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Self-consistent nonperturbative theory for classical systems

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We construct a self-consistent nonperturbative theory for the structure and thermodynamics of a classical system of particles that goes beyond the usual approaches based on perturbation theory. Our theory, which gives accurate predictions for the phase diagram, is based on two ingredients: first, use is made of an exact expression for the free energy of a many-body system in terms of a reference system and a coupling integral connecting the latter to the final system; second, correlation functions may be very accurately approximated using a number of sum rules relating the radial distribution function with thermodynamic quantities. Consistency between the coupling integral expression and the sum rules may be achieved by means of a self-consistent process.

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Prediction of thermodynamic and structural properties of materials from a knowledge of the intermolecular interactions is one of the important goals of statistical mechanics. Available theoretical approaches mostly use a perturbation expansion around a reference system [1] whose properties are used as input information. For systems of particles interacting via central forces, this scheme has been applied many times, with more or less success [1,2]. In particular, systems such as colloids are rather elusive because of their very short-range intermolecular attractions as compared with the large molecular size, a situation where the usual perturbative schemes do not perform well and may in fact lead to qualitatively inaccurate phase diagrams [2]. In the present paper we propose an alternative to perturbation theory that does not involve any perturbative expansion and that can be applied, in principle, to a large variety of systems, not necessarily colloidal in nature.

Our starting point is the following exact expression for the free energy F of a system with pair interactions $\phi(r)$:

$$F=F_{\mathrm{ref}}+\int_0^1 d\lambda\left\langle\frac{\partial U}{\partial\lambda}\right\rangle_\lambda,\qquad U(\lambda)=\sum_{i<j}\phi(r_{ij};\lambda),\tag{1}$$

where $U(\lambda)$ is the total energy of a system whose pair interactions $\phi(r;\lambda)$ depend on a parameter λ such that $U(0)=U_{\mathrm{ref}}$, $U(1)=U$, U_{ref} and F_{ref} being the energy and free energy of a reference system. The latter is assumed to be known for a sufficiently wide range of thermodynamic conditions. The average is to be taken over configurations weighted by an appropriate Boltzmann factor containing $U(\lambda)$. The coupling parameter λ connects the reference to the target system. Using $\phi(r;\lambda)=\phi_{\mathrm{ref}}(r)+\lambda\Delta\phi(r)$, with $\Delta\phi(r)\equiv\phi(r)-\phi_{\mathrm{ref}}(r)$, the relevant expression becomes

$$F=F_{\mathrm{ref}}+\int_0^1 d\lambda\langle\Delta U\rangle_\lambda,\tag{2}$$

with $\Delta U\equiv U-U_{\mathrm{ref}}$. The average may be evaluated either by computer simulation or by theory. For our purposes, it is more convenient to express it as

$$\langle\Delta U\rangle_\lambda=\frac{N\rho}{2}\int d\mathbf{r}\left\{\int_0^1 d\lambda\tilde{g}(r;\lambda)\right\}\Delta\phi(r),\tag{3}$$

where N is the number of particles, ρ the mean density, and $\tilde{g}(r)$ an angle average of the two-body distribution function [3] (for fluid phases, $\tilde{g}$ reduces to the radial distribution function). The usual linear perturbation theory (LPT) amounts to approximating the coupling integral in curly brackets by $\tilde{g}(r;\lambda=0)\equiv\tilde{g}_{\mathrm{ref}}(r)$. A problem that has affected many of the applications of this scheme to ordered phases is that the role of $\tilde{g}$ has been systematically ignored or misinterpreted in the literature, leading to the formulation of qualitatively incorrect perturbation theories [4,5]. As will be discussed later, even the straight implementation of LPT results in a quantitatively inaccurate phase behavior for short-ranged interactions.

