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An application of cell theory to molecular models of n-alkane solids

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Solid phase properties for hard sphere chain molecular models of n-alkanes are calculated using the cell theory, and a numerical method for implementation of cell theory for chain molecules is described. Good agreement with Monte Carlo simulations for solid phase properties is obtained from the theory. By using cell theory for the solid phase and an equation of state for the fluid phase, solid–phase equilibrium can be calculated. The predictions are in quite good agreement with Monte Carlo simulation results. Cell theory is used to assess the impact of an approximate treatment used in earlier work for the effect of the temperature dependence of the molecular flexibility upon the solid phase properties of a hard chain model with a realistic torsional potential.

1. Introduction

Computer simulation studies have been reported dealing with the important problem of calculating solid–fluid phase equilibrium for chain molecules. Malanoski and Monson [1] and Polson and Frenkel [2] have studied solid–fluid equilibrium for chains of tangent spheres. In the work of Malanoski and Monson [1] freely jointed tangent hard sphere chains were considered. The goal was to investigate the feasibility of calculating the free energy in the solid phase. Polson and Frenkel [2] considered the case of tangent Lennard-Jones 12-6 spheres and investigated the effect of variable chain stiffness. They found that increasing the chain stiffness stabilized the solid phase.

The n-alkanes are an important prototypical system for studying the effect of molecular shape and chain length on solid–fluid phase diagrams of chain molecules. The solid phase equilibrium properties of n-alkanes exhibit odd–even effects which are related to the way in which the chains are packed in the solid phase [3]. Such effects cannot be described with models that do not restrict the CCC bond angles. Malanoski and Monson [4] have considered fused hard chain models which give a geometrically realistic model of the n-alkanes. They found that if the hard sphere chain results were used as reference system data in a generalized van der Waals or mean-field theory for the phase diagram, the predictions for the chain length dependence of T_t/T_c were in qualitatively good agreement with the experimental results if, in addition to the chain structure, the torsional potential was modelled realistically.

Calculations of solid–fluid equilibrium via Monte Carlo simulations are a major computational undertaking and it is worthwhile investigating the feasibility of predicting the solid–fluid phase equilibrium for chain molecules using simpler theoretical approaches. One possibility is to use density functional theory [5]. Another is to use cell theory [6] for the solid phase and a theoretical equation of state for the fluid phase. This approach has been used successfully to study a variety of model systems including hard spheres [7], the Lennard-Jones 12-6 potential [8], hard dumbbells [9], and mixtures of hard spheres [10, 11] and Lennard-Jones 12-6 spheres [12]. Generally the quantitative agreement with available Monte Carlo results for these systems is better than for the density functional theory [9]. In cell theory the partition function is factored into a product of cell partition functions for single molecules moving in a cage created by the neighbouring molecules fixed at their lattice positions. Such partition functions are easy to calculate for spherical molecules and rigid non-spherical molecules. For flexible chains, however, the calculations are somewhat more involved and require substantially more computer time. Nevertheless, such calculations are still much less computationally intensive then using full N particle Monte Carlo simulations to determine the solid phase free energy.

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2. Methodology

2.1. *Molecular models*

In this work we use the same molecular models as those reported in [4]. We consider hard sphere chains with the CCC bond angle set at the value for tetrahedral coordination (109.47°) and the bond length at 0.4σ where σ is the hard sphere site diameter. In the work of Malanoski and Monson [4] three treatments of the torsional portential were considered. All the models have a hard sphere repulsive interaction between pairs of sites in a chain separated by three or more sites. For example, in a six-site chain there is a hard sphere interaction between sites one and five, sites one and six and sites two and six. In their first model (model I) there is no additional intramolecular interaction beyond this hard core exclusion. In the second model (model II) there is an additional hard sphere interaction between pairs of sites separated by three sites, yielding a hard core torsional potential. In the third model (model III) they considered a more realistic representation of the torsional potential using two forms which have been used previously in simulations of n-alkanes [13, 14]. In this work we focus on the model II and model III torsional potentials since it is these which give the more realistic treatment of the flexibility effects. For the model III we use the Ryckaert–Bellemans torsional potential.

