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Extending Wertheim's perturbation theory to the solid phase: The freezing of the pearl-necklace model

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An extension of Wertheim's first order perturbation theory [M. S. Wertheim, J. Chem. Phys. **87**, 7323 (1987)] for chain molecules in the solid phase is proposed. In particular the solid phase of a model of freely jointed chains of tangent hard spheres has been considered. The equation of state and free energies from theory are compared with simulation results obtained previously by Malanoski and Monson [A. P. Malanoski and P. A. Monson, J. Chem. Phys. **107**, 6899 (1997)] for chains with up to eight monomer units. The agreement between theory and simulation is good for the densities close to the melting, and deteriorates for densities close to close-packing. We also evaluated theoretically the fluid-solid equilibrium of the pearl-necklace model and compare with simulation results. The theory reproduces reasonably well the trends observed in the simulation results. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1372329]

I. INTRODUCTION

In the early 1980s Wertheim developed a theory to deal with the thermodynamic properties of fluids with association forces,[1–4] for example, hydrogen bonding fluids. It was soon realized that the formalism proposed could lead to an approximate equation of state for a completely different system, namely, that formed by chain molecules. The reason for this surprising relation arises from the fact that chains are formed from a fluid of associating monomers when the strength of the association becomes infinitely strong. This interesting finding was discovered independently by Wertheim[5] and by Chapman, Jackson and Gubbins.[6] It can be stated that since the publication of these two papers a new era has been born for the statistical mechanics of flexible molecules. In the simplest implementation of the theory, which is commonly denoted as the first order perturbation theory[5] (TPT1), the only information required to build an approximate equation of state for the chain fluid is the equation of state and the pair correlation function at contact of the monomer fluid. In the first order perturbation theory, the properties of the chain fluid are independent of the torsional state of the molecule and of the bond angle between three consecutive beads. For hard spheres, both the equation of state (EOS) and the pair correlation at contact are well known, and, therefore, it is simple to derive an equation of state for the fluid phase of chains of tangent hard spheres. This is the reason why the first application of Wertheim's theory of association to flexible molecules was performed on hard flexible chains.[5,6] Further development followed in the early 1990s. Zhou and Stell,[7] and W. Smith *et al.*[8] reformulated Wertheim's theory of association in a different language, namely that of the equilibrium constant. Chapman[9] showed that Wertheim's formalism could also be applied to systems with attractive forces. The work of Johnson *et al.*[10,11] has shown that Wertheim's formalism yields quite a good description for Lennard-Jones (LJ) chains, provided that the EOS and pair correlation function of the reference LJ fluid is accurately known. Gil-Villegas *et al.* have shown that the same holds true for square well chains[12] and recently the same has been shown for Yukawa chains.[13] One can summarize by saying that a good EOS of chain molecules interacting through a given pair potential can be obtained if the EOS and pair correlation function of the monomer fluid are known accurately. Therefore, an approximate but reliable description of flexible chains in the fluid phase can be obtained nowadays in a rather straightforward way. Since the message seems a little bit enthusiastic we should temper our expectations by mentioning that Wertheim's theory describes fluids made up of tangent monomer units, without any restriction in the bond angle or in the torsional energy. We shall denote models like these as fully flexible models. However, from a chemical point of view the models of real interest are those in which the bond angle is fixed, there is a torsional potential and the monomers are not tangent but overlap when forming the chain. For these more realistic models, Wertheim's theory is not yet successful and the situation is far from satisfactory.

In recent years, Wertheim's theory has been used to predict the vapor-liquid equilibrium of fully flexible molecules. Critical properties as obtained from Wertheim's theory have been compared to simulation results. This has been done by Escobedo and de Pablo for Lennard-Jones (LJ) and square well (SW) chains,[14] by Blas and Vega for LJ chains[15] and by MacDowell *et al.* for LJ chains with flexible bond lengths.[16] The theory performs a reasonable job in estimating the coexistence envelope and the critical properties of chain fluids.

Although the fluid phase of fully flexible chains has been studied extensively for hard models and for models with attractive forces, the solid phase has received far less attention (see, for instance, the recent review in Ref. 17). Solid phases of long flexible molecules are of interest since at room temperature and pressure long flexible molecules are in the solid phase. For instance, all linear alkanes with more than 20 carbon atoms are solid at room temperature and pressure and the same is true for polyethylene. Therefore the study of solid phases of flexible chains seems to be interesting not only from a scientific point of view but also from a practical point of view. The same is true for the fluid-solid equilibrium of these kind of systems.

Two recent studies have focused on the fluid-solid equilibrium of two simple models of fully flexible molecules. In the first study Malanoski and Monson[18] have examined the fluid-solid equilibrium of freely jointed chains of tangent hard spheres, the so called pearl-necklace model. These authors have studied the pearl-necklace model in the solid phase, determining the equation of state for $m=3,4,5,6,7,8$. In addition they also performed free energy calculations thus computing the fluid-solid equilibrium for these models. In the solid phase the atoms are arranged in a close packed fcc solid but there is no long range orientation order between the bond vectors of the chains.[17–22] In the other study Polson and Frenkel[23] have studied the fluid-solid equilibrium of a similar model with Lennard-Jones interactions (in place of hard sphere interactions). In addition to fully flexible chains, Polson and Frenkel considered the case of semi-rigid chains (i.e., they introduce a bending potential restricting the position of the bond angles). Taking this research on fluid-solid equilibrium one step further both groups have considered the fluid-solid equilibrium of simple models of *n*-alkanes, with hard interactions[24] and with LJ interactions,[25] respectively.

