

Perturbation Theory for Classical Solids

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The first well founded perturbation theory for classical solid systems is presented. Theoretical approaches to thermodynamic and structural properties of the hard-sphere solid provide us with the reference system. The traditional difficulties of all previous approaches are overcome. The perturbation is a first order term in an expansion of the Helmholtz free energy functional instead of an additive *ad hoc* term and the proper solid reference structure is used instead of some kind of mapping into the fluid structure at some effective density. As the theory reduces to the usual liquid perturbation theory in the uniform limit, it can describe consistently the complete phase diagram. Excellent results are obtained when applied to different model systems. [S0031-9007(96)01105-2]

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In the last two decades, we have witnessed a continuous progress in the theory of nonuniform classical fluids [1,2]. Inside this context, where classical solids are regarded as an extremely nonuniform system, a considerable effort has been devoted to develop a theory for solids. From this point of view, the theory would provide not only a description of solids but a unified view of classical systems [2]. However, due to the inherent difficulties in the nonuniform systems, this progress is still not comparable to that reached in uniform liquids.

An important part of the enormous progress of the theory of simple uniform liquids has been due to the development of perturbation theories. Within this scheme, the liquid properties are described by those of a reference system (usually built with the repulsive part of the interaction potential) modified by a perturbation (usually due to the attractive part of the interaction potential). The usefulness of these theories is based on the knowledge of the thermodynamic and structural properties of the reference system. The foremost, if not the unique, reference system is the hard-sphere fluid, which describes many of the essential features of realistic interacting repulsive potentials. For this reason, much effort has been devoted to understanding its properties. Nowadays, the virial expansion, the analytically solvable Perkus-Yevick approximation and semiempirical approximations supply quite accurate results for thermodynamics and structure up to the crystallization density [1]. The seminal article by Andersen *et al.* [3] establishes the relation between the properties of a hard-sphere fluid and those of realistic repulsive interactions, completing the scheme of the perturbation theory for simple liquids.

The same strategy has been pursued in the solid phase of classical systems. The aims of the theory are essentially two: the formal development of the theory itself and the determination of accurate thermodynamic and structural properties of the reference system. To this end, the density functional formalism has been successfully elaborated to describe the *thermodynamic* properties of the hard-

sphere solid [4]. At present, there are different functional approaches for the Helmholtz free energy which describe the solid phase and reduce to that of the fluid in the homogeneous limit [2]. Recently, it has been showed that the equation of state obtained from these functionals reproduces the simulation results quite well even up to almost close packing [5]. For all that, the thermodynamics of the hard-sphere system can be accurately described from low densities to almost close packing, including the crystallization phase transition.

However, up to very recently, there was neither an accessible theoretical approach to the structural properties of the hard-sphere solid nor a proper perturbation theory [6]. All the perturbation approaches proposed by different authors, two of us included, are rather primitive [7–9]. Basically, they follow the same scheme: the Helmholtz free energy of the solid is written as a sum of two terms, namely, the reference and perturbation free energies. The former is assumed to be any of the available density functionals for the free energy of the hard-sphere solid while the perturbation is an *ad hoc* term built without any connection with the hard-sphere potential which is being assumed as the reference potential. Furthermore, the structure of the reference hard-sphere solid is substituted in the perturbative term by some kind of mapping into the structure of the hard-sphere *fluid* at some effective density. Typically, the Andersen *et al.* (WCA) criterium is used to divide the interacting potential, whereas the Barker-Henderson criterium [1,10] is used to fix the hard-sphere diameter of the reference solid. To worsen things, the Barker-Henderson criterium does not distinguish uniform from nonuniform systems. Any intent to do a consistent approach gives disastrous results.

In spite of the crudeness and the fragility of these approaches, all pieces assembled achieved to describe the phase diagram of the Lennard-Jones system reasonably well [8]. This success is not completely understood though some clues have been suggested [9]. It seems that for large-ranged attractive interactions some kind of

numerical error cancellation should occur. When they are applied to systems with slightly more sophisticated potentials, they merely give a qualitative description of the thermodynamic properties or even fail completely. This is what happens when short-ranged attractive interactions are present. In any case, these theories are far from being satisfactory.

