Physica A 176 (1991) 28–36
North-Holland

STATISTICAL MECHANICAL THEORIES OF FREEZING: WHERE DO WE STAND?

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The basic advantages of the density functional theory over the other statistical mechanical theories of freezing are outlined. The feasibility of a density functional based calculation is illustrated in the case of the hard sphere freezing. The difficulties encountered in the extension of these results to continuous potentials are discussed and a possible solution is presented.

1. Introduction: the theories of freezing

Ordering phase transitions can (and do) occur in many systems made up of subatomic, atomic, molecular or supramolecular items. At sufficiently high pressures and low temperatures, such transitions from disordered to an ordered state usually become unavoidable. Indeed, the loss in configurational entropy resulting from this ordering can then be compensated by the gain in correlational entropy resulting from the more efficient packing, which characterizes the ordered state. Any ordered state can, moreover, usually be described in terms of the broken symmetries corresponding to the "freezing in" of a number of translational, rotational or compositional degrees of freedom. Such states may be further characterized in terms of the underlying "order parameters", for which the corresponding Landau theory [1] can then be constructed.

Although such a theory can give important clues to symmetry-based restrictions and similar qualitative information, it cannot by itself give a *quantitative* description of the ordering phenomena. The reasons for this are well known: the Landau theory was designed to describe second-order phase transitions and hence it considers the order parameters to be small, whereas many ordering transitions have a pronounced first-order character; while the theory also provides no means to compute the coefficients of the expansion of the free energy with respect to these order parameters. As a consequence, a quantitative description of ordering or freezing transitions is possible only within the general framework of equilibrium statistical mechanics.

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Notwithstanding a century long practice of the latter, progress in this general area of molecular physics has been rather slow. Some of the reasons behind this are easily understood. Indeed, in the traditional [1] partition-function based approach to statistical thermodynamics, one is immediately faced with a complicated N-body problem, which has proven to be intractable even for the much simpler disordered phases (except when dilute). The situation is however less trivial for the theories [2] based on the Born–Green–Yvon hierarchy for the N-body distribution functions. Indeed, the celebrated Kirkwood–Monroe truncation [3] of the equivalent Kirkwood hierarchy for a Lennard-Jones solid, performed half a century ago, did describe the solid but failed to produce the proper freezing behaviour and the situation has remained unsatisfactory till now. This could be due to the fact that the solution to this hierarchy has a delicate and explicit dependence on the interaction potential whereas once this solution is known, there is still a long way to go before the final thermodynamic data for the solid can be obtained.

It may thus be considered as a surprise when successful results were announced for freezing by Ramakrishnan and Yussouff [4] within a related but different theory, which today goes under the name of the "density functional theory" because it views the free energy as a functional of the one-body density [5]. It is true that this theory yields a framework which is a priori much better suited to the description of phase transitions than any of the previous theories. Indeed, the central item of this theory is the free energy whereas it is precisely the thermodynamic data which a theory of phase transitions should describe accurately. Within density functional theory, this free energy is moreover obtained in terms of the one- and two-body structural information, avoiding hereby the complicated N-body problems. Finally, the ordered equilibrium state can be found by minimizing this free energy expression without having to solve explicitly for the structural data. This theory is thus fairly close in spirit to the phenomenological Landau theory of which it constitutes so to say a statistical mechanical version.

It is nevertheless also clear today that the enthusiasm following the original success [4] has to be tempered somewhat since many problems have arisen, some of which have been circumvented (see our previous discussions [6, 7]), while others remain and will be considered in more detail below.

2. Density functional theory of freezing: the success story

The general setup of the density functional theory is fairly simple. One starts from a classical equilibrium system of volume V, temperature T and chemical potential μ. Next, all broken symmetry elements are described in terms of a formal external potential, $\phi(\boldsymbol{r})$ (for presentational convenience, we will assume that the molecules have only translational ($\boldsymbol{r}$) degrees of freedom). These include: (i) the finite size of the system, (ii) the location of the coexisting phases and (iii) the symmetries of the ordered phases. Within the Gibbsian equilibrium statistical mechanics, the grand canonical potential of this system, Ω, will be a function of T and a functional of this generalized external field or equivalently of the local chemical potential, $u(\boldsymbol{r}) = \mu - \phi(\boldsymbol{r})$. Indicating this functional dependence by square brackets, we have $\Omega = \Omega(T, [u])$, and omitting for simplicity the T-dependence, we henceforth write: $\Omega = \Omega[u]$. It is then easily seen that the first two functional derivatives of $\Omega[u]$ with respect to $u(\boldsymbol{r})$ read

