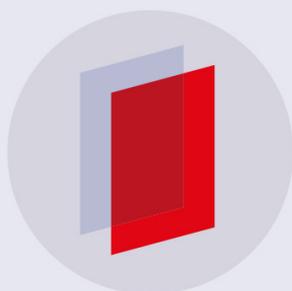# The freezing of soft spheres from a simple hard-sphere perturbation theory

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LETTER TO THE EDITOR

The freezing of soft spheres from a simple hard-sphere perturbation theory

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Abstract. It is shown that a simple perturbation expansion around the free energy of a (BCC/FCC) hard-sphere crystal leads to accurate predictions for the (BCC/FCC) freezing of soft spheres interacting via the inverse-power potential, $V(r) = \varepsilon(\sigma/r)^n$, for all values of n including the extreme case of the one-component plasma ($n = 1$). In particular, we find that for $1 \le n \le 6$ there is both a fluid–BCC and BCC–FCC transition whereas for $n > 6$ the BCC phase is unstable and only the fluid–FCC transition survives, in agreement with the computer simulations.

The theory of the freezing of classical fluids into perfect crystals (see, e.g., [1]) as based on the density-functional approach to non-uniform systems [2], has obtained some mixed success [3–4]. For the case of the hard-sphere (HS) system, usually used as a reference system for the description of more realistic potentials, very good results have recently been obtained from a variety of approaches [3]. The 'brute force' extension of these theories to continuous potentials has, in contrast, produced results of little physical interest especially for those systems for which a body-centred cubic (BCC) phase is expected [4] and to a lesser extent also for the face-centred cubic (FCC) phases [4].

The reason for this failure stems, in our opinion, from the fact that the HS case is a degenerate one for which the free energy and the entropy cannot be distinguished. Because of our present lack of understanding of how to circumvent this difficulty we have, meanwhile, set up a perturbation theory around the HS solid similar to the one currently used in the study of realistic fluids [5]. The theory requires only our previous (BCC/FCC) HS density-functional theory results [3] as input and yields good results for all of the inverse power potentials [5] including the one-component plasma [5]. In this way we are able to study, with little effort, the fluid–BCC, fluid–FCC and BCC–FCC transitions of these systems in a systematic way.

The formulation of a successful perturbation theory has been a major achievement of the theory of fluids [5]. Although many variations of it do already exist, they all have in common a Van der Waals-like splitting of the pair-interaction potential, $V(r) = V_0(r) + W(r)$, into a steep short-ranged, V_0, and a weak long-ranged, $W(r)$, part. Next, the (Helmholtz) free energy F corresponding to the system with the original potential $V(r)$ is rewritten in terms of the free energy F_0 of the system with the potential V_0 as:

$$F = F_0 + \tfrac{1}{2} \int dr_1 \int dr_2 \, \bar{\rho}(r_1, r_2) W(r_{12}) \tag{1}$$

where $r_{12} = |r_1 - r_2|$, $\bar{\rho}(r_1, r_2) = \int_0^1 d\alpha \rho_\alpha(r_1, r_2)$ and $\rho_\alpha(r_1, r_2)$ is the pair density of a

system interacting with the potential $V_\alpha(r) = V_0(r) + \alpha W(r)$. Equation (1) results simply from the fact that the functional derivative of F with respect to the pair potential is equal to one half of the pair density [2]. The final step then, consists in re-expressing the free energy F_0 in terms of the free energy F_{HS} of a fictitious HS system (of 'potential' $V_{HS}(r)$):

$$F_0 = F_{HS} + \frac{1}{2\beta} \int dr_1 \int dr_2 \, \bar{y}(r_1, r_2)\Delta f(r_{12}) \tag{2}$$

where

$$\beta = 1/k_B T \qquad \Delta f(r) = \exp(-\beta V_{HS}(r)) - \exp(-\beta V_0(r)),$$

$$\bar{y}(r_1, r_2) = \int_0^1 d\alpha \, y_\alpha(r_1, r_2) \qquad y_\alpha(r_2, r_2) = \rho_\alpha(r_1, r_2)\exp(\beta\varphi_\alpha(r_{12}))$$