The first step in order to develop a proper theory of perturbations for solids has been carried out recently by determining theoretically the average $\tilde{g}(r)$ of the pair distribution function $\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ [6]. This average is defined by

$$\tilde{g}(r_{12}) = \frac{1}{4\pi V \rho^2} \int d\Omega \int d\mathbf{r}_1 \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2), \quad (1)$$

where V is the volume, ρ is the mean density, and $d\Omega$ the differential solid angle aperture around \mathbf{r}_{12} . Excellent results are obtained for the hard-sphere solid up to almost close packing.

In this Letter, we develop a perturbation theory where, to first order, all the structural information needed is precisely the function $\tilde{g}(r)$. As it is usually done in perturbation theories for uniform liquids, we divide the interacting potential into the reference and the perturbative parts: $\phi(r) = \phi_r(r) + \phi_p(r)$. Then, we start from the general expression for the Helmholtz free energy of a nonuniform system as a functional of the density $\rho(\mathbf{r})$ which is written exactly as [4,11]

$$F[\rho(\mathbf{r})] = F_r[\rho(\mathbf{r})] + F_p[\rho(\mathbf{r})], \quad (2)$$

being $F_r[\rho(\mathbf{r})]$ the Helmholtz free energy of the reference system at density $\rho(\mathbf{r})$ and

$$F_p[\rho(\mathbf{r})] = \frac{1}{2} \int_0^1 d\alpha \int d\mathbf{r}_1 d\mathbf{r}_2 \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2; \alpha) \phi_p(r_{12}), \quad (3)$$

where α is the coupling parameter for the interaction potential $\phi(r; \alpha) = \phi_r(r) + \alpha \phi_p(r)$ and $\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2; \alpha)$ is the pair distribution function when the potential is $\phi(r_{12}; \alpha)$ but the density is $\rho(\mathbf{r})$. To lowest order, Eq. (3) yields

$$F_p[\rho(\mathbf{r})] = \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 \rho_r^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \phi_p(r_{12}), \quad (4)$$

which after an appropriate integration becomes exactly

$$F_p[\rho(\mathbf{r})] = 2\pi\rho N \int dr r^2 \tilde{g}_r(r) \phi_p(r), \quad (5)$$

where N is the number of particles and $\tilde{g}(r)$ is precisely the average of the pair distribution function given by Eq. (1). For any realistic system, the reference interacting potential is chosen to describe the rapidly varying short-ranged repulsive part of the interacting potential. However, the thermodynamic and structural properties of these systems are unknown. Therefore, a treatment to relate these properties to those of a hard-sphere solid is evidently

necessary. The procedure is analogous to that of the theory of liquids. Let $e(\mathbf{r}_1, \mathbf{r}_2) = \exp(-\beta\phi|\mathbf{r}_1 - \mathbf{r}_2|)$ be the Boltzmann factor. It depends only on r_{12} , but for clearness in some of the expressions below it is convenient to keep the formal dependence on the two locations \mathbf{r}_1 and \mathbf{r}_2 . As in the liquid theory, let $\Delta e(\mathbf{r}_1, \mathbf{r}_2)$ be the blip function, i.e., the difference of the Boltzmann factors of the reference potential and the hard-sphere potential of diameter d_{HS} , $e_r(|\mathbf{r}_1 - \mathbf{r}_2|) - e_{\text{HS}}(|\mathbf{r}_1 - \mathbf{r}_2|)$. If this diameter is comparable to the range of the reference potential, the blip function is different from zero in a small range of the order of ξd_{HS} with $\xi < 1$. We can then expand the Helmholtz free energy functional of the reference system in powers of the blip function

$$\begin{aligned} F_r[\rho(\mathbf{r})] &= F_{\text{HS}}[\rho(\mathbf{r})] \\ &+ \frac{1}{2} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \frac{\delta F_{\text{HS}}[\rho(\mathbf{r})]}{\delta e_{\text{HS}}(\mathbf{r}_1, \mathbf{r}_2)} \Delta e(\mathbf{r}_1, \mathbf{r}_2) \\ &+ \text{higher-order terms.} \end{aligned} \quad (6)$$

