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Study of the solid–liquid–vapour phase equilibria of flexible chain molecules using Wertheim's thermodynamic perturbation theory

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The phase diagram of flexible molecules formed by freely-jointed tangent spheres is studied using the first-order thermodynamic perturbation theory of Wertheim for both fluid and solid phases. A mean-field term is added to the free energy of the fluid and solid phase in order to account for attractive dispersion forces. The approach is used to determine the global (solid–liquid–vapour) phase diagrams and triple points of chain molecules of increasing chain length. It is found that the triple point temperature is not affected strongly by the length of the chain, whereas the gas–liquid critical temperature increases dramatically. The asymptotic limits of the phase diagram for infinitely long chains are discussed. The reduced critical temperature of infinitely long chains as given by the mean-field theory is 2/3, and the reduced triple point temperature is 0.048 56, so that an asymptotic value of $T_t/T_c = 0.072\,84$ for the ratio of the triple to critical point temperatures is obtained. This indicates that fully-flexible tangent chains present an enormous liquid range. The proposed theory, while being extremely simple, provides a useful insight into the phase behaviour of chain molecules, showing the existence of finite asymptotic limits for the triple and critical point temperatures. However, since *n*-alkanes present an asymptotic limit of about $T_t/T_c = 0.40$, the agreement with experiment is not quantitative. This suggests that fully flexible models may not be appropriate to model the solid phases of real chain molecules.

1. Introduction

Flexible molecules are important both from a theoretical and from a practical point of view. When considering fluid phases one of the most successful approaches for modelling the phase behaviour of flexible molecules is due to Wertheim [1–5]. The first-order thermodynamic perturbation theory of Wertheim (TPT1) was first developed to study the thermodynamic behaviour of associating fluids, but in the limit of infinite association, the theory also allows one to determine the thermodynamic properties of chain molecules [5–7]. According to TPT1 fully-flexible chain fluids can be described using only thermodynamic information of the reference monomer fluid. The theory is in excellent agreement with computer simulation data of hard chains [7], and it has also been shown to be adequate for modelling chains of soft and attractive monomers [8–14].

Solid phases of chain molecules are of interest since a number of flexible molecules are solids at room temperature and pressure. For instance, all linear alkanes with more than 20 carbon atoms are solids at room temperature and pressure, and the same is true for polyethylene [15]. In many industrial processes one has to deal with fluid–solid separations of alkane mixtures. However, molecular studies of the fluid–solid equilibrium of flexible molecules are rather scarce, and it is only recently that this problem has been considered (see [16–26]). An interesting model, which has played an important role in theoretical studies of the phase behaviour of chain molecules, is that of fully flexible chains of tangent hard spheres [27]. In this model the pair potential between monomers (either in the same or in different chains) is given by the hard sphere potential, and there is no bending or torsional potential between the monomers of the chain (although there is an intramolecular pair interaction between monomers of the same chain separated by more than one bond). Using computer simulations Malanoski and Monson [17] were

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the first to determine the fluid–solid equilibrium of such a model. An unobvious question is the nature of the solid phase of fully flexible chains of tangent spherical monomers. Malanoski and Monson [17] have shown that the stable solid structure of such a model is given by a face-centred cubic (fcc) close-packed arrangement of atoms (spheres) exhibiting no long range order of bonds. The extreme flexibility of the freely jointed model makes the existence of such a solid possible. Any reduction of flexibility, such as fixing the bond angles in the model, would make the existence of the closed-packed solid with random bonds impossible, since it is unlikely that the molecular bonding angle would be compatible with the angles of an fcc arrangement of atoms. The possibility of an ordered solid from the point of view of atoms but not from the point of view of bonds was first proposed by Wojciechowski and co-workers [28–30]; they were able to show that the stable solid structure of tangent hard-disc dimers in two dimensions is formed by a close-packed arrangement of atoms with a disordered arrangement of bonds [28–30]. The same idea holds for hard chains [17].

Following the determination of the fluid–solid equilibrium of fully flexible chains of hard spheres via computer simulations, an interesting question is the possibility of describing theoretically the fluid–solid equilibrium of this model. Since Wertheim's TPT1 is so successful in describing the fluid phase equilibria of chain molecules, one may wonder whether it can be extended also to study the solid phases. Recently, Vega and MacDowell [23] have shown that the approach can be extended to model solid phases of flexible hard chain molecules. Following Wertheim, the free energy of the hard chain system in the solid phase is given in terms of the free energy of a reference monomer hard sphere in the solid phase. The theoretical predictions are found to be in excellent agreement with the simulation data of Malanoski and Monson [17] for the same system. The approach also gives a good description of the solid phases of two-dimensional freely-jointed hard discs [24]. Therefore, the phase diagram of freely-jointed hard chains is well known, both from simulation and from theoretical studies. However, due to the absence of attractive forces, hard bodies do not present vapour–liquid equilibria, and are, in this respect, somewhat unrealistic. Attractive forces need to be incorporated into the model in order to study the fluid–solid equilibria of real molecules. Little is yet known about the fluid–solid equilibria of flexible models with attractive forces. Polson and Frenkel have recently studied by computer simulation the fluid–solid equilibrium of semiflexible Lennard-Jones (LJ) chains [20], and the fluid–solid equilibrium of *n*-alkane molecules [21]. We have recently extended Wertheim's TPT1 to model fully flexible LJ chains in the solid phase [25]. Our theory allows the prediction of the global phase diagram of LJ chains; we were able to predict the global phase diagram of chains of finite size ($m = 2, 4, 8$) and to estimate the triple point temperatures in each case. The theoretical predictions suggest that the solid–liquid coexistence curves tend to an asymptotic behaviour for increasing chain lengths [25]. The theory predicts an asymptotic limit of $T_t/T_c = 0.14$ for LJ chains when the number of monomer units of the chain m goes to infinity, which corresponds to an enormous liquid range. However, the results of our theoretical development [25] should be taken with caution. It should be noted that, although the theory provides a good description of the equation of state (EOS) and the internal energies of the dimer in the solid phase, the free energies were not tested. Furthermore, due to the lack of simulation data for LJ chains in the solid phase, it is not clear if the theory works equally well for longer chains in the solid phase as it does for dimers. Unfortunately, the numerical character of the theory means that it is difficult to assess clearly the existence of asymptotic limits for the freezing properties of infinitely long LJ chains.