with $\rho_\alpha(r_1, r_2)$ denoting the two-body distribution function corresponding to the potential $\varphi_\alpha(r) = V_{HS}(r) + \alpha(V_0(r) - V_{HS}(r))$. Equation (2), similarly, expresses the fact that the functional derivative of the free energy with respect to the Mayer function $(f(r_{12}))$ is equal to one half of the y function [2, 5]. Equations (1) and (2) can then be turned into perturbation series by expanding $\rho_\alpha(r_1, r_2)$ in (1) and $y_\alpha(r_1, r_2)$ in (2) around their values at $\alpha = 0$. As already exemplified by the above notation, such a perturbation theory is equally applicable to the liquid [5] and to the solid phases although very little work has been done in the latter case [6, 7], especially for the BCC phases. Notice, however, that within perturbation theory only free energies can be obtained, while some structural information about the solid is lost.

For the first step of our perturbation theory, we proceed as usual and determine the HS diameter d to be used in (2) by the Weeks–Chandler–Anderson prescription [8] that the first-order correction to $F_0 \simeq F_{HS}(d)$ in (2), i.e. the second term in the RHS of (2) evaluated with $\bar{y}(r_1, r_2) \simeq y_0(r_1, 2)$, should vanish. This yields an implicit equation for d and we then expand this d-value around its Barker–Henderson approximation [9] d_{BH} as proposed by Verlet–Weis [10]: $d = d_{BH}(1 + 2\delta(1 + \ldots))$, where the ellipsis denotes a density-dependent correction term which depends on the structure of the HS solid via $y_0(r_1, r_2)$. For the densities of interest here this correction terms is usually small and we propose therefore to use for d the value given by:

$$d = d_{BH}(1 - 2\delta) \tag{3}$$

$$d_{BH} = \int_0^\infty dr \left(1 - \exp(-\beta V_0(t))\right) \tag{4}$$

$$\delta = \int_0^\infty dr \left(\frac{r}{d_{BH}} - 1\right)^2 \frac{d}{dr}\exp(-\beta V_0(r)) \tag{5}$$

which has the great advantage of being determined by the potential $V_0(r)$ only. For the latter we adopt the Kang–Lee–Ree–Ree [11] separation, $V(r) = V_0(r) + W(r)$, defined by:

$$V_0(r) = \{V(r) - V(\lambda) - (r - \lambda)V'(\lambda)\}\theta(\lambda - r) \tag{6}$$

where λ is a break point and $\theta(\lambda - r) = 1$ for $\lambda \geqslant r$ and zero otherwise. This form of $V_0(r)$ guarantees that both $V_0(r)$ and $V_0'(r) = dV_0(r)/dr$ vanish at $r = \lambda$. For the break point λ we adopt the simple approximation [11]:

$$\lambda = (\sqrt{2}/\rho)^{1/3} \tag{7}$$

which corresponds to the nearest-neighbour distance of a compact lattice structure with

ρ being the average number density. Notice that this choice of λ makes $V_0(r)$, and hence also d, density-dependent quantities. We now substitute the result, $F_0 \simeq F_{HS}(d)$, back into (1) and approximate the second term in the RHS of (1) by taking $\bar{\rho}(r_1, r_2) \simeq \rho_{\alpha=0}(r_1, r_2)$. Whereas, in a liquid, all of the structural information contained in $\rho_0(r_1, r_2)$ is produced by the pair correlation function [5] $(\rho_0(r_1, r_2) = \rho^2 g_0(r_{12}))$, this is not the case for a solid where $\rho_0(r_1, r_2) = \rho(r_1)\rho(r_2)g_0(r_1, 2)$ and the product $\rho(r_1)\rho(r_2)$ almost entirely exhausts the structural information: in this case, the main purpose of $g_0(r_1, r_2)$ is to produce a correlation hole for r_{12} smaller than the range of $V_0(r_{12})$ $(g_0(r_1, r_2) \sim \theta(r_{12} - d))$. If, moreover, the particles are well localized (as one expects to be the case for a solid) then $\rho(r)$ will resemble a set of delta functions at the lattice sites. Using this rough approximation for $\rho_0(r_1, r_2)$ in (1) the latter becomes

$$F = F_{HS}(d) + \frac{N}{2} \sum_{r_j > d} W(r_j) \tag{8}$$

where r_j is the distance of the jth lattice site to the site at $r = 0$ and N is the total number of particles. In the course of going from F_0 to $F_{HS}(d)$ we have consistently approximated in (1) the range of $V_0(r)$ by d so that the restriction $r_j > d$ in (8) expresses the existence of a correlation hole. Our final approximation (8) is thus very simple since it requires only the evaluation of the integrals (4) and (5) involving $V_0(r)$, a lattice sum for $W(r)$ and $F_{HS}(d)$ for which we can use the results of our previous HS density-functional theory [3].