$$\frac{\delta\Omega[u]}{\delta u(\boldsymbol{r})} = -\rho(\boldsymbol{r}) , \tag{1}$$

$$\frac{\delta^2\Omega[u]}{\delta u(\boldsymbol{r})\, \delta u(\boldsymbol{r}')} = -\beta\{\rho(\boldsymbol{r}, \boldsymbol{r}') - \rho(\boldsymbol{r})\, \rho(\boldsymbol{r}') + \rho(\boldsymbol{r})\, \delta(\boldsymbol{r} - \boldsymbol{r}')\} , \tag{2}$$

where $\beta = 1/k_B T$ and $\rho(\boldsymbol{r})$, $\rho(\boldsymbol{r}, \boldsymbol{r}')$ denote respectively the one- and two-body densities. On the basis of (1), we are tempted to view $\rho(\boldsymbol{r})$ and $u(\boldsymbol{r})$ as a pair of conjugate variables, and to eliminate the more formal variable $u(\boldsymbol{r})$ in favor of the physically more accessible variable $\rho(\boldsymbol{r})$ by performing a functional Legendre transformation from the grand potential Ω to the (Helmholtz) free energy F according to

$$F[\rho] = \Omega[u] - \int \mathrm{d}\boldsymbol{r}\, u(\boldsymbol{r})\, \frac{\delta\Omega[u]}{\delta u(\boldsymbol{r})} , \tag{3}$$

where $F = F[\rho]$ is now viewed as a functional of the density, $\rho(\boldsymbol{r})$, obtained by eliminating $u(\boldsymbol{r})$ in the r.h.s. of (3) in favor of $\rho(\boldsymbol{r})$ by formally solving (1). The relations conjugate to (1)–(2) can then be shown to read:

$$\frac{\delta F[\rho]}{\delta\rho(\boldsymbol{r})} = u(\boldsymbol{r}) , \tag{4}$$

$$\beta\, \frac{\delta^2 F[\rho]}{\delta\rho(\boldsymbol{r})\, \delta\rho(\boldsymbol{r}')} = \frac{\delta(\boldsymbol{r} - \boldsymbol{r})}{\rho(\boldsymbol{r})} - C(\boldsymbol{r}, \boldsymbol{r}'; [\rho]) , \tag{5}$$

where $C(\boldsymbol{r}, \boldsymbol{r}')$ is the Ornstein–Zernike direct correlation function (d.c.f.) Eq. (5) can, finally, be functionally integrated in the space of $\rho(\boldsymbol{r})$ functions to yield (Λ being the thermal wavelength)

$$\begin{aligned} \beta F[\rho] &= \int \mathrm{d}\boldsymbol{r}\, \rho(\boldsymbol{r})\, (\ln\{\Lambda^3\rho(\boldsymbol{r})\} - 1) \\ &\quad - \int \mathrm{d}\boldsymbol{r} \int \mathrm{d}\boldsymbol{r}\, \int_0^1 \mathrm{d}\lambda \int_0^\lambda \mathrm{d}\lambda'\, \rho(\boldsymbol{r})\, \rho(\boldsymbol{r}')\, C(\boldsymbol{r}, \boldsymbol{r}'; [\lambda'\rho]) , \end{aligned} \tag{6}$$

which is the integral form corresponding to the differential relation (5). Eq. (6) provides us with a compact and first principles link between the free energy (or the thermodynamic data) and the structural information embodied in $\rho(\boldsymbol{r})$ and $C(\boldsymbol{r}, \boldsymbol{r}'; [\rho])$. It is this relation which is at the basis of the most recent density functional theories of freezing [8]. In order to implement eq. (6), one can evaluate its r.h.s. with a suitably parametrized expression for the one-body density $\rho(\boldsymbol{r})$. The nature of this expression will depend on the type of order present; for instance, for a crystalline ordering, one can use Gaussian density profiles around the lattice sites $\{\boldsymbol{r}_j\}$, so that

$$\rho(\boldsymbol{r}) = \sum_j \left(\frac{\alpha}{\pi}\right)^{3/2} \exp\{-\alpha(\boldsymbol{r} - \boldsymbol{r}_j)^2\} , \tag{7}$$

where the inverse width parameter α is playing the role of an order parameter ($\alpha > 0$ for the ordered phase and $\alpha = 0$ for the disordered phase), which, just as in Landau's theory, can be determined by minimizing the free energy with respect to α. As such, eq. (7) is only approximate but there is no difficulty in systematically improving it (at the expense of introducing more order parameters, usually with little gain, at least in the freezing context [7]). The crux of the method now rests on our ability to also (analytically) implement the two-body information contained in the d.c.f. appearing in (6). Today, the d.c.f. of the ordered phases are however still unknown and therefore we will take advantage of the fact that, in (6), they appear only under the integral signs in order to approximate them in terms of the d.c.f. of the disordered phase. At present, the value of this approximation is not known but, in principle, it could be tested as soon as more information about the structure of the ordered phases becomes available.