In this work we continue to investigate the large liquid range exhibited by fully-flexible chains. The approach we shall follow is a well-established one. Longuet-Higgins and Widom [31] added a simple mean-field term to the free energies of hard spheres in the fluid and solid phases (this seminal paper has been reprinted recently in *Molecular Physics* [32]). Following this simple approach they were able to obtain a qualitative picture of the global phase diagram of a spherical fluid (argon), including an estimate of the T_t/T_c ratio. These ideas have also been used by Paras *et al.* to understand trends in the variation of the T_t/T_c ratio in diatomic [33], and linear quadrupolar molecules such as carbon dioxide [34], and Malanoski and co-workers have used the same ideas to understand the even–odd effects in the T_t/T_c ratio of *n*-alkanes [18, 19]. As suggested by Longet-Higgins and Widom the theoretical idea is relatively simple. First the fluid–solid equilibrium of a hard model is obtained with accuracy, either from computer simulation or from theoretical arguments, and a mean-field term is added both in the fluid and in the solid phase in order to obtain the global (gas–liquid–solid) phase diagram (see the review of Monson and Kofke for further details [22]). Obviously, and due to the crude nature of the mean-field approximation, only a qualitative understanding of the phase diagram can be obtained in such a way. The advantage of the procedure is that it is simple both from a conceptual and from a mathematical point of view. In this work we use the extension of Wertheim's TPT1 proposed by Vega and MacDowell [23] to describe freely jointed chains of hard spheres in the fluid and solid phases, and, in order to study the global phase equilibria, a segment–segment mean-field contribution is incorporated both in the fluid and in the solid phase. The addition of a mean-field term to an accurate EOS of hard fluids (Wertheim's TPT1) yields a simple and tractable theory. The approach has been used previously to study the fluid phase behaviour of chain fluids (such as *n*-alkanes and *n*-perfluoroalkanes [35, 36]), and strongly associated fluids (such as hydrogen fluoride [37], water + *n*-alkane [38] and water + surfactant mixtures [39, 40]). In this work we address principally two questions involving the solid phases: do fully flexible chains of tangent hard spheres present a large liquid range as suggested in our previous study and, do the triple point temperatures of infinitely long flexible chains reach an asymptotic limit?

This paper is organized as follows: in section 2 the extension of Wertheim's theory to model solid phases of hard-chain molecules with attractive segment–segment mean-field interactions is discussed. The calculated phase behaviour for varying chain lengths is presented in section 3. Conclusions are given in section 4.

2. Wertheim's first-order perturbation theory

Consider a system of fully-flexible chains of m tangent spherical segments (monomers). The system has a volume V and is at a temperature T. The spherical segments interact through a pair potential $u^{\mathrm{ref}}(r)$; in this work the spherical segments are modelled as hard spheres of diameter σ, so that $u^{\mathrm{ref}}(r)$ is given by the hard sphere potential. The chains are modelled as fully flexible, with a fixed bond length $L=\sigma$, but with no other constraints (i.e. there is no restriction in either the bonding angles or in the torsional angles), so that each monomer of a certain chain interacts with all other monomers in the system (i.e. in the same molecule or in other molecules with the only exception of the monomer(s) to which it is bonded) with the pair potential $u^{\mathrm{ref}}(r)$. In order to be able to study the fluid phase behaviour in this system, dispersive attractive interactions must also be taken into account. The simplest approach is to incorporate the Helmholtz free energy contribution due to the attractive interactions at the mean-field level of van der Waals. The Helmholtz free energy of the proposed system can be written as [7]

$$\frac{A}{Nk_{\mathrm{B}}T}=\frac{A^{\mathrm{ideal}}}{Nk_{\mathrm{B}}T}+m\frac{A^{\mathrm{ref}}_{\mathrm{residual}}}{N^{\mathrm{ref}}k_{\mathrm{B}}T}-(m-1)\ln y^{\mathrm{ref}}(\sigma)-m\eta\left(\frac{\epsilon_{\mathrm{mf}}}{k_{\mathrm{B}}T}\right), \tag{1}$$