One interesting issue is the theoretical description of flexible molecules in the solid phase. Recently Malanoski *et al.*[26] have illustrated how cell theory can be successfully implemented for the determination of the properties of flexible molecules in the solid phase. This is certainly a route which deserves further work. Another possibility is the extension of Wertheim's first order perturbation theory,[5] TPT1, to solid phases. In an interesting paper, Sear and Jackson combined ideas from TPT1 and from cell theory and proposed an EOS for the rigid dimer in the solid phase.[27] The results were highly encouraging. They suggest ideas for extending the theory to longer chains, although results were not presented. In this work, we shall propose an extension of Wertheim's first order perturbation theory to the solid phase. In particular, we shall show how the theory can be implemented for the pearl-necklace model. The EOS and free energies obtained from this extension will be compared with the simulation results from Malanoski and Monson.[18] Once the TPT1 has been extended to the solid phase, it is possible to compute the fluid-solid equilibrium of the pearl-necklace model theoretically and to compare with the simulation results.

II. BRIEF DESCRIPTION OF WERTHEIM'S PERTURBATION THEORY

We shall summarize the main ideas contained within Wertheim's theory by following the formulation introduced by Zhou and Stell.[7,28] Let us assume that we have a certain number, N^{ref}, of spherical monomer particles within a certain volume V at temperature T. These spherical particles interact through a spherical pair potential $u(r)$. We shall denote this fluid as the reference fluid and the properties of this reference fluid will be labeled by the superscript ref. Let us also assume that in another container of volume V and temperature T, we have $N=N^{\mathrm{ref}}/m$ fully flexible chains of m monomers each. By fully flexible chains we mean chains of m monomers, with a fixed bond length of $L=\sigma$, and no other constraints (i.e., there is no restriction in either bonding or in the torsional angles). Each monomer of a certain chain interacts with all the other monomers in the system (i.e., in the same molecule or in other molecules) with the pair potential $u(r)$. The variable σ is a value of r for which the function $u(r)$ starts to increase strongly towards positive values (i.e., for a hard sphere it corresponds to the hard diameter whereas for a LJ bead it corresponds to the distance where the pair potential vanishes). The chain system described so far will be denoted as the chain fluid.

The Helmholtz free energy of the reference fluid A^{ref} can be divided into an ideal and a residual part as follows:

$$\frac{A^{\mathrm{ref}}}{N^{\mathrm{ref}}kT}=\frac{A^{\mathrm{ref}}_{\mathrm{ideal}}}{N^{\mathrm{ref}}kT}+\frac{A^{\mathrm{ref}}_{\mathrm{residual}}}{N^{\mathrm{ref}}kT}=\ln(\rho^{\mathrm{ref}}\sigma^3)-1+\frac{A^{\mathrm{ref}}_{\mathrm{residual}}}{N^{\mathrm{ref}}kT}, \qquad (1)$$

where ρ^{ref} is the number density of the reference fluid and where we arbitrarily assigned the value of thermal de Broglie wavelength to σ. The residual term represents the difference between the reference fluid and that of a system without intermolecular interactions at the same temperature and density.

The free energy of the chain fluid A can also be divided into an ideal and a residual part as follows:

$$\frac{A}{NkT}=\frac{A_{\mathrm{ideal}}}{NkT}+\frac{A_{\mathrm{residual}}}{NkT}=\ln(\rho\sigma^3)-1+\frac{A_{\mathrm{residual}}}{NkT}, \qquad (2)$$

where ρ is the number density of chains. Thermodynamic properties without any superscript refer to the chain fluid. The residual term represents the difference between the chain fluid and an ideal gas of chains at the same temperature and number density. In the ideal gas of chains there are no intermolecular interactions, whereas intramolecular interactions are still present. Let us assume at this point that the properties (thermodynamic and structural) of the reference fluid are known. Can we obtain an approximation for A_{residual} of the chain fluid from the properties of the monomer fluid? Following Zhou and Stell, the residual properties of the chain fluid are given after several approximations as

$$\frac{A_{\mathrm{residual}}}{NkT}=m\frac{A^{\mathrm{ref}}_{\mathrm{residual}}}{N^{\mathrm{ref}}kT}-(m-1)\ln y^{\mathrm{ref}}(\sigma), \qquad (3)$$

where $y^{\mathrm{ref}}(\sigma)$ is the background correlation function[29] of the reference fluid at contact. The background correlation function is related to the pair correlation function by

$$y(r)=\exp(\beta u(r))g(r). \qquad (4)$$

Therefore, the free energy of the chain fluid is given by

$$\frac{A}{NkT}=\ln(\rho\sigma^3)-1+m\frac{A^{\mathrm{ref}}_{\mathrm{residual}}}{N^{\mathrm{ref}}kT}-(m-1)\ln y^{\mathrm{ref}}(\sigma). \qquad (5)$$