2.2. *Implementation of cell theory for chain molecules*

In cell theory the partition function of the solid is evaluated by assuming that each molecule of the solid interacts with its nearest neighbours in their static lattice positions [6, 9, 15]. For hard core potentials this approximation works best for dense solid states. The partition function for the entire solid can then be factorized into single molecule partition functions. We have

$$Q_N = q^N Z_1^N, \tag{1}$$

where N is the number of molecules and q is part of the molecular partition function that is independent of the density. In the case of a chain molecule, Z_1 can be written as

$$Z_1 = \int \cdots \int \exp\left[-\beta u(\mathbf{r}_1, \ldots \mathbf{r}_m)\right] \Phi(\mathbf{r}_1, \ldots \mathbf{r}_m)\, \mathrm{d}\mathbf{r}_1 \cdots \mathrm{d}\mathbf{r}_m, \tag{2}$$

where $\mathbf{r}_j$ refers to the cartesian coordinates of the jth site in the central molecule of the cell, m is the total number of sites in the chain, r_c is the bond length, θ_c is the CCC bond angle, and $u(\mathbf{r}_1, \ldots \mathbf{r}_m)$ is the potential energy which consists of two contributions. The first is the potential energy of interaction of the molecule with its neighbours. The second contribution is from the intramolecular potential energy. The function $\Phi(\mathbf{r}_1, \ldots \mathbf{r}_m)$ imposes constraints on the chain configuration due to fixed bond lengths and bond angles, and is given by

$$\Phi(\mathbf{r}_1, \ldots \mathbf{r}_m) = \prod_{i=2}^{m} \delta(|\mathbf{r}_i - \mathbf{r}_{i-1}| - r_c) \times \prod_{j=3}^{m} \delta\left(\frac{(\mathbf{r}_j - \mathbf{r}_{j-1}) \cdot (\mathbf{r}_{j-2} - \mathbf{r}_{j-1})}{|\mathbf{r}_j - \mathbf{r}_{j-1}||\mathbf{r}_{j-2} - \mathbf{r}_{j-1}|} - \cos\theta_c\right). \tag{3}$$

We calculate Z_1 numerically using Monte Carlo integration. In order to enforce the bond length and bond angle constraints it is convenient to use a combination of Cartesian and spherical polar coordinates. The coordinates used are illustrated in figure 1. We use Cartesian coordinates to specify the location of the first atom in the chain. For each subsequent atom l the coordinates are expressed relative to those of the previous atom $l-1$, using spherical polar coordinates, r_l, θ_l, ϕ_l. Z_1 can be rewritten using this coordinate system as

$$\begin{aligned} Z_1 = \int \cdots \int & \exp\left[-\beta u(\mathbf{r}_1, r_2, \theta_2, \phi_z, \ldots r_m, \theta_m, \phi_m)\right] \\ & \times \Phi(\mathbf{r}_1, r_2, \theta_2, \phi_2, \ldots r_m, \theta_m, \phi_m) \\ & \times \mathrm{d}\mathbf{r}_1 r_2^2 \sin\theta_2\, \mathrm{d}r_2\, \mathrm{d}\theta_2\, \mathrm{d}\phi_2 \cdots r_m^2 \sin\theta_m\, \mathrm{d}r_m\, \mathrm{d}\theta_m\, \mathrm{d}\phi_m, \end{aligned} \tag{4}$$

where $\Phi(\mathbf{r}_1, r_2, \theta_2, \phi_2, \ldots r_m, \theta_m, \phi_m)$ is given by

$$\Phi(\mathbf{r}_1, r_2, \theta_2, \phi_2, \ldots r_m, \theta_m, \phi_m) = \prod_{i=2}^{m} \delta(r_i - r_c) \prod_{j=3}^{m} \delta(\theta_j - \theta_c). \tag{5}$$

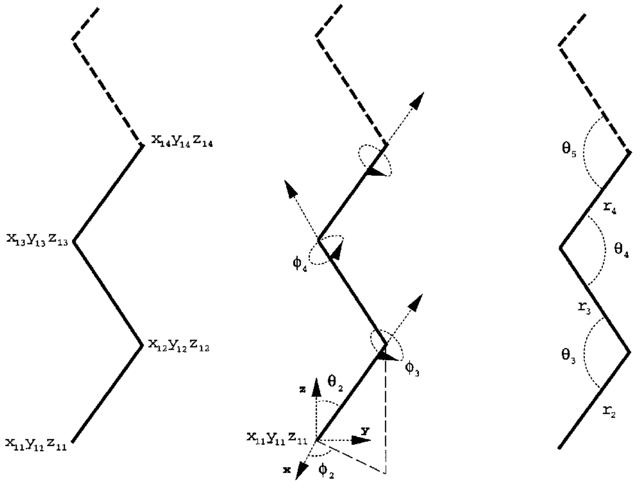

Figure 1. Schematic representation of the coordinate system used to represent a chain in our cell theory calculations.