where N is the number of chain molecules, k_{B} is Boltzmann's constant, A^{ideal} is the Helmholtz free energy of an ideal system of flexible chains, $A^{\mathrm{ref}}_{\mathrm{residual}}$ is the residual free energy of the reference monomer system formed by $N^{\mathrm{ref}}=Nm$ hard-sphere molecules and $y^{\mathrm{ref}}(\sigma)$ is the contact background correlation function [41] of the reference system (note that in the case of hard-sphere monomers $y^{\mathrm{ref}}(\sigma)=g_{\mathrm{hs}}(\sigma)$, where $g_{\mathrm{hs}}(\sigma)$ is the pair correlation function). The dispersion interactions are treated at the mean-field level of van der Waals, so that ϵ_{mf} is the integrated van der Waals mean-field energy, and $\eta=\rho^{\mathrm{ref}}\sigma^3\pi/6$ is the packing fraction, with $\rho^{\mathrm{ref}}=N^{\mathrm{ref}}/V$. The corresponding equation of state is given by

$$Z=mZ^{\mathrm{ref}}-(m-1)\left\{1+\rho^{\mathrm{ref}}\frac{\partial\ln y^{\mathrm{ref}}(\sigma)}{\partial\rho^{\mathrm{ref}}}\right\}-m\eta\left(\frac{\epsilon_{\mathrm{mf}}}{k_{\mathrm{B}}T}\right). \tag{2}$$

Vega and MacDowell [23] noted that the arguments used to arrive at equations (1) and (2) make no special mention of the actual nature of the phase considered. Following their work, we use these equations to model both fluid and solid phases of chain molecules. As can be seen from the expressions, a knowledge of the residual free energy and compressibility factor of the monomer hard-sphere system, and of its radial distribution function at contact, are required, both in the fluid and in the solid phase. Expressions for these have been presented in detail elsewhere [23]; here we give a short summary of the main expressions. The Carnahan–Starling equation of state [42],

$$Z^{\mathrm{ref}}_{\mathrm{fluid}}=\frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3}, \tag{3}$$

is used to describe the compressibility factor of the hard-sphere system in the fluid phase. The residual free energy in this phase can be easily obtained from this expression by integration; i.e.

$$\frac{A^{\mathrm{ref}}_{\mathrm{res,fluid}}}{N^{\mathrm{ref}}k_{\mathrm{B}}T}=\int_0^{\eta}\frac{(Z^{\mathrm{ref}}_{\mathrm{fluid}}-1)\,\mathrm{d}\eta}{\eta}, \tag{4}$$

and the virial route

$$Z^{\mathrm{ref}}_{\mathrm{fluid}}=1+4\eta g^{\mathrm{ref}}_{\mathrm{fluid}}(\sigma) \tag{5}$$

can be used to obtain the contact distribution function. The compressibility factor of the hard sphere reference system in the solid phase is described using the equation of Hall [43],

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

where

$$\alpha = 4\left(1 - \frac{\eta}{\eta_{\mathrm{CP}}}\right), \tag{7}$$

and $\eta_{\mathrm{CP}} = 2^{1/2}\pi/6$. Once the EOS of hard spheres in the solid phase is known, then the contact value of the radial distribution function can be obtained from the virial theorem (as in equation (5) but replacing the compressibility factor of the fluid phase by that of the solid phase). The free energy of hard spheres in the solid phase can be obtained by integrating the EOS of Hall, provided that the free energy at a certain reference density is known. Polson *et al.* [44] have performed free energy calculations for hard spheres in the solid phase, and report a residual free energy (in $Nk_{\mathrm{B}}T$ units) of 5.918 89 for $\eta = 0.5450$. We use this state and value as a reference state for the free energy of hard spheres in the solid phase. See [23] for more details.

3. Results

Using the expressions presented in the previous section and in [23], we have calculated the solid–liquid–vapour phase equilibria of flexible hard chains with mean-field attractive interactions. Throughout this section we use the integrated mean-field dispersion energy ϵ_{mf} as the unit of energy and the hard-sphere diameter of the monomers σ as the unit of length. According to this, we define the reduced temperature and pressure as $T^* = k_{\mathrm{B}}T/\epsilon_{\mathrm{mf}}$ and $p^* = p\sigma^3/\epsilon_{\mathrm{mf}}$. The phase equilibria between two phases can be calculated by equating the pressure and chemical potentials, and the coexistence densities are given in terms of the packing fraction η.

The phase diagram for chain molecules of $m = 1$ to $m = 8$ as obtained from the theoretical treatment of this work are presented in figure 1. It is noticeable that the increase in chain length results in a more dramatic variation of the vapour–liquid coexistence densities, than of those corresponding to the solid–liquid and solid–gas phase transitions. This behaviour has been observed previously in systems of fully flexible Lennard-Jones chains [25]. Since the theoretical predictions corresponding to the vapour–liquid coexistence have been discussed in detail elsewhere [7], in this work we concentrate on the study of the solid–liquid and solid–vapour phase behaviour. As can be seen, the coexistence packing fractions corresponding to the solid–liquid and solid–vapour transitions increase as the chain lengths increase. The largest increase is observed when going from the monomer to the dimer system. The calculated triple point temperatures are also predicted to increase for increasing chain lengths; an increase of 8% is observed between the monomer system and a system of chains of $m = 8$ segments (see figure 1 and table 1). It is important to point out that in our previous implementation of Wertheim's TPT1 theory for Lennard-Jones chains a decrease, instead of an increase, in the triple point temperatures was observed [25] (in going from a monomer system to a chain of $m = 8$ segments the