The above equation shows that the free energy of the chain fluid may be obtained from a knowledge of the residual free energy of the reference fluid and the pair background correlation function of the reference fluid at the bonding distance of the chain. The equation of state which follows from Eq. (5) is given by

$$Z=mZ^{\mathrm{ref}}-(m-1)\left(1+\rho^{\mathrm{ref}}\frac{\partial \ln y^{\mathrm{ref}}(\sigma)}{\partial\rho^{\mathrm{ref}}}\right), \tag{6}$$

where we have defined Z^{ref} as $Z^{\mathrm{ref}}=p/(\rho^{\mathrm{ref}}kT)$. We shall denote Eqs. (5) and (6) as Wertheim's TPT1 theory.[4,6]

We note that the arguments used to arrive at Eqs. (5) and (6) make no special mention whatsoever of the actual nature of the phase considered.[7,28] What we suggest is to use these two equations for *both* the fluid phase and the solid phase. All that is then needed to obtain a fully unified theory for the phase equilibria of chain molecules is the residual free energy, compressibility factor and pair correlation function of the monomer fluid both for the fluid and solid phases. Note that in this way we depart from the approach proposed by Sear and Jackson,[27] as we do not find it necessary to invoke a cell theory for the solid phase.

We shall now show how to obtain the fluid and solid phase residual free energy, compressibility factor and radial distribution functions for use in Eqs. (5) and (6).

A. The fluid phase

Implementation of TPT1 for the fluid phase has been performed previously by a number of authors so we shall only provide the main ideas.

For the pearl-necklace model, the reference fluid is that of hard spheres in the fluid phase. The fluid phase of hard spheres is described quite accurately by the Carnahan–Starling[30] EOS:

$$Z_f^{\mathrm{ref}}=\frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3}, \tag{7}$$

where the subscript f denotes properties of the fluid phase and η is the volume fraction of the hard spheres, defined as

$$\eta=\frac{\pi}{6}\sigma^3\rho^{\mathrm{ref}}=\frac{\pi m}{6}\sigma^3\rho. \tag{8}$$

Notice that for tangent hard spheres the volume fraction of the chain fluid and that of the reference fluid are the same. The residual free energy of the hard sphere reference fluid is obtained from the thermodynamic relation:

$$\frac{A_{\mathrm{res},f}^{\mathrm{ref}}}{N^{\mathrm{ref}}kT}=\int_0^{\eta}\frac{Z_f^{\mathrm{ref}}-1}{\eta}d\eta. \tag{9}$$

When using the Carnahan–Starling EOS for the hard sphere fluid one obtains

$$\frac{A_{\mathrm{res},f}^{\mathrm{ref}}}{N^{\mathrm{ref}}kT}=\eta\frac{(4-3\eta)}{(1-\eta)^2}. \tag{10}$$

The virial route to the pressure of hard spheres[31] reads

$$Z_f^{\mathrm{ref}}=1+4\eta g_f^{\mathrm{ref}}(\sigma). \tag{11}$$

For hard spheres $g_f^{\mathrm{ref}}(\sigma)$ and $y_f^{\mathrm{ref}}(\sigma)$ adopt the same value. By substituting Eq. (7) in Eq. (11) the value of $g_f^{\mathrm{ref}}(\sigma)$ is obtained as a function of η. By substituting Eq. (7) and $g_f^{\mathrm{ref}}(\sigma)$ in Eq. (6) one obtains the well known TPT1 EOS for hard sphere chains which reads

$$Z_f=m\frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3}-(m-1)\frac{1+\eta-0.5\eta^2}{(1-\eta)(1-0.5\eta)}. \tag{12}$$

The residual free energy of the chain fluid is then given by

$$\frac{A_{\mathrm{res},f}}{NkT}=(m-1)\ln\frac{2(1-\eta)^3}{(2-\eta)}-(m)\frac{(2\eta-3)}{(1-\eta)^2}-3m. \tag{13}$$

Equations (13) and (12) give the residual free energy and EOS of the hard chains in the fluid phase. By adding the ideal term as given by Eq. (2) one obtains the free energy of the hard chain fluid.

B. The solid phase

Implementation of TPT1 for the solid phase is made as follows. For the pearl-necklace model in the solid phase, the reference system is that of hard spheres in the solid phase. The solid phase of hard spheres is described quite accurately by the EOS proposed by Hall,[32] which is essentially a least squares fit to the simulation results of hard spheres obtained by Alder.[33] The EOS for hard sphere solid reads

$$\begin{aligned}Z_s^{\mathrm{ref}}=&(12-3\alpha)/\alpha+2.557\,696\alpha+0.125\,307\,7\alpha\\&+0.176\,239\,3\alpha^2-1.053\,308\alpha^3+2.818\,621\alpha^4\\&-2.921\,934\alpha^5+1.118\,413\alpha^6,\end{aligned} \tag{14}$$

where α has been defined as

$$\alpha=4\left(1-\frac{\eta}{\eta_{\mathrm{cp}}}\right), \tag{15}$$

where $\eta_{\mathrm{cp}}=\pi/6\sqrt{2}$ is the volume fraction at close packing for hard spheres.