The functional derivative of the Helmholtz free energy with respect to the Boltzmann factor is easily obtained

$$-\beta \frac{\delta F[\rho(\mathbf{r})]}{\delta e(\mathbf{r}_1, \mathbf{r}_2)} = \frac{1}{2} \rho(\mathbf{r}_1) \rho(\mathbf{r}_2) y(\mathbf{r}_1, \mathbf{r}_2), \quad (7)$$

where the $y(\mathbf{r}_1, \mathbf{r}_2)$ function is the generalization of the $y(r_{12})$ function in uniform systems. This last one is defined by $e^{-\beta\phi(r_{12})} g(r_{12})$, whereas the former is defined by $e(\mathbf{r}_1, \mathbf{r}_2) \frac{\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2)}{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}$. Introducing Eq. (7) into Eq. (6) and after some simple algebraic steps, it is found that

$$\begin{aligned} F_r[\rho(\mathbf{r})] &= F_{\text{HS}}[\rho(\mathbf{r})] \\ &+ 2\pi\rho N \int dr r^2 \tilde{y}_{\text{HS}}(r) \Delta e(r) \\ &+ \text{higher-order terms,} \end{aligned} \quad (8)$$

where $\tilde{y}_{\text{HS}}(r)$ is the average of the $y_{\text{HS}}(\mathbf{r}_1, \mathbf{r}_2)$ function which can also be expressed as

$$\tilde{y}_{\text{HS}}(r) = \exp[\beta\phi_{\text{HS}}(r)] \tilde{g}_{\text{HS}}(r).$$

Until here, the hard-sphere diameter has remained arbitrary. Now we specify it by imposing that the first order term in the functional expansion Eq. (8) be zero. This yields

$$\int_{d_{\text{HS}}}^{\infty} dr r^2 \tilde{y}_{\text{HS}}(r) = \int_0^{\infty} dr r^2 \tilde{y}_{\text{HS}}(r) \exp[\beta\phi_r(r)]. \quad (9)$$

Notice that it is analogous to the well known WCA criterium [3] in liquid theory except that the $\tilde{y}(r)$ function instead of the $y(r)$ function is used. From Eqs. (6) and (7) and after averaging, we find

$$\tilde{y}_r(r) = \tilde{y}_{\text{HS}}(r) + \text{higher-order terms,} \quad (10)$$

which can be used to lowest order to evaluate the perturbation term Eq. (5). It is interesting and easy to

prove that, if Eq. (9) holds, the convergence properties of the expansions (8) and (10) are similar to those found in the uniform limit [12], i.e.,

$$F_p[\rho(\mathbf{r})] = F_{HS}[\rho(\mathbf{r})] + 2\pi\rho N \int dr r^2 \tilde{y}_{HS}(r) \Delta e(r) + O(\xi^4), \quad (11)$$

$$\tilde{y}_r(r) = \tilde{y}_{HS}(r) + O(\xi^2). \quad (12)$$

With the above expressions the theoretical formalism is completed. It is straightforward to see that in the uniform limit the theory reduces to the WCA perturbation theory of simple liquids. Observe also that all the problems of previous approaches are automatically overcome: the formalism provides a proper expansion of the free energy with precise thermodynamic and structural properties of a reference solid, namely, any of the functionals for the Helmholtz free energy and the correlation function $\tilde{g}(r)$, and the criterium to determine the appropriate reference system enhances the convergence of the expansion.

We have applied the theory to the Lennard-Jones (LJ) system and to an extremely short-ranged square well potential. In Table I we show the LJ liquid (ρ_l) and solid (ρ_s) densities at coexistence at several temperatures (all in LJ parameter units) obtained from the present theory, using the Tarazona functional [13] for the reference hard-sphere solid, compared to simulation data of Hansen and Verlet [14]. The theoretical predictions are quite good and the small deviations are quantitatively similar to those obtained by previous *ad hoc* approaches. Nevertheless, contrary to what it is predicted by the latter, the present theory gives the correct slopes of the coexistence densities as functions of the temperature. This improvement is undoubtedly due to the adequate dependence of the hard-sphere diameter with the density. Table I also shows the solid Lindemann parameter at coexistence. It is significantly smaller than the simulation result. This is due to the functional approach we have used for the reference hard-sphere solid, as it is well known. If any other functional were used, the Lindemann parameter would improve but no significant changes would be detected for the energies and, therefore, for the coexistence densities

TABLE I. Lennard-Jones liquid (ρ_l) and solid (ρ_s) densities at coexistence at several temperatures (all in Lennard-Jones parameters units) as predicted by the simulations of Hansen and Verlet [14] and the present theory. The Lindemann parameter L of the solid phase at coexistence is also shown.