It is, moreover, fairly obvious that the (angular) *averaged* structures of the coexisting ordered and disordered phases should be fairly similar because of the similar packings. The problem then boils down to finding which disordered phase yields a structure which can mimic the (angular) averaged structure of a given ordered phase. The difficulty now is that there does not appear to exist a systematic recipe to find the "effective" disordered phase which does this. Therefore, a certain amount of guessing is necessary at this stage. One thing which is certain however is that, in the ordered phase, the two-body *correlations* are weaker and of shorter range than in the coexisting disordered phase, and therefore this "effective" disordered phase has to correspond to a different thermodynamic state than the coexisting disordered phase. It so happens that, in the particular case of the freezing of a hard sphere fluid, the range of the direct correlations in both phases is given to a good approximation (see the Percus–Yevick theory) by the hard sphere diameter, i.e., the shortest range possible, whereas the amplitude of these correlations is completely determined by the density (packing fraction), which reduces the search of the effective hard sphere fluid to the determination of its effective density alone. In the hard sphere case, it is thus only necessary to find the hard sphere fluid whose density is small enough so that its correlations can describe (both with respect to its amplitude and its range) those of the angular averaged solid. One recipe (but not the only one), which appears to do this fairly well, is to determine the effective density, $\hat{\rho}$, corresponding to a given solid density, $\rho(r)$, from the following self-consistency relation:

$$\phi_{\mathrm{sol}}[\rho] = \phi_{\mathrm{liq}}(\hat{\rho}) , \tag{8}$$

between the excess free energy per particle (ϕ) of the solid ($\phi_{\mathrm{sol}}[\rho]$) and of this effective liquid or fluid ($\phi_{\mathrm{liq}}(\hat{\rho})$). This then leads to hard sphere freezing results which are quite spectacular [8]; e.g. the packing fractions of the fluid (0.495) and the (fcc) solid (0.545) are within the error bars of the simulation results (respectively 0.494 and 0.545). The corresponding hard sphere equation of state is shown in fig. 1. The underlying freezing mechanism is seen to be a competition between the configuration entropy (favoring disorder) and the excess or correlation entropy (favoring ordered packings) [6].

Not only the above scheme [8] but also several other variations on the same theme (see ref. [7]) do lead to similar hard sphere freezing results, which

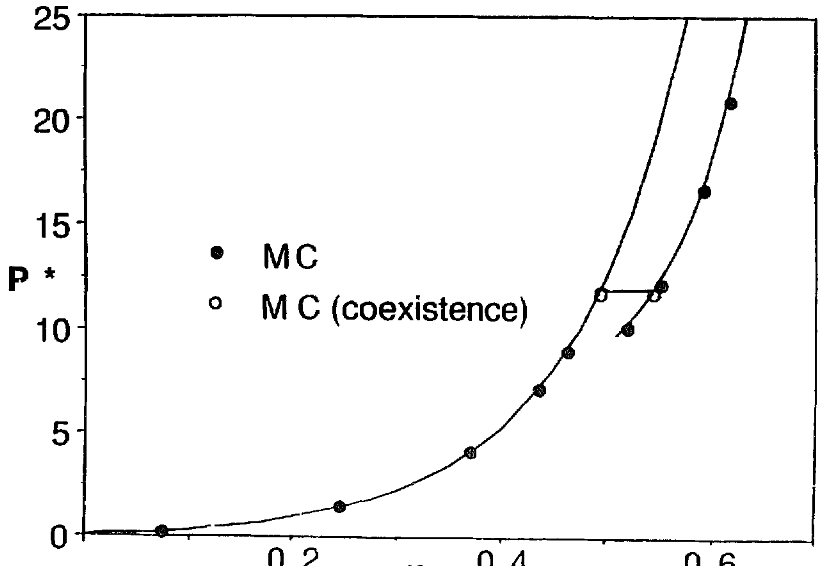

Fig. 1. The complete hard sphere phase diagram in the pressure($p^* = \beta p \sigma^3$)-density($\eta = \frac{1}{6}\pi\rho\sigma^3$) plane. The stable and metastable portions of the fluid and (fcc) solid branches are separated by the tie-line. The full lines correspond to the theoretical results (see text) and the dots represent the computer simulation results [8].

