggest that the thermodynamic formula for the volume change, that we have proposed above, could be used to check the degree of internal consistency in practical calculations using the density-wave theory of freezing.

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