The virial route to the pressure of hard spheres reads

$$Z_s^{\mathrm{ref}}=1+4\eta g_s^{\mathrm{ref}}(\sigma). \tag{16}$$

By replacing Eq. (14) in Eq. (16) the value of $g_s^{\mathrm{ref}}(\sigma)$ is obtained as a function of η. By replacing Eq. (14) and $g_s^{\mathrm{ref}}(\eta)$ in Eq. (6) the EOS for chains in the solid phase Z_s is obtained. The expression of Z_s is straightforward although rather lengthy and can be determined easily by using an algebraic manipulations program such as Maple.[34]

Let us now focus on the determination of the free energy of the chain solid. As it can be seen in Eq. (3) all that is needed is an expression for $g_s^{\mathrm{ref}}(\sigma)$ and for the residual free energy of the hard sphere solid. The residual free energy of the hard sphere solid can be obtained from the thermodynamic relationship:

$$\frac{A_{\mathrm{res},s}^{\mathrm{ref}}(\eta)}{N^{\mathrm{ref}}kT}=\frac{A_{\mathrm{res},s}^{\mathrm{ref}}(\eta_0)}{N^{\mathrm{ref}}kT}+\int_{\eta_0}^{\eta}\frac{(Z_s^{\mathrm{ref}}-1)}{\eta}d\eta, \tag{17}$$

where $A_{\mathrm{res},s}^{\mathrm{ref}}(\eta_0)$ is the residual free energy of a reference hard sphere solid at a certain reference volume fraction η_0. For hard spheres in the solid phase the residual free energy has been evaluated by free energy calculations by a number of authors. The latest and most accurate calculations[35] have

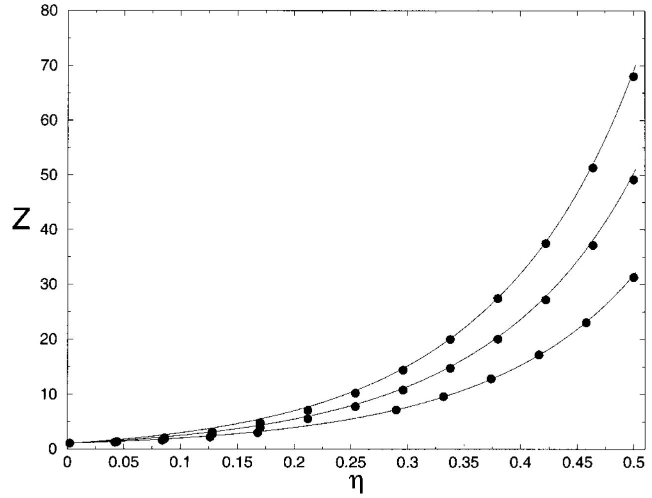

FIG. 1. Equation of state of chains with $m=3,5,7$ in the fluid phase as obtained from simulation (Ref. 18) (symbols) and from TPT1 (lines). The results from bottom to top correspond to $m=3,5,7$.

yielded $A_{\mathrm{res},s}^{\mathrm{ref}}(\eta_0)/(N^{\mathrm{ref}}kT)=5.918\,89$ for a reference packing fraction of $\eta_0=0.5450$. Therefore, the residual free energy of the reference hard sphere solid can be obtained as

$$\frac{A_{\mathrm{res},s}^{\mathrm{ref}}(\eta)}{N^{\mathrm{ref}}kT}=5.918\,89+\int_{0.5450}^{\eta}\frac{(Z_s^{\mathrm{ref}}-1)}{\eta}d\eta. \tag{18}$$

The integral of Eq. (18) can be evaluated again by using an algebraic package such as Maple.[34]

One may summarize by saying that all that is needed for implementing Wertheim's TPT1 to the solid phase of hard chains is the EOS of the hard sphere reference solid and the value of the residual free energy at a certain density. By using Eqs. (16) and (18) the rest of the properties of the reference hard sphere solid are obtained. By substituting these properties of the hard sphere reference solid into Eqs. (6) and (5) the properties of the hard sphere chain solid are obtained. All the final expressions of the thermodynamic properties of the chain model, in the fluid and in the solid phase, are obtained analytically, although for the solid phase they are rather lengthy. We should mention that the theory used in this work is identical to that of Sear and Jackson[27] for the fluid phase. However, for the solid phase, although the EOS is identical to that proposed by Sear and Jackson, our expression for the free energy differs from that proposed by Sear and Jackson[27] [see, for instance, Eq. (30) of their paper].

III. RESULTS

In this section we shall compare the results obtained from the theory described in the previous section with the simulations results of Malanoski and Monson[18] for the pearl-necklace model. These authors have provided empirical fits to their simulation results for the fluid and solid phases of chain molecules with m ranging from $m=3$ up to $m=8$. Therefore when plotting simulations results it should be understood that they were obtained by using these fits.