Since each of the delta functions is now associated with one variable, these variables can be integrated over immediately. So we can rewrite equation (4) as

$$Z_1 = r_c^{m-1}(\sin\theta_c)^{m-2}\int\cdots\int \exp(-\beta u)\mathrm{d}\mathbf{r}_1 \times \sin\theta_2\,\mathrm{d}\theta_2\,\mathrm{d}\phi_2\,\mathrm{d}\phi_3\cdots\mathrm{d}\phi_m. \tag{6}$$

The quantities r_c^{m-1} and $(\sin\theta_c)^{m-2}$ can be removed from Z_1 and grouped with q as they are not dependent on the density. We then have

$$Z_1' = \int\cdots\int \exp(-\beta u)\mathrm{d}\mathbf{r}_1 \sin\theta_2\,\mathrm{d}\theta_2\,\mathrm{d}\phi_2\,\mathrm{d}\phi_3\cdots\mathrm{d}\phi_m \tag{7}$$

The single chain partition function can now be determined numerically using Monte Carlo integration via

$$Z_1' = \frac{V_s}{M}\sum_{i=1}^{M}\exp(-\beta u_i), \tag{8}$$

where M is the total number of randomly generated sample configurations and V_s is the hypervolume from which the coordinates are sampled. In evaluating Z_1', only configurations that place the molecule close to its lattice position will be significant. We can introduce importance sampling by limiting the range from which each coordinate is sampled to values close to the lattice value of that coordinate. V_s is then given by

$$V_s = \Delta x_1 \Delta y_1 \Delta z_1 \Delta\cos\theta_2 \prod_{i=2}^{m}\Delta\phi_i \tag{9}$$

where, for example,

$$\Delta\phi_i = \phi_i^{\max} - \phi_i^{\min}. \tag{10}$$

In order to determine V_s a Monte Carlo simulation is run for a single chain in its cell, recording the minimum and maximum values of the coordinates encountered [9]. These minimum and maximum values of the variables can then be used to compute V_s. This importance sampling technique works very well for shorter chains, but for longer chains V_s determined in this way can be much larger than the hypervolume of the cage formed by the neighbouring molecules. When this happens the number of samples that must be taken in the Monte Carlo integration becomes prohibitively large. We have been able to obtain satisfactory accuracy from large Monte Carlo samples for chains with up to eight atoms.

Before calculating the free energy it is convenient to divide Z_1' by the intramolecular contribution in the ideal gas limit. This contribution is given by

$$Z_{\mathrm{intra}}' = \int\cdots\int \exp(-\beta u_{\mathrm{intra}})\sin\theta_2\,\mathrm{d}\theta_2\,\mathrm{d}\phi_2\,\mathrm{d}\phi_3\cdots\mathrm{d}\phi_m. \tag{11}$$

Alternatively, the corresponding contribution to the free energy should be added to the configurational free energy obtained from the equation of state of the fluid phase prior to performing a solid–fluid phase equilibrium calculation.

The simulations to determine the maximum and minimum values of the generalized coordinates were carried out using a modification of algorithm used for the molecular simulations of the previous work on models of n-alkanes [4]. The simulations used were 10-50 × 10^6 trials depending on the chain length. The minimum and maximum values of the coordinate variables were increased by a safety margin to ensure that the sample space contained all of the chain configurations that generate no overlaps with neighbouring chains. This value varied from 0.05 to 0.03 of the values determined in the simulation. To evaluate equation (8) the number of sample configurations required to achieve sufficient accuracy increased with chain length. For the butane models, 20×10^6 sample configurations were sufficient. For the octane models, 100-1000 × 10^6 sample configurations were required. This increase in the number of trials required reflects the decrease in the number of configurations that contribute significantly to the integral for longer chains using the sampling scheme described above. It is possible that a more efficient importance sampling procedure could be developed, although we have not investigated that possibility. Eight atoms appears to represent an upper limit to the chain length for which the present sampling method can be used.

The lattice structure for the cell theory calculations was obtained from the close packed configuration generated by the method described in [4]. This solid structure was isotropically expanded to the required density. Relaxation of the solid structure from the close packed geometry was not studied in these calculations.