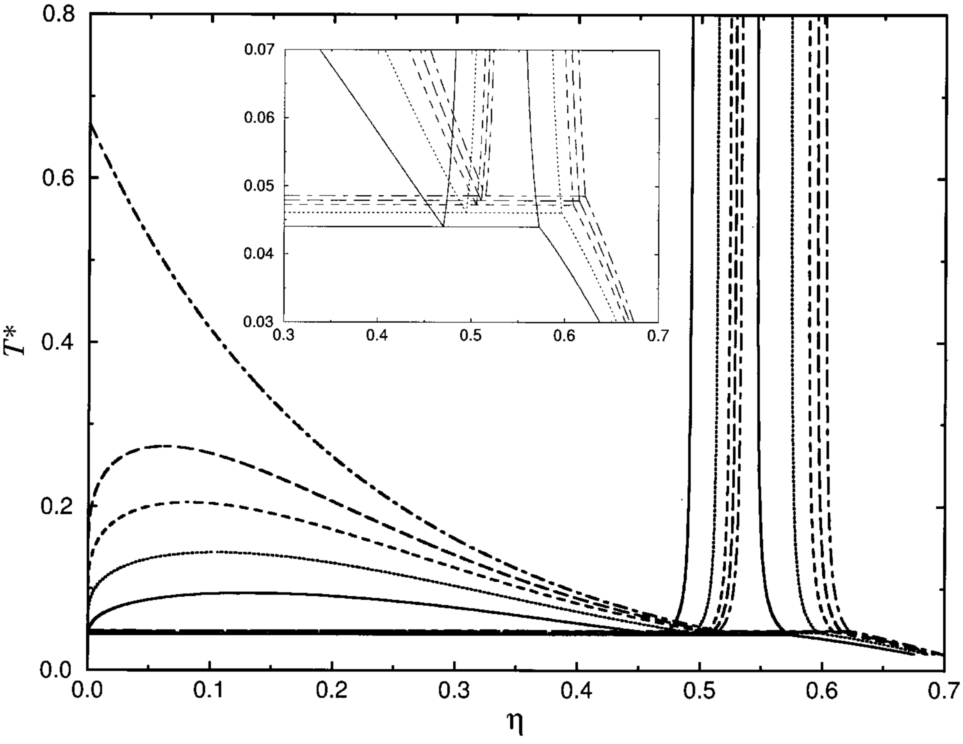

Figure 1. T^*_η projection of the global (solid–liquid–vapour) phase diagram of fully-flexible chain molecules of lengths $m = 1$, 2, 4 and 8 as obtained from the theoretical treatment of this work. The phase behaviour corresponding to chains of infinite length is also included. The solid curves correspond to $m = 1$, the dotted curves to $m = 2$, the dashed curves to $m = 4$, the long-dashed curves to $m = 8$ and the dot-dashed curves to $m \to \infty$. The inset shows the region close to the triple point.

Table 1. Critical and triple point reduced temperatures obtained using Wertheim's TPT1 for fully flexible hard chains together with an attractive segment–segment mean-field term. The coexistence densities of the liquid and solid phases at the triple point are given in terms of the packing fractions, η_l and η_s, respectively. The properties corresponding to the asymptotic $m \to \infty$ limit are also presented.

m	T^*_c	T^*_t	η_l	η_s	T^*_t/T^*_c
1	0.094 360	0.044 060	0.470 164	0.572 547	0.466 935
2	0.143 920	0.046 120	0.494 469	0.596 665	0.320 456
4	0.204 952	0.047 252	0.505 484	0.609 241	0.230 552
8	0.273 078	0.047 878	0.510 642	0.615 542	0.175 327
16	0.342 580	0.048 210	0.513 129	0.618 691	0.140 726
32	0.408 230	0.048 383	0.514 349	0.620 261	0.118 519
64	0.466 200	0.048 470	0.514 950	0.621 050	0.103 968
∞	0.666 667	0.048 560	0.515 553	0.621 831	0.072 840

decrease was about 7%). It is difficult at this stage to assess which is the correct trend. Simulation results of fully-flexible attractive chains are not available, and the phase diagram and triple point temperatures of this type of chain are unknown. One may suspect that the mean-field treatment is too simple, and that the more sophisticated Lennard-Jones treatment [25] should be qualitatively correct, but only simulation data can settle this issue.

In figure 2 the phase diagrams of chains formed by $m = 16$, 32 and 64 monomers are presented. It is seen that the fluid–solid coexistence densities rapidly reach an asymptotic limit (note that the volume fractions at melting and freezing are almost independent of m for $m > 16$). The same is true for the solid coexistence densities along the sublimation line and for the orthobaric densities at low temperatures. However, it is also clear from figure 2 that, at intermediate and high temperatures, the vapour–liquid coexistence densities strongly depend on m. In table 1 the critical and triple point temperatures, as obtained from the theory of this work, are shown together with the volume fractions of the fluid and solid phases at the triple point. A number of interesting conclusions can be noted from the data of