In Fig. 1 the EOS as obtained from TPT1 and from simulation is presented for $m=3,5,7$ chains in the fluid phase. The reduced pressure, defined as $p^*=p/(kT/\sigma^3)$, is plotted as a function of the volume fraction η for chains with $m=3,5,7$ monomers. As can be seen the agreement is quite good and this has been previously noticed by other authors.

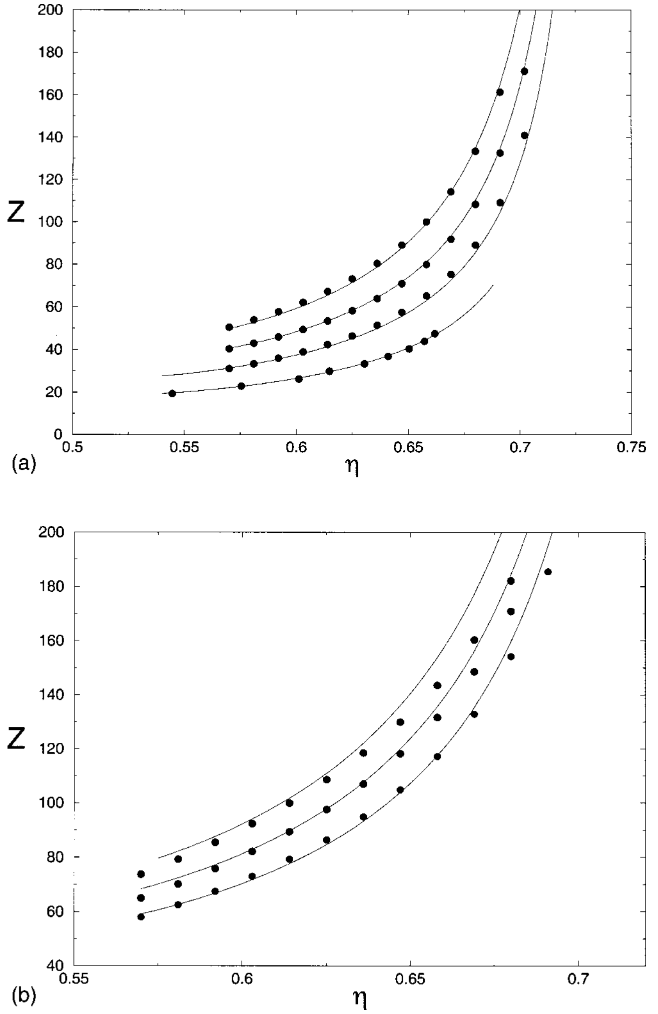

FIG. 2. Equation of state of chains in the solid phase as obtained from simulation (Ref. 18) (symbols) and from TPT1 (lines). (a) Results from bottom to top correspond to $m=2,3,4,5$. (b) Results from bottom to top correspond to $m=6,7,8$.

In Fig. 2 the EOS as obtained from the extension of TPT1 to solid phases described in this work and from the simulations results of Malanoski and Monson is presented. The reduced pressure is plotted as a function of the volume fraction for $m=2,3,4,5$ [Fig. 2(a)] and for $m=6,7,8$ [Fig. 2(b)]. Simulations results for $m=2$ were taken from Vega, Paras and Monson[36] and correspond to an ordered solid since no simulation results are yet available for the equation of state of a disordered fcc solid dimer. For short chains [Fig. 2(a)] the agreement between theory and simulation is quite good for all the considered range of densities. For longer chains, the results are good for the low densities (those close to the melting point) but deteriorate significantly at high densities and as the molecules become longer. Obviously, the deficiencies of the theory become more evident for longer chains.

In Table I, the free energies of the chains in the solid

TABLE I. Free energies of the pearl-necklace model in the solid phase as obtained from simulation (Ref. 18) $A/(NkT)$ and from the extension of Wertheim's theory to the solid phase performed in this work $A^{\mathrm{TPT1}}/(NkT)$.

m	η	$A/(NkT)$	$A^{\mathrm{TPT1}}/(NkT)$
3	0.6754	21.70	21.92
4	0.6806	29.13	29.53
5	0.6859	36.52	37.69
6	0.6806	43.01	43.67
7	0.6806	49.33	50.79
8	0.6806	55.67	57.93

phase as obtained from TPT1 are compared with the free energies determined by Malanoski and Monson by free energy calculations.[18] The agreement may be considered as satisfactory. Again, results seem to be better for shorter chains and deteriorate somewhat for longer chains. Taking into account the simplicity of the theory, and the complexity of the free energy calculations (in fact, the paper by Malanoski and Monson probably contains the first free energy calculations for the solid phase of flexible molecules) one is surprised even by such a good agreement. Table I illustrates that the extension of TPT1 to solid phases proposed in this work does not only provide a reasonable EOS for the solid phase but also reasonable free energies.

One of the consequences of Wertheim's TPT1 for fluid and solid phases is that it predicts that, for a fixed value of the volume fraction, η, the compressibility factor should be a linear function of m for sufficiently long chains for the fluid phase that has already been illustrated by Hall *et al.*[37] Let us now show that this also holds for the solid phase. In Fig. 3 the compressibility factor Z is plotted as a function of m, for several volume fractions $\eta = 0.6, 0.62, 0.64, 0.66, 0.68, 0.7$. It is seen that the behavior of Z versus m seems to be linear for low volume fractions but deviates significantly at high densities.