The procedure presented in this paper involves calculating the coupling integral as accurately as possible by performing *explicitly* the integration in λ, which involves knowledge of $\tilde{g}(\lambda)$ in the *entire* range $0\leqslant\lambda\leqslant1$, an information that is not available *a priori*. We propose to solve this admittedly complicated problem based on the observation that the radial distribution functions may be very accurately constructed by using a number of sum rules for $\tilde{g}$. One such relation is the virial equation for the pressure P. Another relation, valid for the solid phase and applicable with reasonable accuracy to the *dense* fluid, is a normalization of the first correlation shell to the average coordination number. One other relation that we have found particularly useful is to demand that the first moment of r in the $\tilde{g}$ and $\tilde{g}_0$ distributions (the latter corresponding to the uncorrelated system, see below) be equal, $\langle r\rangle_{\tilde{g}}=\langle r\rangle_{\tilde{g}_0}$, which we have shown to be very accurate. In previous work [5], we have exploited these three relations to construct $\tilde{g}$ for a solid made up of hard spheres (HS) of diameter σ. Since our approach for more general potentials shares some of the technicalities with the latter problem, we briefly summarize the procedure involved. The starting point is the one-particle distribution function $\rho(\mathbf{r})$ that, for the hard-sphere solid, can be very accurately represented by a sum of (normalized) Gaussian peaks centered on the set of lattice sites, $\{\mathbf{R}\}$, and a Gaussian width parameter α. In the absence of correlations, $\rho^{(2)}(\mathbf{r},\mathbf{r}')=\rho(\mathbf{r})\rho(\mathbf{r}')$, and the radial distribution function is [5]

$$\tilde{g}_0(r)=\sum_{i\geqslant 0}\tilde{g}_0^{(i)}(r),\quad \tilde{g}_0^{(i)}(r)=\left(\frac{\alpha}{2\pi}\right)^{1/2}\frac{e^{-\alpha(r-R_i)^2/2}}{4\pi\rho r R_i}. \tag{4}$$

When correlations are present, it is reasonable to assume, and justified *a posteriori*, that the corresponding $\tilde{g}(r)$ may also be written as a sum of peaks, each with the same functional form, except that there will exist: (i) a correlation hole in $r<\sigma$, and (ii) some rearrangements in the width parameter, position, and prefactor of the first peak, α_1, r_1, and A, respectively, which are taken as free parameters

$$\tilde{g}^{(1)}(r)=\frac{A}{4\pi\rho}\left(\frac{\alpha_1}{2\pi}\right)^{1/2}\frac{e^{-\alpha_1(r-r_1)^2/2}}{r}\Theta(\sigma-r). \tag{5}$$

The other peaks $\tilde{g}^{(i)}(r)$, $i>1$ are assumed to be identical to the uncorrelated peaks $\tilde{g}_0^{(i)}(r)$ (this assumption, which turns out to be extremely accurate, has only a practical basis and could be relaxed by using additional conditions on $\tilde{g}$). Now, using any of the available values for the pressure and Gaussian parameter of the fcc hard-sphere solid (either from density-functional theory [6] or free-volume approximation [7]), the conditions provide three nonlinear equations from which α_1, r_1, and A may be obtained. Comparison of the ensuing $\tilde{g}$ with simulation results demonstrates that this procedure is sound and, in fact, highly accurate [5].

Let us consider in the following a *general* interaction potential. Suppose that we somehow parametrize $\tilde{g}$ in terms of a number of free parameters that provide a faithful representation in a wide range of densities and temperatures (the actual parameters need not be the same in different phases). We propose the following strategy. First, the coupling integral in Eq. (3) is discretized with step-size h and approximated using the trapezoidal rule; defining $F(\lambda,T,\rho)$ as the free energy of a system with interactions $\phi(r;\lambda)$ and thermodynamic conditions T,ρ (T being the temperature), Eq. (2) leads to

$$F^{[n+1]}(\lambda+h,T,\rho)=F(\lambda,T,\rho)+N\pi h\int_0^\infty[\tilde{g}(r;\lambda,T,\rho)+\tilde{g}^{[n]}(r;\lambda+h,T,\rho)]\Delta\phi(r;\lambda)r^2\,dr \tag{6}$$

with $n=0,1,2,\ldots$. Assume both $F(\lambda,T,\rho)$ and $\tilde{g}(r;\lambda,T,\rho)$ are known in a region of the T-ρ plane. Then the above expression defines a self-consistent iterative scheme in n which on convergence provides *both* $F(\lambda+h,T,\rho)$ and $\tilde{g}(r;\lambda+h,T,\rho)$. For each value of T and ρ, the scheme starts by taking $\tilde{g}^{[0]}(\lambda+h,T,\rho)=\tilde{g}(\lambda,T,\rho)$ and obtaining $F^{[1]}(\lambda+h,T,\rho)$. This procedure is used to compute whatever derivatives of the free energy are necessary in order to apply the required sum rules (e.g., an approximation for the pressure in the case of the virial equation). These sum rules along with other structural relations (which, taken together, have to be equal in number to the number of parameters describing $\tilde{g}$) provide a set of nonlinear equations (in the manner described above for the HS solid) that, once solved, give an improved $\tilde{g}^{[1]}(\lambda+h,T,\rho)$. The scheme is iterated until convergence; then λ is increased and the whole process repeated. At the end of the calculations $F(\lambda,T,\rho)$ and $\tilde{g}(\lambda,T,\rho)$, corresponding to all systems from the reference to the target systems, are obtained in the defined region of the T-ρ plane.