appear therefore to be fairly robust. The extension of this approach to other, more complicated, hard core systems has produced results which, although more difficult to check, appear to be equally sound. This is the case for, e.g., the freezing of hard spheres in the presence of an external field, the partial freezing of hard sphere mixtures, the freezing of hard sphere mixtures into substitutionally disordered solids, the freezing of hard "spheres" of various spatial dimensionalities, etc. (for a recent review, see ref. [7]). This remains true also for the studies concerning the orientational freezing of systems composed of non-spherical objects with purely hard core interactions (see e.g. ref. [9]) although it should be realized that, for such systems, the description of the disordered phase is already far less accurate than for the simple hard sphere system, while the consequences of this for the density functional description of the ordered phases are more difficult to estimate.

In conclusion, it can be stated that, between all the statistical mechanical approaches to freezing, it is the density functional approach which, for the reasons given above, has reached its goal with the most success.

3. Density functional theory of freezing: the difficulties

Some of the difficulties encountered in the early applications of the density functional techniques to freezing problems can be qualified as purely technical. For instance, the use of a Fourier series representation for the local density instead of the real space representation given in eq. (7) has produced Fourier series with slow oscillatory convergence properties. Similarly, expansions of the free energy (6) around the free energy of the disordered phase, as in the Landau theory, has produced series which are presumably only asymptotic in nature. As shown above, such difficulties can easily be circumvented (for a detailed discussion see ref. [7]). The real problem of the density functional theory of freezing, in its present stage, is concerned instead with the extension of the theory to systems with continuous, and hence more realistic, interaction potentials. Indeed, some recent studies (see ref. [10]) have shown that a straightforward (or brute force) extension of the hard sphere theory to more realistic potentials leads to results of very limited value. It is important to realize here that the problem appears to be unrelated to the presence of attractive forces, since it is present already for purely repulsive continuous potentials, such as the inverse power potentials. It is our opinion that what is at stake here is the proper definition of the effective liquid whose correlations are supposed to model those of the solid. It is, indeed, well known that, in the liquid, the amplitude and the range of the correlations are tightly bound to each other, whereas in the solid the corresponding relation is unknown. This then raises the question of how to consistently relate the amplitude to the range of correlations in the effective liquid corresponding to a given potential. In the hard sphere case, this problem was very much simplified because the range of the correlations was fixed by the hard sphere diameter, leaving only the density as a free parameter to adjust the amplitude self-consistently. In the case of the more general potentials, it could then well be that another effective parameter, besides the effective density, needs to be introduced in order to achieve the required self-consistency between the amplitude and the range of the direct correlation function of the effective liquid. Since it is, at present, not obvious how to do this, we will now describe one way to circumvent the problem in a more pedestrian manner.

Since we know how to compute the free energy of the hard sphere solid, we will now try to compute the free energy of the solid corresponding to a continuous potential, say $V(r)$, by thermodynamic perturbation theory [11]. In other words, we will proceed for the solid in the same way as usually done for the liquid [12]. Although thermodynamic perturbation does not always work, even for the liquid, we can nevertheless hope to learn something more about the above difficulties by applying it to the solid. In order to avoid having to face too many problems at one time, we will consider the $n = 12$ soft spheres, $V(r) = \epsilon(\sigma/r)^n$, which in many aspects behave similarly to hard spheres (corresponding to $n \to \infty$), except that the purely repulsive potential is now continuous and of slightly longer range. Let us expand then the free energy of the $1/r^{12}$ solids as

$$\beta F \simeq \beta F_{\mathrm{HS}}(\delta) - \frac{1}{2\rho V} \int \mathrm{d}\boldsymbol{r}_1 \int \mathrm{d}\boldsymbol{r}_2 \, y_{\mathrm{HS}}(\boldsymbol{r}_1, \boldsymbol{r}_2; \delta) \times (\exp\{-\beta V(r_{12})\} - \exp\{-\beta V_{\mathrm{HS}}(r_{12})\}) , \tag{9}$$

where $y_{\mathrm{HS}}(\boldsymbol{r}_1, \boldsymbol{r}_2; \delta) = \rho(\boldsymbol{r}_1, \boldsymbol{r}_2; \delta) \exp\{\beta V_{\mathrm{HS}}(r_{12})\}$ and δ denotes the hard sphere (HS) diameter corresponding to the soft sphere diameter σ ($\neq \delta$). Next, we split $V(r) = V_0(r) + W(r)$ into a core part, $V_0(r) = V(r)\,\theta(\lambda - r) + F(r) \times \theta(\lambda - r)$, and a repulsive tail, $W(r) = V(r)\,\theta(r - \lambda) - F(r)\,\theta(\lambda - r)$, with λ a cutoff parameter, $F(r)$ a linear interpolation function [12] and $\theta(x)$ the Heaviside step function. We then determine δ in such a manner that