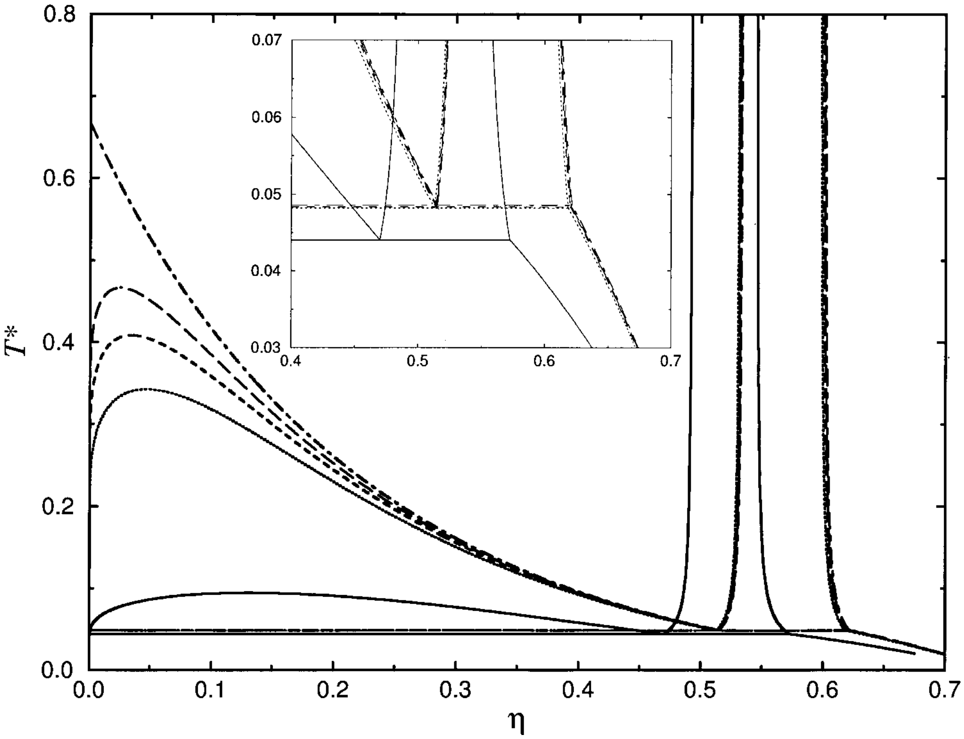

Figure 2. T^*_η projection of the global (solid–liquid–vapour) phase diagram of fully-flexible chain molecules of lengths $m = 16$, 32 and 64 with attractive interactions described at the mean-field level of van der Waals. The phase behaviour corresponding to the monomer $m = 1$ and to infinite length are also included. The solid curves correspond to $m = 1$, the dotted curves to $m = 16$, the dashed curves to $m = 32$, the long-dashed curves to $m = 64$ and the dot-dashed curves to $m \to \infty$. The inset shows the region close to the triple point.

table 1. It can be seen that the triple point temperature in the case of $m = 64$ is 10% larger than that of the monomer ($m = 1$). As mentioned, in our previous work we estimated the triple point temperature of very long LJ chains to be 7% lower than that of the monomer. Although it is not clear whether the correct trend corresponds to an increase or a decrease of the triple point temperatures, all evidence suggests that the triple point temperatures of very long chains formed by tangent spheres are not further than 10% of the triple point temperature of the monomer. In contrast with this, it can be seen in table 1 that the critical temperature of chains with $m = 64$ segments is four times higher than the critical temperature of the monomer (this means a 400% variation in the critical point temperature). In summary, concerning models of fully flexible chain molecules, small variations of the triple point temperatures are seen for varying chain lengths, while variations of chain length dramatically affect the gas–liquid critical point. We have been able to confirm these trends both in our present model and in the case of flexible chains of Lennard-Jones segments [25].

It is useful to consider at this stage the phase behaviour of chains of infinite length ($m \to \infty$). The existence of asymptotic limits in the liquid–solid coexistence densities of fully-flexible hard chains [23] and Lennard-Jones chains [25] of infinite length has already been suggested. The simplicity of our present model means that it is possible to calculate explicitly the phase behaviour at $m \to \infty$, so that the asymptotic limit can be readily known. Let us start by determining the critical temperature in the limit of infinite chain length. MacDowell *et al.* [14] and Vega and MacDowell [45] have shown that in Wertheim's TPT1 the Boyle temperature (the temperature at which the second virial coefficient is zero) of an infinitely long polymer is equal to the Θ temperature of the system (the gas–liquid critical temperature in the limit of infinite chain length). This is equivalent to the behaviour observed in the Flory–Huggins lattice theory [46], in which the critical temperature of the infinitely long chain is also that where the second virial coefficient vanishes. Following the expressions presented in section 2, the second virial coefficient of a fully flexible chain formed by hard-sphere monomers with segment–segment attractive interactions treated at the mean-field level of van der Waals is obtained as

$$B_2(T) = \lim_{\rho \to 0} \left(\frac{\partial Z}{\partial \rho} \right)_{TN} = bm^2 \left\{ \frac{3}{2} + \frac{5}{2m} - \left(\frac{\epsilon_{\mathrm{mf}}}{k_{\mathrm{B}}T} \right) \right\}, \quad (8)$$

where $b = (\pi/6)\sigma^3$ is the hard-sphere volume. The Boyle temperature of the system can be easily obtained as $B_2(T_{\mathrm{Boyle}}) = 0$, thus

$$T^*_{\mathrm{Boyle}} = \frac{k_{\mathrm{B}} T_{\mathrm{Boyle}}}{\epsilon_{\mathrm{mf}}} = \frac{2m}{3m + 5}, \quad (9)$$

so that the Θ temperature of the system is

$$\Theta^* = \frac{k_{\mathrm{B}}\Theta}{\epsilon_{\mathrm{mf}}} = \frac{2}{3}. \quad (10)$$

According to this then, when Wertheim's TPT1 theory for hard-sphere chains is combined with a segment–segment mean-field term, the reduced critical temperature of the infinite chain is just 2/3.