$k_B T$	Simulation			Theory		
	ρ_l	ρ_s	L	ρ_l	ρ_s	L
0.75	0.875	0.973	0.145	0.884	0.970	0.087
1.15	0.936	1.024	0.139	0.974	1.049	0.082
1.35	0.964	1.053	0.137	0.996	1.077	0.083
2.74	1.113	1.179	0.140	1.116	1.199	0.090

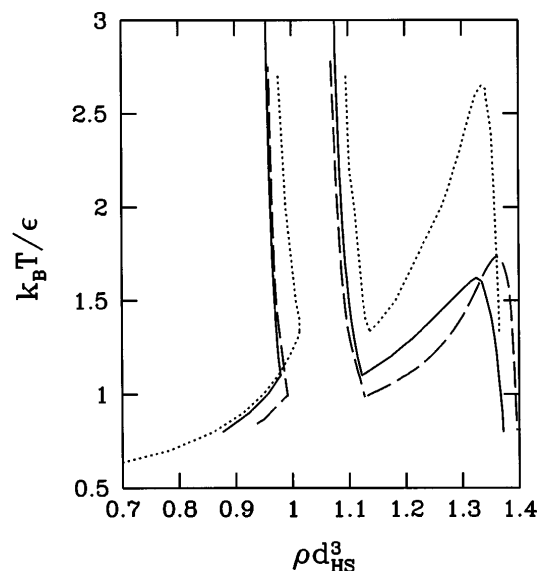


FIG. 1. Phase diagram of the square well system for the well width $\delta/d_{HS} = 0.02$. The temperature is given in well depth units. The solid line is the prediction of the present theory. The dashed line corresponds to the simulations by Bolhuis and Frenkel [15]. The dotted line is the prediction of the PWDA.

shown in Table I. However, the important point is that, for the first time, a classical system can be studied with a unique, proper, and consistent theory.

Much more impressive are the results obtained by the theory when it is applied to a system with an extremely short-ranged attractive interaction. Simulation results have recently proved [15] that this kind of system presents quite interesting isostructural solid-solid transitions. Up to now, as one could expect, no theory had been able to give a reasonable quantitative account of this behavior [16,17]. Therefore, these systems offer an interesting and stringent test for the present theory. Figure 1 shows the phase diagram of the square well potential characterized by a short width $\delta/d_{HS} = 0.02$. The dashed lines of this figure, which correspond to simulation results [15], show the coexistence densities of the liquid-solid transition and, inside of the solid region, the coexistence curve of the solid-solid transition. Observe that, due to the weakness of the attractive potential, there is no fluid condensation. However, the solid-solid transition is a kind of solid condensation which arises from a different mechanism than the usual fluid condensation. It is related to the commensurability of the lattice parameter of the solid structure with the well width of the potential [15,16]. The dotted lines correspond to the perturbation weighted density approximation (PWDA) [9,16] which was, to our knowledge, the best approach so far able to describe the complete phase diagram of this system. The continuous lines correspond to the present theory using the Tarazona functional [13] for the reference hard-sphere solid. The results using any other functional would be

indistinguishable in the scale of this figure. The dramatic improvement is clear and the global agreement of the theoretical predictions with the simulation results is quite good. Equivalent quantitative agreement is obtained for the phase diagrams corresponding to square wells of different widths.

In summary, we have developed a perturbation theory with remarkable characteristics. It is the first well founded perturbation theory for classical solids. It reduces to the well known WCA perturbation liquid theory in the appropriate uniform limit. Its versatility allows its use with any of the functional approaches available for the Helmholtz free energy of hard spheres. It gives quite good results even for systems where other *ad hoc* approaches have failed. Finally, but not less important, the computational effort is drastically reduced. The cumbersome mapping of the structure of the solid into the structure of the liquid at certain effective density, which usually involves tedious autoconsistent and recursive processes, is replaced by a simple integral.

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