To illustrate the above theory, we now consider a square-well (SW) potential of hard-core diameter σ and attractive well of width δ. For $\delta\sim\sigma$ shows the usual Lennard-Jones-like phase diagram. However, as δ decreases below a critical value $\delta_c\sim 0.07\sigma$, simulation studies [8] indicate that the liquid-vapor transition disappears and that a transition between two solids of fcc crystal symmetry arises. This system has been studied theoretically by a number of workers using a properly formulated LPT [9] or variations thereof [10,11], with HS as a reference system. When $\delta\ll\sigma$ these theories are not expected to perform well since only a narrow region $\sigma<r<\sigma+\delta$ contributes to the attractive energy, which is basically dictated by the value of $\tilde{g}_{\mathrm{HS}}(\sigma)$; this is expected to be very different from the contact value of $\tilde{g}$ for the actual potential.

We now apply our self-consistent approach to this system. For values of δ not exceeding σ, only the structure of $\tilde{g}$ in the vicinity of the contact distance (i.e., the first peak) has to be taken care of. Assuming a Gaussian form in the solid, suitably modified to take account of the discontinuity at $r=\sigma+\delta$,

$$\tilde{g}(r)=\begin{cases}0, & r<\sigma\\ Ae^{-\alpha_1(r-r_1)^2}/r, & \sigma<r<\sigma+\delta\\ Be^{-\alpha_1(r-r_1)^2}/r, & r>\sigma+\delta,\end{cases} \tag{7}$$

we are left with four parameters, A,B,α_1, and r_1, to be determined from the three conditions together with the exact *discontinuity equation*, which gives the ratio between the values of $\tilde{g}$ at the discontinuity as the Boltzmann factor $\exp(-\epsilon/kT)$. For the liquid, we have found it more convenient to use a simple exponential form with three parameters,

$$\tilde{g}(r)=\begin{cases}0, & r<\sigma\\ Ae^{-\alpha_1(r-\sigma)}/r, & \sigma<r<\sigma+\delta\\ Be^{-\alpha_1(r-\sigma)}/r, & r>\sigma+\delta,\end{cases} \tag{8}$$

and obtain $A,B,$ and α_1 by applying the virial and the normalization conditions, and the discontinuity equation. The normalization condition is clearly approximate, even for the dense liquid, but this does not turn out to be very critical. The corresponding conditions lead, for each phase, to a system of nonlinear equations (to be integrated into the pro-