Let us now analyse the possibility of determining the asymptotic limits of the coexistence curves. Vega and MacDowell have shown [23] that if the compressibility factor and residual free energies are linear functions of the number of monomer units m for a given monomer density, the coexistence curves must reach an asymptotic limit for large values of m. In such a case it is possible to write the residual free energy and compressibility factors as

$$A = A_1(\eta, T) + mA_2(\eta, T) \quad (11)$$

and

$$Z = Z_1(\eta, T) + mZ_2(\eta, T), \quad (12)$$

where A_1, A_2, Z_1 and Z_2 depend only on η and T as indicated. In the limit of infinite chain length ($m \to \infty$), the phase equilibria conditions for coexistence between phases I and II ($P^{\mathrm{I}} = P^{\mathrm{II}}$ and $\mu^{\mathrm{I}} = \mu^{\mathrm{II}}$) can also be written as [23]

$$\eta^{(\mathrm{I})} Z_2^{(\mathrm{I})}(\eta^{(\mathrm{I})}, T) = \eta^{(\mathrm{II})} Z_2^{(\mathrm{II})}(\eta^{(\mathrm{II})}, T) \quad (13)$$

and

$$\frac{A_2^{(\mathrm{I})}(\eta^{(\mathrm{I})}, T)}{k_{\mathrm{B}}T} + Z_2^{(\mathrm{I})}(\eta^{(\mathrm{I})}, T) = \frac{A_2^{(\mathrm{II})}(\eta^{(\mathrm{II})}, T)}{k_{\mathrm{B}}T} + Z_2^{(\mathrm{II})}(\eta^{(\mathrm{II})}, T). \quad (14)$$

The solid–liquid phase equilibria in the limit of infinite chain length can be obtained numerically from equations (13) and (14) using an algebraic manipulations program such as Maple [47]. Note that in the derivation of equation (14) it has been assumed that the coexistence densities of both phases are different from zero (otherwise the ideal term as given by $\ln(\eta)$ will appear in equation (14)).

In the case of the sublimation and orthobaric curves, equation (14) cannot be used since the volume fraction of the vapour phase goes to zero in the infinite-chain limit, and hence, the ideal $\ln(\eta)$ term cannot be neglected. In this case a different approach is required. The vapour pressures along the sublimation line are so low that, instead of determining the coexistence curve, the densities of the solid along the sublimation line can be determined by calculating the zero-pressure densities of the solid phase. This amounts to setting to zero the compressibility factor for each temperature and solving numerically the corresponding value of the density. A similar approach is often used in computer simulations, where the solid densities along the sublimation curve are obtained by performing isobaric–isothermal *NpT* simulations at zero pressure [48]. In the limit $m \rightarrow \infty$ setting to zero the compressibility factor corresponds to setting to zero the Z_2 term of the solid EOS (see equation (12))

$$Z_2^{(\text{solid})}(\eta, T) = 0. \tag{15}$$

Equation (15) can be solved analytically, giving

$$T^* = \frac{k_\mathrm{B} T}{\epsilon_\mathrm{mf}} = \eta \left[Z^\mathrm{ref}_\mathrm{solid} - \left\{ 1 + \rho^\mathrm{ref} \frac{\partial \ln g^\mathrm{ref}_\mathrm{solid}(\sigma)}{\partial \rho^\mathrm{ref}} \right\} \right], \tag{16}$$

where T^* is the reduced temperature at which, for a given packing fraction η, sublimation would occur in a system of infinitely long chains. $Z^\mathrm{ref}_\mathrm{solid}$ is the compressibility factor of the hard-sphere solid phase given by Hall [43], and $g^\mathrm{ref}_\mathrm{solid}(\sigma)$, as before, is the contact pair correlation function obtained via the virial route from $Z^\mathrm{ref}_\mathrm{solid}$ (see section 2).

In order to determine the liquid densities along the orthobaric curve a similar approach can be used. Liquid densities (at low temperatures) are often estimated from zero-pressure *NpT* simulations. More importantly, it has been shown that, in the case of infinitely long chains, the pressure at the critical point, which follows from Wertheim's TPT1 approach, goes asymptotically to zero [14, 45, 49–51], so that the orthobaric densities of the vapour–liquid coexistence curve for very long chains are simply the zero-pressure densities. Thus,

$$Z_2^{(\text{liquid})}(\eta, T) = 0 \tag{17}$$

for the entire gas–liquid envelope. This equation can be solved analytically, and the temperature T^*, for a given packing fraction η, at which the liquid is in coexistence with the vapour in the limit of infinite chain length, is obtained as

$$T^* = \frac{k_\mathrm{B} T}{\epsilon_\mathrm{mf}} = \eta \left[Z^\mathrm{ref}_\mathrm{liquid} - \left\{ 1 + \rho^\mathrm{ref} \frac{\partial \ln g^\mathrm{ref}_\mathrm{liquid}(\sigma)}{\partial \rho^\mathrm{ref}} \right\} \right], \tag{18}$$

where $Z^\mathrm{ref}_\mathrm{liquid}$ is the compressibility factor of the hard-sphere fluid given by the Carnahan–Starling equation of state [42] and $g^\mathrm{ref}_\mathrm{liquid}(\sigma)$ is the contact pair correlation function obtained via the virial route from $Z^\mathrm{ref}_\mathrm{liquid}$ (see section 2). Using these equations the triple point temperature of the infinitely long chain system is obtained as $T^*_\mathrm{t} = 0.048\,560$ (see table 1). In the case of a chain of 64 monomers ($m = 64$), the triple point temperature is $T^*_\mathrm{t} = 0.048\,470$, which indicates that the asymptotic limit is obtained for reasonably short finite chain systems. In contrast with this (see table 1 and figure 2), the calculated critical temperature for a chain of $m = 64$ monomers is $T^*_\mathrm{c} = 0.4642$, while the Θ temperature (the critical temperature of the infinite chain) is 0.6666 (see equation (10)).