It is useful to fit Z_1' to a function so that the free energy can be differentiated to give the pressure. For this purpose we use the expression

$$Z_1' = C\alpha^D \exp(a_1\alpha + a_2\alpha^2 + a_3\alpha^3), \tag{12}$$

where C, a_1, a_2, and a_3 are adjustable constants and α is given by

$$\alpha = \frac{\rho_0 - \rho}{\rho_0}, \tag{13}$$

where ρ is the number density of molecules and ρ_0 is its value at close packing. In the rest of this paper ρ will always refer to the number density of molecules. The densities at close packing were determined by the algorithm described in [4]. Equation (12) is a generalization of the expression used by Alder *et al.* [16] to fit the equation of state of hard spheres from molecular dynamics simulations at high pressure. For rigid molecules, the exponent D is the number of degrees of freedom of the central molecule [17]. We calculated D as the number of variables required to describe the position of the central molecule which, for a chain of n atoms with fixed bond lengths and bond angles, is $n + 3$. Making D an adjustable parameter did not improve the quality of the fit. Values of the coefficients for the fits of our results for Z_1' are tabulated elsewhere [18].

2.3. *Fluid equation of state*

In order to calculate this solid–fluid transition, a fluid phase equation of state is required. Vega and coworkers [19] developed an extension of the equation of state for freely jointed chains of tangent hard spheres obtained from Wertheim's thermodynamic perturbation theory [20, 21]. For chains of length m the tangent hard sphere equation of state is given by

$$\frac{PV}{NkT} = m\frac{(1 + y + y^2 - y^3)}{(1 - y)^3} - (m - 1)\frac{(1 + y - y^2/2)}{(1 - y)(1 - y/2)}, \qquad (14)$$

where y is the packing or volume fraction. Vega *et al.* [19] chose a value of $m(T)$ so that the second virial coefficient obtained from equation (14) was the same as that of the model n-alkane molecule in the rotational isomeric states (RIS) approximation. More details of this approach can be found in [4, 19].

In the case of model II the hard sphere torsional potential leads to conformers which are quite similar in shape. Thus it is possible for this model to approximate the second virial coefficient of the fluid by using the values for one conformer, the all-*trans* conformation. Using this approximation results in a theoretical equation of state that agrees very well with Monte Carlo simulation results.

3. Results and discussion

3.1. *Equation of state and solid–fluid equilibrium for hard sphere chains*

Figure 2 shows a comparison of the results from the theoretical approach described in the previous section with Monte Carlo simulations [4] for hard chain models of n-butane and n-octane with the hard sphere torsional potential. In the case of n-butane the solid phase considered corresponds to the low temperature experimental structure. These results are representative of the kind of agreement we obtained for all chain lengths considered ($m = 4$, 5, 6, 7 and 8). The predictions for solid–fluid equilibrium for all systems studied are compared with those from Monte Carlo simulation in table 1.

Figure 3 presents the results for the Helmholtz free energy versus density from cell theory and Monte Carlo simulations [4] for the hard chain models of n-butane and n-heptane with the hard sphere torsional potential length. For the model of n-butane we see that the agreement between cell theory and simulation remains good throughout the density range, but in the case of the model for n-heptane the agreement worsens at lower densities. This larger error for the longer chain lengths coincides with the slightly worse agreement for the solid–fluid phase equilibrium parameters seen in table 1 for the longer chains. The fact that the present cell theory calculations do not allow for solid structure relaxations away from the close packed geometry [9] could contribute to this difference.

3.2. *Generalized van der Waals theory*

As in our previous work we can use the results for the hard sphere chains in a generalized van der Waals (GVDW) or mean-field theory to model the contribution from the dispersion forces to the phase diagram [22, 23]. We write the Helmholtz free energy per molecule as

$$A = A_{\mathrm{HC}} - a\rho \qquad (15)$$

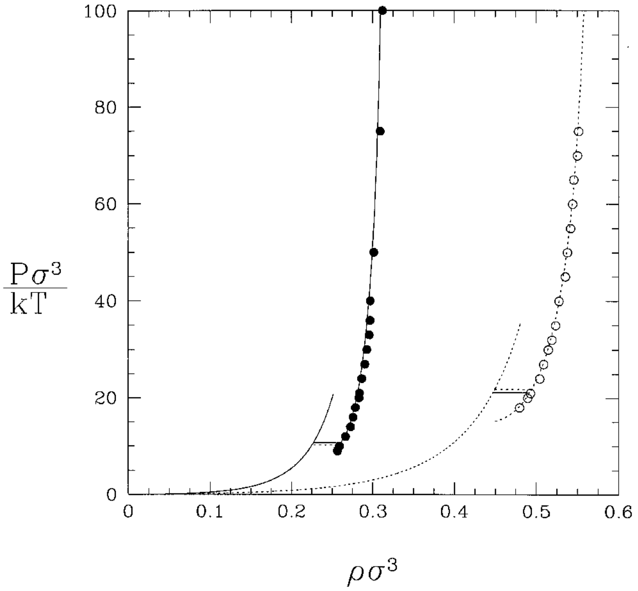

Figure 2. Pressure $P\sigma^3/kT$ versus density ρd^3 for the hard chain models of n-butane and n-octane using the model II torsional potential. The lines for the solid and fluid phases (——, n-octane; - - -, n-butane) are from cell theory and the equation of state. The points (●, n-octane; ○ n-butane) give the simulation results for the solid phase. In the fluid phase the simulation results are not plotted since they are indistinguishable from the theoretical results on the scale of the plots. Tie lines for solid–fluid equilibrium are also shown for each chain length (full line, theory; dashed line, simulation).