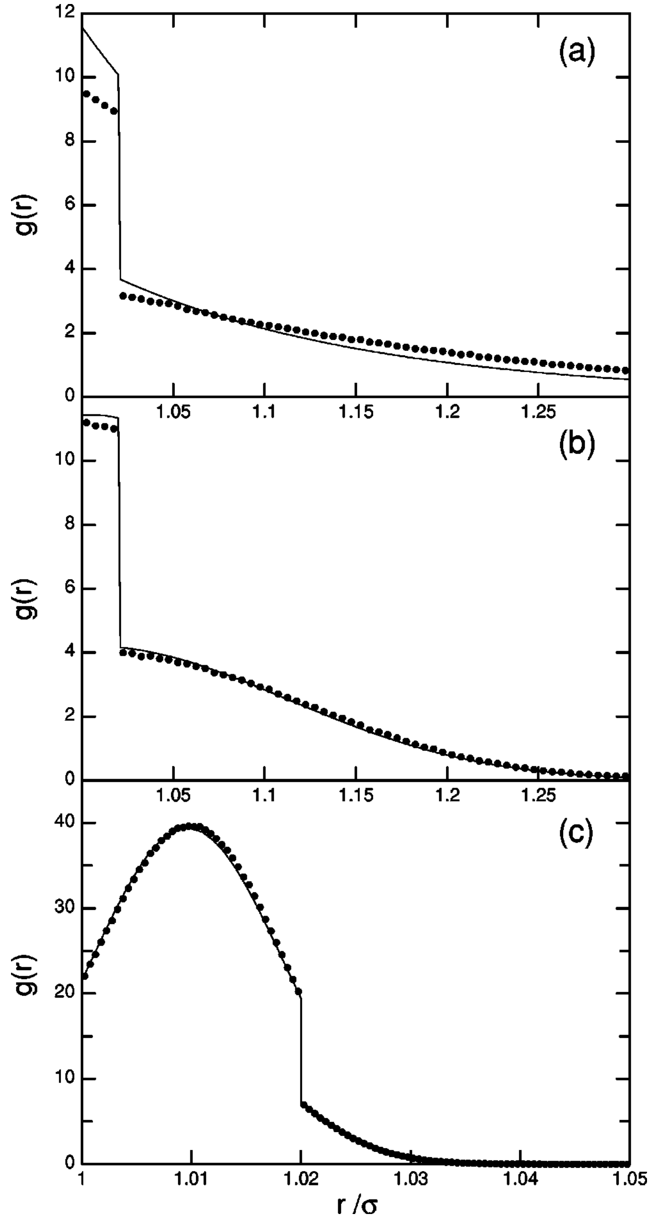

FIG. 1. $\tilde{g}(r)$ for (a) liquid, (b) expanded solid, and (c) dense solid (all at the triple point), for a square-well system with $\delta/\sigma = 0.02$. Solid line: present theory. Symbols: results from computer simulations [14].

posed self-consistent scheme) that may be easily solved by standard numerical techniques. The iterative, self-consistent procedure is started using a reference HS system; free energies for the latter are taken from the Carnahan-Starling [12] (liquid) and Hall [13] (solid) expressions, whereas the HS radial distribution functions are constructed following the same methodology as explained before. The whole scheme is numerically very simple and convergence for a single isotherm is obtained in a few iterations; the entire phase diagram is calculated in less than three minutes of CPU time on a 500-MHz Pentium PC.

Figure 1 shows $\tilde{g}$, along with simulation results, for the liquid, expanded, and compressed solids that coexist at the triple point for a SW system with $\delta = 0.02$. For the solid phases, the agreement is quite impressive; for the liquid, though less accurate, the theory describes reasonably well the main features of $\tilde{g}$. A further check for the accuracy of our theory is to compare the free energy with that obtained from simulation; this is seen in Fig. 2 [these simulation results along with those for $\tilde{g}$ were obtained by us using a standard Monte Carlo technique [14] and Eq. (2)], which corresponds to the same system. The figure shows a perfect agreement at the scale of the graph (save liquid points beyond the transition that are metastable states). A more definite test, however, is to look at the phase diagram since phase boundaries depend very sensitively on numerical details of the free energy (note the extremely linear behavior of the solid branch in Fig. 2). Figure 3 presents our results for the phase diagram for $\delta = 0.02$, together with results from other theories. The comparison with computer simulation is very satisfactory; only in the critical region are the results at variance with the simulation results (note that the theory is still mean field in character since higher-order fluctuations, arising from subtle details of the higher-order peaks of $\tilde{g}$, are not accounted for). Also, our theory dramatically improves on the results from both linear perturbation theory [9] (using the Carnahan-Starling approximation for the liquid and a free volume approximation for the solid phase) and the PWDA (perturbative weighted-density approximation—an effective perturbation theory with a density-functional treatment for the reference system [11]).

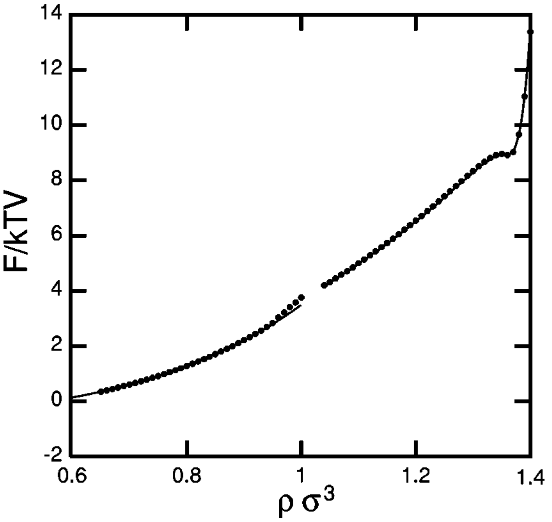

FIG. 2. Fluid and solid free energies of a SW system with $\delta/\sigma = 0.02$ at $kT/\epsilon = 1$. Solid line: results from the proposed theory. Symbols: results from computer simulation [14].