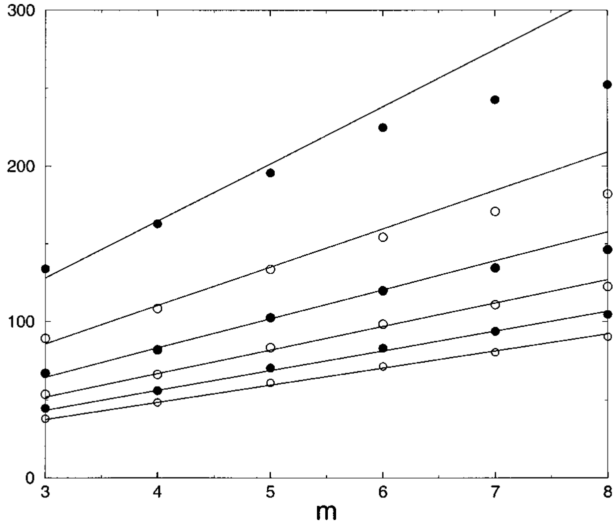

FIG. 3. Compressibility factors, Z, as a function of m for the pearl-necklace model in the solid phase. Symbols: simulation results from Malanoski and Monson (Ref. 18). Lines: TPT1 theory for the solid phase. Lines from top to bottom corresponds to $\eta = 0.70, 0.68, 0.66, 0.64, 0.62$, and 0.60, respectively.

TABLE II. Fluid-solid equilibrium of the pearl-necklace model determined from simulation and from TPT1 theory. η_f and η_s denotes the volume fractions of the fluid and solid phases at coexistence, respectively. $p^* = p/(kT/\sigma^3)$ corresponds to the reduced pressure at coexistence. $\mu/(kT)$ corresponds to the chemical potential at coexistence. For each value of m the first row presents the simulation results from Malanoski and Monson (Ref. 18) whereas the second one corresponds to the theoretical predictions.

m	Method	η_f	η_s	p^*	$\mu/(kT)$
1	MC	0.4939	0.5451	11.70	16.20
1	TPT1	0.4932	0.5451	11.69	16.19
2	TPT1	0.5147	0.5728	12.24	32.06
3	MC	0.5288	0.5864	12.90	49.01
3	TPT1	0.5215	0.5824	12.42	48.12
4	MC	0.5289	0.5917	13.00	65.82
4	TPT1	0.5247	0.5870	12.48	64.20
5	MC	0.5341	0.5969	13.63	84.18
5	TPT1	0.5268	0.5900	12.54	80.41
6	MC	0.5393	0.6021	13.88	101.75
6	TPT1	0.5279	0.5917	12.54	96.48
7	MC	0.5393	0.6074	14.16	121.8
7	TPT1	0.5288	0.5930	12.56	112.66
8	MC	0.5393	0.6021	13.43	133.9
8	TPT1	0.5293	0.5938	12.56	128.73

Let us now present the results for the fluid-solid equilibrium. In Table II the coexistence densities and pressures of the fluid-solid equilibria of hard sphere chains as obtained from theory and from simulation are presented. As can be seen, the agreement between theory and simulation is reasonable. In Fig. 4 coexistence densities are plotted. In general the theory underestimates the densities at which the fluid-solid equilibrium occurs. The theory predicts a slight increase of the freezing densities with m. In fact, the theory predicts an increase from $\eta = 0.4939$ for $m = 1$ (the freezing density for hard spheres[31]) to $\eta = 0.5293$ for $m = 8$ for the volume fractions of the fluid phase at freezing. It also predicts a slight increase of the volume fraction of the solid phase at melting. Similar trends are observed in the simulations results. Trends observed in Fig. 4 may explain why a

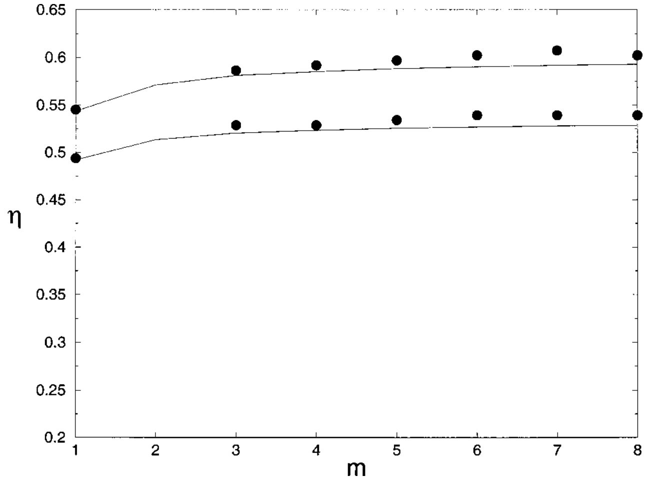

FIG. 4. Coexistence densities of the fluid-solid equilibrium of the pearl-necklace model. The densities are presented as volume fractions, i.e., η. Results are presented for several values of m. Lines corresponds to theoretical predictions from TPT1 for the fluid and solid phases. Symbols: Simulations results from Malanoski and Monson (Ref. 18).