We will now use (8) for the evaluation of the free energy of the soft-sphere solids. Soft spheres are systems of point particles interacting via repulsive inverse-power potentials of the form, $V(r) = \varepsilon(\sigma/r)^n$, where ε and σ fix the energy and length scales, respectively, while the index n determines the range of the potential. In the limit where $n \to \infty$ the soft spheres become hard spheres of diameter σ. When $n \leqslant 3$ the soft-sphere system has to be stabilized by a continuous background in which case $n = 1$ will reproduce the one-component plasma (OCP) [12] of ions of charge e such that $e^2 = \varepsilon\sigma$. For $n > 3$ the equilibrium properties of soft spheres are usually described [5] in terms of the dimensionless density, $x = (\beta\varepsilon)^{3/n}\rho\sigma^3$, whereas for $n \leqslant 3$ one usually uses [12] the coupling parameter, $\Gamma = \beta\varepsilon(\sigma/a)^n$, with $x = (3/4\pi)\Gamma^{3/n}$, $a = (\frac{4}{3}\pi\rho)^{-1/3}$ and ρ being the average number density. From (8) with $F_{HS}^{BCC}(d)$ and $F_{HS}^{FCC}(d)$ taken from our previous [3] HS density-functional theory, we find that for all n-values $(1 \leqslant n \leqslant \infty)$ there is a first-order BCC–FCC transition from a low-density BCC phase to a high-density FCC phase with a small density change which decreases with decreasing n. Near melting, the BCC phase is thus favoured, just as in the Alexander–McTague theory [13], but since the BCC–FCC transition could still be pre-empted by the fluid–BCC and fluid–FCC transitions we have investigated the latter by using the fluid free energies obtained from the Rogers–Young (PY-HNC interpolation) theory [14]. We then find that for $n > 6$ the BCC phase is metastable so that only the fluid–FCC transition survives while for $n \leqslant 6$ there is a fluid–BCC transition followed at higher densities by a BCC–FCC transition. This is consistent with the $n = 4, 6, 9$ and 12 computer simulation findings of Hoover–Gray–Johnson [15]. Notice, however, that in their present stage both the theory and the simulation probe only the stability of these solids with respect to particle localization while some of these phases could be shear unstable [16]. In figures 1 and 2 we show the free energies and pressures of the different phases. Notice from figure 1 that the pressures obtained from (8) agree extremely well with the available simulation results [15]. We also find that the value of the coexisting fluid–solid densities are extremely sensitive to the input free
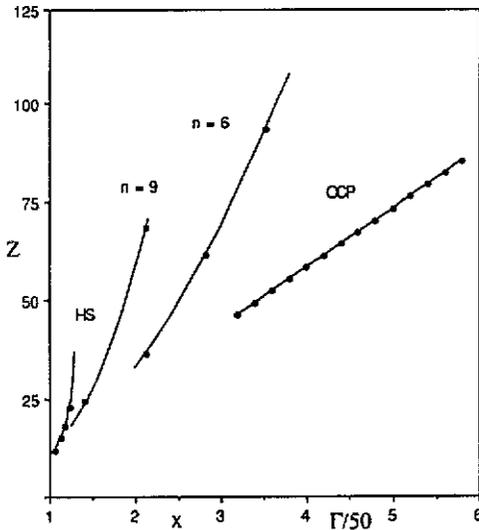
Figure 1. The compressibility factor, $Z = \beta P/\rho$, for the FCC phases of the inverse-power potentials of index n as functions of the reduced density x (for the OCP, we show $-Z$ versus $\Gamma/50$ where Γ is the coupling parameter). The curves have been calculated from the perturbation theory while the points are from simulation [15, 17]. Note that the available BCC pressures cannot be distinguished from the FCC results shown here.
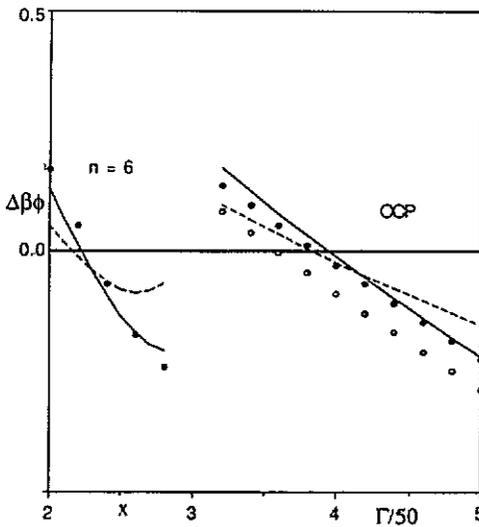