Table 1. Solid–fluid equilibrium data for hard chain models of n-alkanes with the model II torsional potential. Calculations using cell theory for the solid phase and an equation of state for the fluid phase are compared with Monte Carlo simulation results. In defining dimensionless pressure and density here we use d, the diameter of the sphere with the same volume as the chain under consideration in its all-*trans* conformation.

m	$\rho_f d^3$ [a]	$\rho_s d^3$ [a]	$\frac{Pd^3}{kT}$ [a]	$((\rho_s - \rho_f)/\rho_f)$ [a]	$\rho_f d^3$ [b]	$\rho_s d^3$ [b]	$\frac{Pd^3}{kT}$ [b]	$((\rho_s - \rho_f)/\rho_f)$ [b]
4[c]	1.169	1.274	47.8	0.090	1.120	1.147	36.3	0.024
4[d]	1.200	1.320	56.7	0.100	1.206	1.316	58.2	0.091
5	1.300	1.347	113.	0.036	1.278	1.380	111.	0.080
6	1.135	1.279	49.0	0.127	1.136	1.283	48.6	0.129
7	1.196	1.304	75.0	0.090	1.206	1.328	80.4	0.101
8	1.116	1.281	52.7	0.148	1.112	1.257	48.7	0.130

[a] Results from cell theory.

[b] Results from simulation.

[c] Results using the high temperature solid structure for n-butane.

[d] Results using the low temperature solid structure for n-butane.

where the subscript HC denotes properties of the hard chain reference system and a measures the strength of the attractive intermolecular forces. In [4] we used this theory with Monte Carlo simulations for the reference system to study the chain length dependence of the n-alkane phase diagrams. For the model II reference system the implementation of the theory is straightforward but for model III the reference system properties are temperature dependent because of the torsional potential. To reduce the number of simulations required for the reference system we introduced an approximate treatment of this temperature dependence, which we will describe below. We can use cell theory to assess the impact of this approximate treatment.

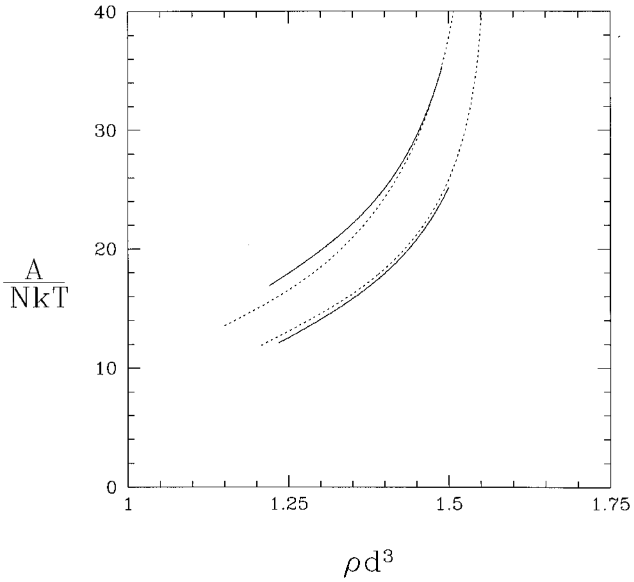

Figure 3. Solid phase free energies A/NkT versus density ρd^3 for the hard chain models of n-butane and n-heptane using the model II torsional potential (– – –, cell theory; ——, simulation). The lower set of curves is for n-butane and those that lie at higher free energy are for n-heptane.