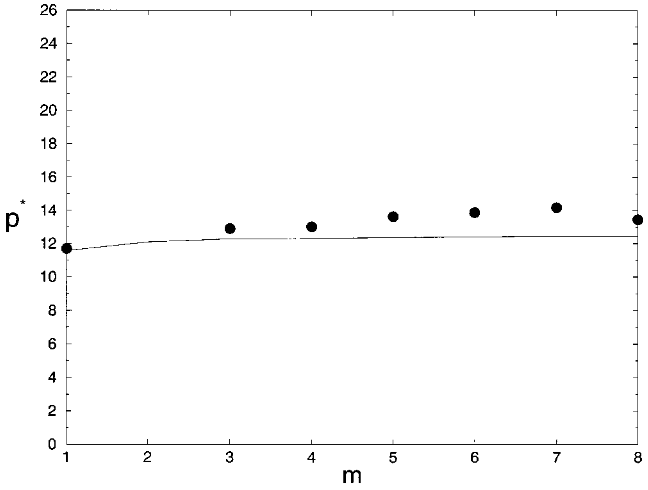

FIG. 5. Coexistence pressures of the fluid-solid equilibrium of the pearl-necklace model. The pressures are presented in reduced units $p^* = p/(kT/\sigma^3)$. Results are presented for several values of m. Lines corresponds to theoretical predictions from TPT1 for the fluid and solid phases. Symbols: Simulations results from Malanoski and Monson (Ref. 18).

previous estimate of the fluid-solid equilibrium of the dimer[36] gave volume fractions at coexistence very close to that of hard spheres.

In Fig. 5 the reduced coexistence pressures are shown as a function of m. Again, the theory underestimates the coexistence pressures.

An interesting feature which appears in Figs. 4 and 5 is the fact that densities (i.e., volume fractions) and pressures seems to reach asymptotic values for large values of m. This is an interesting feature which seems to be also observed in the simulation results. Let us explain the origin of this asymptotic limit. In Wertheim TPT1 the compressibility factor can be written in the form[38]

$$Z = Z_1(\eta) + mZ_2(\eta), \tag{19}$$

where Z_1 and Z_2 are functions which depend only on η. This is true for the solid and for the fluid phase. We shall use Z_1 and Z_2 for the fluid phase and Z_1' and Z_2' for the solid phase. The prime will denote properties of the solid phase, whereas variables without prime refer to the fluid phase. Let us define the reduced pressure as

$$p^* = \frac{p\sigma^3}{kT}. \tag{20}$$

One of the conditions for equilibrium between the fluid and solid phases is that $p^* = p^{*'}$ which can be written after Eq. (19):

$$\eta\left(Z_2(\eta) + \frac{Z_1(\eta)}{m}\right) = \eta'\left(Z_2'(\eta') + \frac{Z_1'(\eta')}{m}\right). \tag{21}$$

For sufficiently long values of m Eq. (21) reads

$$\eta Z_2(\eta) = \eta' Z_2'(\eta'), \tag{22}$$

where any dependence with respect to m has disappeared.

The residual free energy of a chain is given from TPT1 theory as[14]

$$A_{\mathrm{res}} = A_1(\eta) + mA_2(\eta). \tag{23}$$

Equation (23) holds for the fluid and for the solid phase. To this residual term, one must add the ideal term, given by $\ln(\rho\sigma^3) - 1 = \ln(\eta) - \ln(\pi m/6) - 1$. The condition of equal chemical potentials in the fluid and solid phases, $\mu/(kT) = \mu'/(kT)$, gives

$$\ln(\eta) + (A_1(\eta) + mA_2(\eta) + Z_1(\eta) + mZ_2(\eta)) \\ = \ln(\eta') + (A_1'(\eta') + mA_2'(\eta') + Z_1'(\eta') + mZ_2'(\eta')). \tag{24}$$

For long values of m Eq. (24) can be rewritten as

$$A_2(\eta) + Z_2(\eta) = A_2'(\eta') + Z_2'(\eta'), \tag{25}$$

where again any dependence with m has disappeared. For infinitely long chains the volume fractions at coexistence, η and η', are obtained by solving Eqs. (22) and (25), which do not contain any m dependence. Therefore, according to TPT1 the volume fractions of the fluid and solid phases at coexistence must reach asymptotic finite values for very long chains.

The reduced pressure at coexistence can be obtained from the expression

$$p^* = \frac{6\sigma^3}{\pi}\left(\frac{(Z_1(\eta) + mZ_2(\eta))}{m}\right)\eta, \tag{26}$$

so that when m tends to infinity it reads

$$p^* = \frac{6\sigma^3}{\pi} Z_2(\eta)\eta. \tag{27}$$

According to Eq. (27) the reduced pressure must also reach an asymptotic finite value for infinitely long chains. In essence, if the EOS of the fluid and solid phases is a linear function of m for a fixed value of η, then the coexistence volume fractions and pressures must reach an asymptotic value. The same is true for the chemical potential per monomer unit at coexistence [i.e., $\mu/(kTm)$] which increases (according to the simulation results) from 16.3 for $m=3$ to 16.7 for $m=8$ as can be inferred from the results of Table II.