A possible source of error involves integration in temperature (note that for the SW system, the coupling integral may be written as an integral in scaled temperature). Even if a very accurate equation of state for the HS system is used, the discretized temperature integral will be prone to accumulating errors whose impact on the phase behavior at temperatures $kT/\epsilon \sim 1$ would be interesting to investigate. In order to check this, we have used a different reference system, namely, that corresponding to a square-well potential at a temperature ($kT/\epsilon = 1.8$) slightly above the critical tempera-

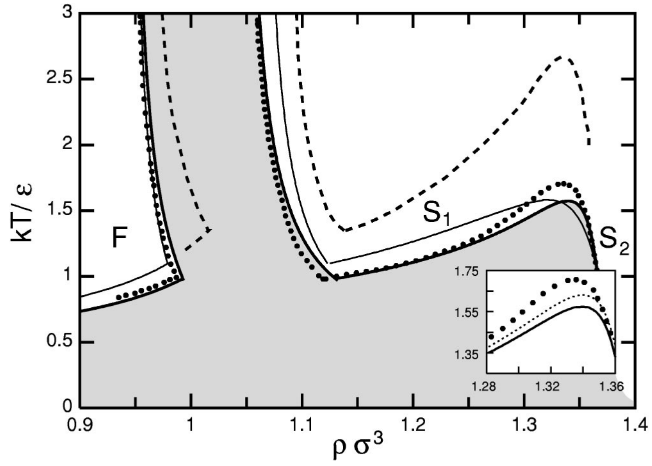

FIG. 3. Phase diagram in the temperature T density ρ plane for a SW system with $\delta/\sigma = 0.02$. Shaded regions are coexistence regions between two phases, according to the present theory. Boundary coexistence lines are indicated as follows: black circles, simulation results [8]; thick continuous lines, present theory; thin continuous line, LPT [9]; dashed lines, PWDA [11]. Indicated by letters are the fluid (F), expanded solid (S_1) and dense solid (S_2). The inset is an enlargement of the critical region, showing results from: simulation (black circles), present theory (continuous line), and present theory using a different reference system (dotted line), as explained in the text.

ture for the solid-solid transition (the necessary input data for the free energy were obtained by simulation). Interestingly, the phase boundary for the solid-solid transition is not modified except close to the critical region where differences with respect to simulation are reduced by a factor of 2, as seen in the inset in Fig. 3 (note that the simulations in [8] were performed with a rather small system size—108 atoms—so that the real critical temperature should actually be lower than shown).

Our theory may be easily extended to incorporate other thermodynamic relations, and self consistency may be formulated on other statistical ensembles. Also, as mentioned before, the theory may be extended to general pair potentials, provided an accurate reference system is available and a suitable set of conditions for liquid and solid phases found. A practical point to solve arises when the potential is more long ranged than allowed by consideration of only the first peak of $\tilde{g}$. Except in extreme cases, we believe there is in principle no need to extend the number of parameters (hence, conditions) to describe $\tilde{g}(r)$ since it should be numerically accurate to replace its second and additional peaks by those of the reference, uncorrelated, radial distribution function. An important example, where this assumption certainly holds, is the Lennard-Jones potential, where a standard WCA division allows use of a reference HS system. Results will be reported elsewhere.

Finally, it is interesting to note that our theory may be regarded as an easy-to-implement alternative to computer simulation. In fact, the route that connects the free energy to that of a reference system is often used in computer simulation, where the coupling integral is evaluated numerically by quadrature or otherwise (as in our method) but the integrand (average excess energy) is evaluated on the computer. Here, the integrand is calculated using an accurate self-consistent procedure that, similar to the simulational strategy, depends sensitively upon having an accurate reference system but, by contrast, is numerically very simple and involves minor computational work as compared to computer simulation.

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[14] 256 spheres were used in a rectangular box with periodic boundary conditions. After equilibration, average runs consisted of 10^4 MC steps. The coupling integral was evaluated by the trapezoidal rule with step size $h = 0.1$.