In figure 4, predictions for the reduced triple-point temperature (T_t/T_c) versus chain length from the GVDW theory are shown for the hard sphere torsional potential when: (i) Monte Carlo simulations are used for the hard chain reference system; and (ii) cell theory and the fluid phase equation of state are used for the hard chain reference system. The results of this approach for

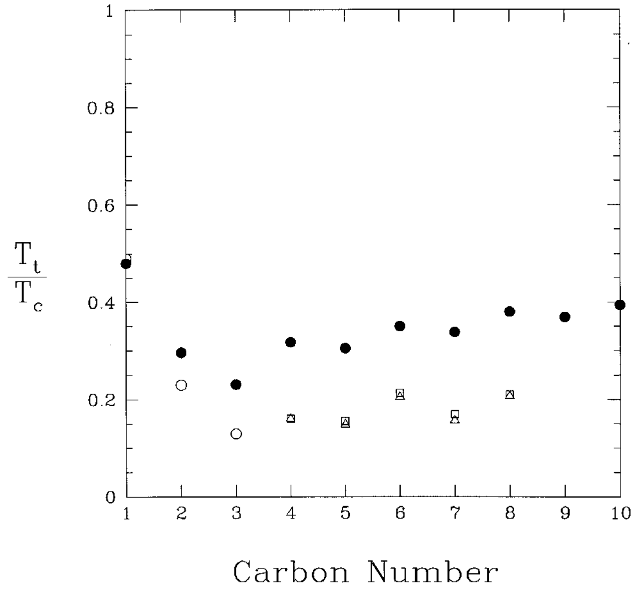

Figure 4. Reduced triple-point temperature T_t/T_c versus chain length (carbon number) for n-alkanes: •, experiment; ○, GVDW theory for rigid molecules; △, GVDW theory using Monte Carlo simulations for the hard chain reference system properties with the model II torsional potential; and □, GVDW theory using theory for the hard chain reference system properties with the model II torsional potential.

methane, ethane and propane are from Paras *et al.* [23] and Shen and Monson [24]. The experimental data [3] are shown also. Given the results presented earlier for the hard chain properties we should expect that the two versions of the GVDW theory would be in good agreement with each other, and this is what we see.

Of more interest is to use cell theory to study the contribution to the phase diagram from the temperature dependence of the molecular flexibility effects when a more realistic torsional potential is used. In this case we consider the torsional potential of Ryckaert and Bellemans [13]. In the work of Malanoski and Monson [14] the solid phase free energy for model III was calculated by assuming that the configurational properties for the hard chain system with this torsional potential and the hard chain system with a hard sphere torsional potential would be approximately equal. This approximation will be correct if the chain conformations in the solid phase are close to the all-*trans* conformation, as will be the case at high solid densities. We may expect more significant errors for lower solid densities at low temperatures, where the realistic torsional potential will make the chains more rigid than the hard sphere torsional potential, and at high temperatures, where the realistic torsional potential will make the chains less rigid. For convenience we will refer to this approximation as the 'all-*trans*' approximation.

We now examine the accuracy of this approximation within the context of cell theory. In cell theory it is possible to calculate the solid phase free energy, including the torsional energy, over a range of temperatures simultaneously. In order to fit the results over temperature and density the parameters a_1, a_2, a_3, and C in equation (12) were fitted with cubic polynomials in inverse temperature. The values of the coefficients for the various chain lengths are tabulated elsewhere [18].

We compare the pressure versus density fom cell theory with and without the all-*trans* approximation in figures 5 and 6. In each case the two sets of results do not differ very much. This is consistent with the findings in our previous work using molecular simulations [4], where we showed that the model II and model III results at the triple point temperature for n-heptane (182.5 K) gave similar results. The differences in the predictions of the two models increase slightly with chain length and, for a given chain length, as the temperature is decreased.

We now consider the free energies from cell theory with and without the all-*trans* approximation. The results are shown in figures 7 and 8, where we see behaviour that is expected. At higher densities the two sets of results agree closely since each molecule is more tightly restricted to configurations near the all-*trans* configurations. At lower densities, this is no longer true and the torsional potential begins to contribute significantly to the free energy. Under these conditions, the all-*trans* approximation, which uses the hard sphere torsional potential, underpredicts the free energy.