Finally, in Fig. 6 the fluid-solid equilibrium of the pearl-necklace model as obtained from TPT1 theory is plotted for $m=1,2,4,8$. The results for $m=1,2$ are clearly distinguishable from the results for $m=4,8$. However, it is seen that there is little difference between the results for $m=4$ and the results for $m=8$. This indicates that the fluid-solid equilibrium for these models are close to the asymptotic limit.

The preceding discussion illustrates that freezing properties of chains must reach asymptotic values when m tends to infinity. As an example of a real system with this property, we should mention the case of polyethylene. In fact, it is well known that the triple point temperature of polyethylene reaches an asymptotic finite value.

IV. CONCLUSIONS

In this article Wertheim's theory has been extended to solid phases. The theory requires knowledge of the residual free energy of the reference fluid and of the contact value of the radial distribution function. For hard spheres, both the

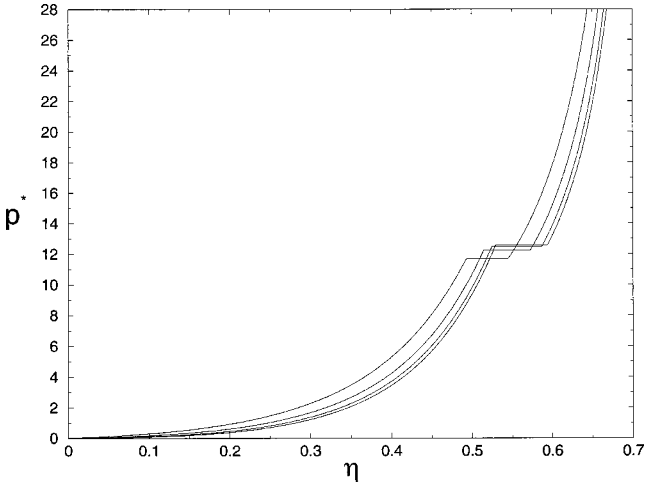

FIG. 6. Fluid-solid equilibrium of the pearl-necklace model as obtained from TPT1 for the fluid and solid phases. For the fluid phase results correspond (from top to bottom) to $m=1,2,4,8$. For the solid phase results correspond (from top to bottom) to $m=1,2,4,8$. The pressures are presented in reduced units $p^*=p/(kT/\sigma^3)$.

residual free energy and the contact value of $g(\sigma)$ are well known for both the fluid and the solid phases. To check the accuracy of the theory, we have compared the theoretical predictions with recent simulation data for the pearl-necklace model in the solid phase. It is found that the extension of TPT1 to the solid phase yields a good EOS, although the results deteriorate significantly at very high densities and for long chains. Also, the free energies of the theory seem to be in rather good agreement with these simulations. In this way, it has been possible to theoretically determine the fluid-solid equilibrium of the pearl-necklace model. Good agreement with simulation is found. It is found that the theory predicts asymptotic values for coexistence properties such as volume fractions and pressures when m is sufficiently large. An explanation for this behavior has been proposed. Simulation results seem to support the existence of these limits when m goes to infinity. Although the theory does not show quantitative agreement with simulation, the results are at least qualitatively correct, and this is especially satisfactory when one considers the complexity of the problem of the fluid-solid equilibrium of hard chains, and the simplicity of the theory. The usefulness of this approach should not be overlooked, as free energy calculations for the solid phase of pearl-necklace chains is not at all a trivial matter. There are at least two important difficulties. The first is that one must select several random arrangements of the molecules in the solid phase and then perform averages of the free energies and densities (for a given pressure) of each possible configuration. Second, some approximate expression for the combinatorial entropy that arises when considering these possible arrangements is needed. Interestingly TPT1 does not require such combinatorial entropy, because it is based on a reference system made of unbounded monomers; the molecules appear naturally as a consequence of association reactions, and all free energy contributions that result from their formation are accounted for by the $\ln y(\sigma)$ term, whether in the fluid or in the solid phase. The combinatorial entropy is required when the reference system consists of chains with atoms which are distributed over a fcc lattice, but not when the reference system consists of individual atoms arranged in a fcc lattice.

The main message of this article is that a qualitative view of the freezing of hard sphere chains can be obtained from the knowledge of the phase diagram of the much simpler hard sphere model.

Some possible extensions of this work are the extension to two dimensional systems and the extension to systems with attractive forces. Such extensions seem rather straightforward.

Some other interesting issues concern the possibility of extending Wertheim's first order perturbation theory to second order. That requires knowledge of the three body correlation function of the hard sphere reference system. Although for the fluid phase the three body correlation function is well known, rather little or nothing is known about the three body correlation function of the hard sphere system in the solid phase. Of course, the role of flexibility on solid phases also deserves further research. It is not clear at this point whether flexible and rigid chains differ significantly in the EOS and structure of the solid phase, and whether Wertheim's theory could also be extended or not to ordered solids formed by linear rigid molecules. We hope this work encourages further research in the area of solid phases of flexible molecules.

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