A convenient way to study the asymptotic limits of the phase behaviour of chain molecules is given by the Schultz–Flory extrapolation diagrams [52]. These are presented in figure 3. The triple point temperature of the monomer system ($m = 1$) is $T^*_\mathrm{t} = 0.044\,06$, while $T^*_\mathrm{t} = 0.048\,56$ for $m \rightarrow \infty$, indicating that the triple point temperature of an infinitely long chain is 1.1 times larger than that of its monomer system. In the case of the vapour–liquid critical point temperatures a

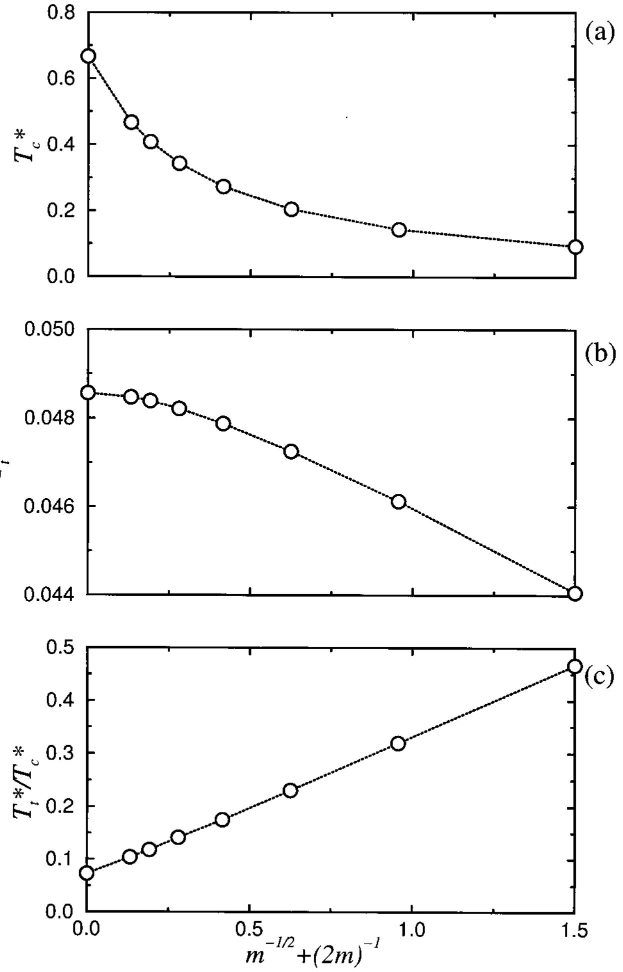

Figure 3. Shultz–Flory diagrams for (*a*) the critical temperature T^*_c, (*b*) the triple temperature T^*_t and (*c*) the $T^*_\mathrm{t}/T^*_\mathrm{c}$ ratio, as functions of the chain length. The circles represent the predictions from Wertheim's theory while the dotted curves guide the eye.

much larger variation is observed. The critical temperature of the monomer fluid is $T_c^* = 0.094\,360$, which is more than 7 times smaller than that of the infinite chain, $T_c^* = 2/3$. The increase of the critical temperature of the system can be understood in terms of the increment associated with the attractive interactions between the monomers that form the chains. More difficult to explain is the small variation of the triple temperature for increasing chain lengths. As can be seen in figure 1, for a given increase in chain length, the increase in packing fraction corresponding to the liquid phase in coexistence with the vapour phase at low temperatures is almost identical to the increase in the packing fraction at freezing (solid–liquid). In this way the triple point temperature remains practically unaffected. This explanation, while not exact, provides a simple view as to why the triple point temperature is approximately constant.

An interesting property is the ratio between the triple point and critical point temperatures. A linear dependence is observed in the Schultz–Flory representation of the T_t^*/T_c^* ratio for our flexible chain molecules (figure 3 (*c*)). The asymptotic limit of this ratio is $T_t^*/T_c^* \to 0.072\,840$. Our previous, more sophisticated, treatment involving LJ chains [25] suggested $T_t^*/T_c^* = 0.14$. Given the simple nature of the mean-field approximation used here, quantitative agreement between the two theoretical treatments cannot be expected. It has already been noted [22, 33] that mean-field treatments tend to underestimate the value of T_t^*/T_c^* of spherical and diatomic fluids. It is likely that the same occurs here. In the case of LJ chains, the critical temperature of infinitely long chains is about 3.5 higher than that of the monomer fluid [53]. The treatment of this work, however, predicts a critical temperature 7 times higher for the infinitely long chain than for the monomer. This might explain the factor of two difference between the value of T_t^*/T_c^* of this work and that of our previous work on LJ chains. In any case, a value of T_t^*/T_c^* of about 0.10 means that fully flexible tangent chains present a liquid phase over an extremely wide range of temperatures. For comparison, it is useful to note that one of the liquids with the largest liquid regime is propane, for which T_t^*/T_c^* is about 0.23 [54].