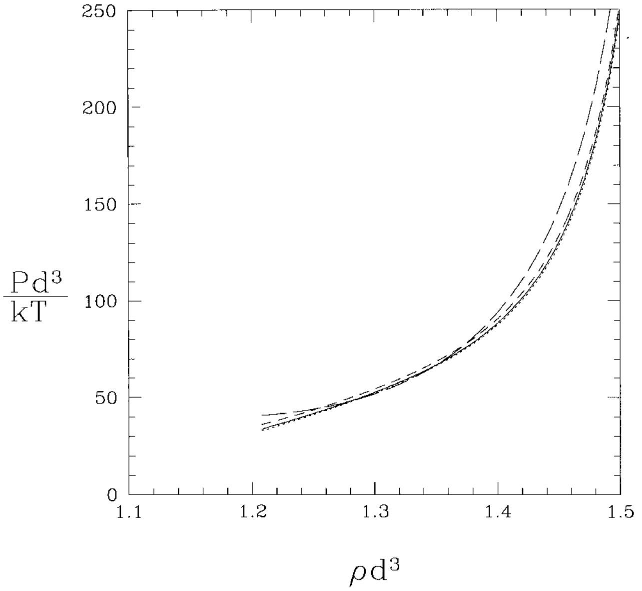

Figure 5. Pressure Pd^3/kT versus density ρd^3 for the hard chain model of n-butane in the solid phase from cell theory with the model II torstional potential (— —) and model III torsional potential at $T = 300$ K (- -), $T = 135$ K (———) and $T = 100K$(– – –).

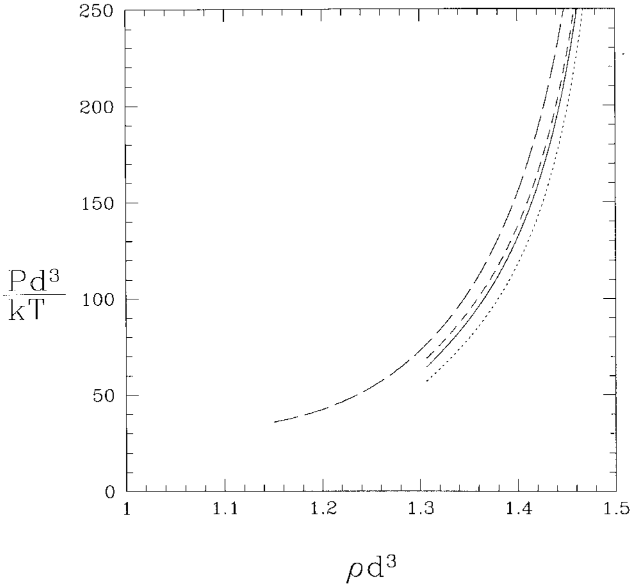

Figure 6. Pressure Pd^3/kT versus density ρd^3 for the hard chain model of n-heptane in the solid phase from cell theory with the model II torsional potential (— —) and model III torsional potential at $T = 300$ K (- -), $T = 182$ K (——) and $T = 100$ K (- - -).

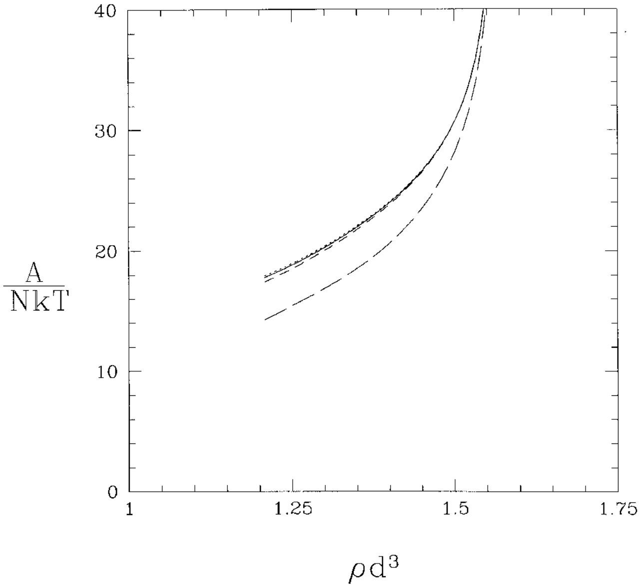

Figure 7. Free energy A/NkT versus density ρd^3 for the hard chain model of n-butane in the solid phase from cell theory with the model II torsional potential (— —) and model III torsional potential at $T = 300$ K (- -), $T = 135$ K (——) and $T = 100$ K (- - -).

When model III is used for the reference system the phase diagram in mean-field theory depends on the ratio $\alpha = \varepsilon\sigma^3/a$, where ε is the characteristic energy of the torsional potential (the Ryckaert–Bellemans can be written in the form $U(\chi) = \varepsilon f(\chi)$ where χ is the torsional angle) [4]. With ε fixed we adjust a iteratively until the calculated critical temperature matches the experimental value. In figure 9 we show the effect of the all-*trans* approximation within the context of the mean-field theory results for the reduced triple-point temperature versus chain length. The reduced triple-point temperature decreases when the all-*trans* approximation is removed. The odd–even behaviour is still present but the upward trend is less apparent and the reduction in the triple-point temperature is much larger for n-heptane and n-octane. On the basis of our analysis of the solid phase free energy given above this should be expected. The all-*trans* approximation underestimates the free energy of the hard core reference system and thus overestimates the stability of the solid phase.