Figure 2. The free energy per particle φ relative to the liquid phase, $\Delta\beta\varphi = \beta\varphi_{\text{solid}} - \beta\varphi_{\text{liquid}}$ for the FCC (full curves) and BCC (broken curves) solid phases of the inverse 6th potential and the OCP. The variable x is defined as in figure 1 and the simulation data, full circles for the FCC phases and open circles for the BCC phase of the OCP, are taken from the same sources. Note the scale: the relative difference between the theory and simulation is in the order of 0.1% in all cases. Also, the apparent non-monoticity is due to errors in extrapolating the liquid-state free energies into the supercooled region.

Table 1. The reduced densities, $x = (\beta\varepsilon)^{3/n}\rho\sigma^3$, for $n \geqslant 6$ and coupling parameters, $\Gamma = (\frac{4}{3}\pi x)^{1/3}$, for $n = 1$ of the various coexistencies for the inverse-power potentials of index n compared to the available simulation results (the other values of n have been deleted here because they add very little to the trends already displayed). For $n \geqslant 4$ the simulation results are taken from [15] while for $n = 1$ they are taken from [17]. Notice that the fluid–FCC transitions for $n \leqslant 6$ refer to metastable solids.

n	fluid–FCC		fluid–BCC		BCC–FCC
	equation (8)	SIM	equation (8)	SIM	equation (8)
∞	0.96–1.04	0.94–1.04	—	—	—
9	1.24–1.28	1.33–1.37	—	—	—
6	2.22–2.24	2.12–2.21	2.14–2.16	—	2.32–2.33
1	194.3–194.0	192	187.2–187.0	178	207.0–207.1

energies for the fluid phases. For instance, the small discrepancies between the fluid free energies obtained from the Rogers–Young scheme (with a density-independent interpolation constant) [14] and those of the simulation results [15] lead to very large shifts in the coexisting fluid–solid densities. In order to make sure that we are testing (8) we have calculated the coexisting densities by taking the simulation results [15] for the fluid-phase free energies as input. As can be seen from table 1 the agreement is fair over the whole range of n-values. Unfortunately, no data, either from simulations or theory, are available to test our fluid–BCC and BCC–FCC transition values for $1 < n < \infty$. In the particular case of the OCP ($n = 1$) such data do exist for the fluid–BCC [17] and the (metastable) fluid–FCC [17, 18] transitions but not for the BCC–FCC transition. Here also, the agreement obtained from (8) is good (see figures 1 and 2 and table 1). One minor defect of the present approach is that for $n = 1$ the width of the transition ($\Delta\Gamma$) is very small ($\Delta\Gamma/\Gamma \sim 10^{-3}$) but not strictly zero as expected theoretically [19].

The scheme presented here is extremely simple, being the result of many approximations and yet gives fair agreement with simulations without using any input from simulation with respect to the solid phase. We believe that most of the approximations are as good as the underlying perturbation theory with the clear exception of the replacement of the two-body distribution function by a sum of delta functions. We hope to discuss in a future publication a slightly more complicated approximation for the two-body distribution function which, while still based solely on HS density-functional theory results, improves the prediction for the fluid–FCC transition in the case of large n ($n > 6$) where at present the discrepancy with simulation is the greatest. We also hope to investigate the application of the present scheme to more complicated continuous potentials but it may be observed here that de Kuijper *et al* [4] have already shown that treating the attractive tail of the Lennard-Jones potential perturbatively gives better results than treating the full potential within density-functional theory.

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