$$\int \mathrm{d}\boldsymbol{r}_1 \int \mathrm{d}\boldsymbol{r}_2 \, y_{\mathrm{HS}}(\boldsymbol{r}_1, \boldsymbol{r}_2; \delta) (\exp\{-\beta V_0(r_{12})\} - \exp\{-\beta V_{\mathrm{HS}}(r_{12})\}) = 0 \tag{10}$$

so that (9) can be rewritten, to the same level of approximation [11], as

$$\beta F \simeq \beta F_{\mathrm{HS}}(\delta) + \frac{1}{2\rho V} \int \mathrm{d}\boldsymbol{r}_1 \int \mathrm{d}\boldsymbol{r}_2 \, \rho_{\mathrm{HS}}(\boldsymbol{r}_1, \boldsymbol{r}_2; \delta) (1 - \exp\{-\beta W(r_{12})\}) , \tag{11}$$

or treating βW as a small perturbation:

$$\beta F = \beta F_{\mathrm{HS}}(\delta) + \frac{1}{2\rho V} \int \mathrm{d}\boldsymbol{r}_1 \int \mathrm{d}\boldsymbol{r}_2 \, \rho_{\mathrm{HS}}(\boldsymbol{r}_1, \boldsymbol{r}_2; \delta) \, \beta W(r_{12}) \,, \tag{12}$$

which we rewrite finally as

$$\beta F = \beta F_{\mathrm{HS}}(\delta) + 2\pi\rho \int_0^\infty \mathrm{d}r \, r^2 \hat{g}_{\mathrm{HS}}(r; \delta) \, \beta W(r) \,, \tag{13}$$

where $\hat{\rho}_2(r; \delta) = \rho^2 \hat{g}_{\mathrm{HS}}(r; \delta)$ is the angular averaged pair density,

$$\hat{\rho}_2(r; \delta) = \frac{1}{V} \int \mathrm{d}\boldsymbol{r}_1 \int \mathrm{d}\boldsymbol{r}_2 \, \rho_{\mathrm{HS}}(\boldsymbol{r}_1, \boldsymbol{r}_2; \delta) \, \frac{\delta(r - r_{12})}{4\pi r^2} \,, \tag{14}$$

and ρ the average density of the solid. Eq. (10) becomes then

$$\int_0^\infty \mathrm{d}r \, r^2 \hat{y}_{\mathrm{HS}}(r; \delta) \left(\exp\{-\beta V_0(r)\} - \theta(r - \delta) \right) = 0 \tag{15}$$

with $\hat{y}_{\mathrm{HS}}(r; \delta) = \hat{g}_{\mathrm{HS}}(r; \delta) \exp \beta V_{\mathrm{HS}}(r)$. The structure of the solid is now completely buried in $\hat{g}_{\mathrm{HS}}(r; \delta)$, for which we use the Weis parametrization [13] with the parameters fixed in such a way that the pressure equation and the compressibility equation as obtained from the HS density functional theory be satisfied while $\hat{g}_{\mathrm{HS}}(r; \delta)$ also yields the correct number of nearest neighbours. The final expression (13) is then ultimately minimized with respect to the cutoff distance λ (the latter comes out to be virtually identical to the nearest neighbour distance). The same theory can then be used for the fluid phase also and the fluid–solid coexistence can then be constructed as usual by equating the pressures and the chemical potentials of both phases. In terms of the reduced density, $x = (\beta\epsilon)^{3/n} \rho\sigma^3$, the fluid–fcc coexisting densities found in this way for the $n = 12$ soft sphere system are $x(\text{fluid}) = 1.165$ and $x(\text{fcc}) = 1.215$, which is to be compared to the simulation results [12] $x(\text{fluid}) = 1.141$ and $x(\text{fcc}) = 1.193$. This clearly shows that the freezing of the $n = 12$ soft spheres (and presumably also of the Lennard-Jones system) is still monitored by the freezing of the underlying hard sphere system and that the density functional theory of freezing can indeed be extrapolated to continuous potentials by using a hard sphere perturbation theory. The question which remains open however is what will happen to the hard sphere perturbation theory for continuous potentials, which introduce a qualitatively new feature (such as bcc freezing)? Can this still be reached by starting from (the metastable bcc) hard sphere solid?

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