4. Summary and conclusions

We have presented an implementation of cell theory for hard sphere chain models of n-alkanes in the solid phase. The approach gives quite an accurate description of the solid phase properties and, when combined with an equation of state for the fluid phase, good predictions of the solid–fluid phase equilibrium.

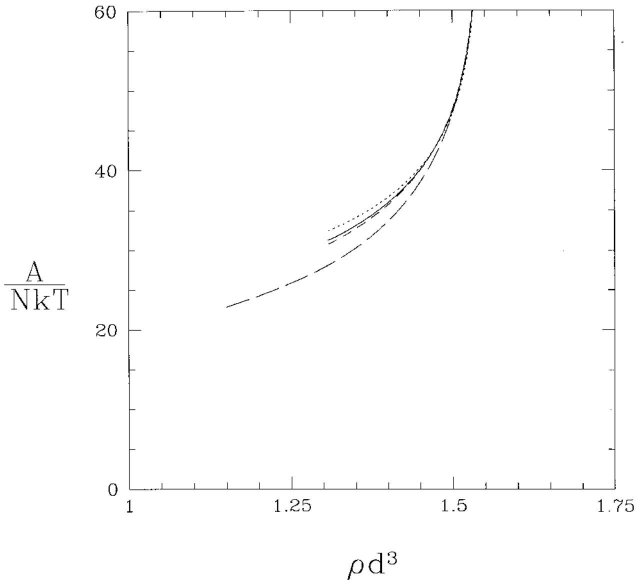

Figure 8. Free energy A/NkT versus density ρd^3 for the hard chain model of n-heptase in the solid phase from cell theory with the model II torsional potential (— —) and model III torsional potential at $T = 300$ K (- -), $T = 182$ K (——) and $T = 100$ K (- - -).

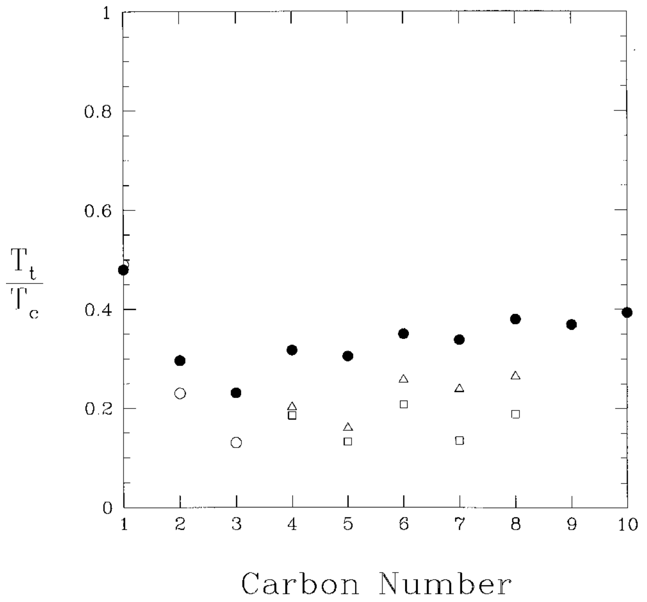

Figure 9. Reduced triple-point temperature T_t/T_c versus chain length (carbon number) for n-alkanes: •, experiment, ○, GVDW theory for rigid molecules; △, GVDW theory using theory for the hard chain reference system properties with the model III torsional potential and the all-*trans* approximation; and □, GVDW theory using theory for the hard chain reference system properties with the model III torsional potential but without the all-*trans* approximation.

We have used cell theory to test an approximate treatment (the all-*trans* approximation) of the temperature dependent effect of the torsional potential upon the solid phase free energy. The all-*trans* approximation underestimates the free energy of the solid phase at low temperatures, and hence overestimates its stability. In the context of the phase diagram for n-alkanes calculated in mean-field theory this leads to an overestimation of the reduced triple-point temperature relative to the case where the all-*trans* approximation is not used.

The phase diagram predictions (in the form of values of T_t/T_c) for the n-alkanes presented here and in [4], although qualitatively correct, are limited in accuracy by the mean-field approximation for the effect of attractive forces between the chains. It may be worthwhile to consider some improvements to the theory. One possibility which has been explored by MacDowell and Vega [25] is to improve the calculation of the perturbation term to the free energy for chain fluids by using pair correlation functions of the reference system in the low density limit. Another is to incorporate a temperature dependent hard sphere site diameter. We hope to explore some of these possibilities in future work.

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