Once the global phase behaviour of chains has been determined, a comparison of the theoretical trends and experimental data can be carried out. It is found experimentally that critical temperatures and triple point temperatures tend to asymptotic finite limits for infinitely long chains. The simple theory of this work is able to capture and explain qualitatively these features. Unfortunately, the theory presented here, as well as that of our previous work, does not provide the correct asymptotic values observed in real systems. For instance the typical value of T_t/T_c for polyethylene [51, 54] is about 0.35–0.4 (there is large uncertainty in the precise value of the critical temperature of polyethylene, which affects the estimate of this ratio [51]). This is far from the value $T_t/T_c = 0.07$ of this work. In our opinion the large discrepancy between both values is probably not due to a failure of the theory, but rather to a failure of the model. It would be useful to obtain simulation results of the freezing properties of fully flexible tangent chains to determine if the predictions of the theory concerning T_t/T_c are correct. The fact that two different treatments yield similar results for the T_t/T_c ratio, seem to indicate that, in the case of fully-flexible chains of tangent spherical monomers, the ratio is always of the order of 0.10. The discrepancy with experimental data is probably due to the fact that fully flexible chain models are not adequate to describe the solid phases of real chain molecules such as *n*-alkanes or polyethylene. The extreme flexibility of the chains allows the existence of a singular solid with ordering of atoms (monomers) but disorder of bonds, which is not seen experimentally. Such a solid cannot be constructed using real polymers; overlap between contiguous monomers, whose distance is less than the sum of their van der Waals radii, and the existence of bond angles and torsional potentials make such a high-density disordered solid an impossibility. When these geometrical constraints are included in the model, the only way of obtaining a highly-packed solid is to generate an ordered solid, i.e. a solid with bond order. Obviously, the chemical and geometrical details of the molecule crucially determine the stability of the solid phase.

4. Conclusions

The global (solid–liquid–vapour) phase behaviour of fully flexible chains is obtained using Wertheim's TPT1 to model the fluid and solid phase of fully-flexible chains of tangent hard spheres with segment–segment mean-field attractive interactions. In other words, we follow the seminal approach of Longuet-Higgins and Widom [31] for hard spheres and apply it to flexible chains.

We have obtained the phase diagram of flexible chain molecules of varying chain lengths. The main effect of increasing the chain length is to increase the coexistence packing fractions corresponding to the liquid and solid phases, and to decrease the coexistence packing fraction of the vapour phase. These changes become negligible for the larger chain lengths and an asymptotic phase behaviour is observed. For increasing chain lengths the asymptotic limits are reached first in terms of the solid–liquid and solid–gas transitions than for the gas–liquid phase coexistence. The simplicity of the Helmholtz free energy in the van der Waals approximation allows the study of the asymptotic behaviour of fully flexible chains in a straightforward way. We have obtained analytically the critical temperature of the infinite chain (i.e. the Θ temperature), as well as the coexistence densities of the solid phase along the sublimation line, and those corresponding to the liquid phase along the vapour–liquid coexistence curve for chains of infinite length. The solid–liquid coexistence has been obtained numerically in this limit. The Θ temperature of the system is found to be 2/3, and the triple temperature of the infinite chain is $T_t^* = 0.048\,560$, so that the T_t/T_c ratio is equal to 0.072 840; note that this corresponds to an enormous fluid range. Although the model used is rather crude, it captures some of the features observed in the phase behaviour of real flexible molecules: the triple point temperature reaches a finite value and the solid–fluid coexistence densities become similar for long chain molecules. However, the large fluid range obtained suggests that fully-flexible chain models are not adequate to describe solid phases of real chain molecules. Nevertheless, we have been able to show that a fundamental understanding of the global phase diagram of long flexible chain molecules can be obtained by using the well-known properties of hard-sphere monomer systems in the fluid and solid phases.

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References

[1] Wertheim, M. S., 1984, *J. stat. Phys.*, **35,** 19.
[2] Wertheim, M. S., 1984, *J. stat. Phys.*, **35,** 35.
[3] Wertheim, M. S., 1986, *J. stat. Phys.*, **42,** 459.
[4] Wertheim, M. S., 1986, *J. stat. Phys.*, **42,** 477.
[5] Wertheim, M. S., 1987, *J. chem. Phys.*, **87,** 7323.
[6] Wertheim, M. S., 1986, *J. chem. Phys.*, **85,** 2929.
[7] Chapman, W. G., Jackson, G., and Gubbins, K. E., 1988, *Molec. Phys.*, **65,** 1057.
[8] Chapman, W. G., 1990, *J. chem. Phys.*, **93,** 4299.
[9] Johnson, J. K., Müller, E. A., and Gubbins, K. E., 1994, *J. phys. Chem.*, **98,** 6413.
[10] Gil-Villegas, A., Galindo, A., Whitehead, P. J., Mills, S. J., Jackson, G., and Burgess, A. N., 1997, *J. chem. Phys.*, **106,** 4168.
[11] Davies, L. A., Gil-Villegas, A., and Jackson, G., 1999, *J. chem. Phys.*, **111,** 8659.
[12] Blas, F. J., and Vega, L. F., 1997, *Molec. Phys.*, **92,** 135.
[13] Blas, F. J., and Vega, L. F., 2001, *J. chem. Phys.*, **115,** 4355.
[14] MacDowell, L. G., Müller, M., Vega, C., and Binder, K., 2000, *J. chem. Phys.*, **113,** 419.
[15] Hiemenz, P. C., 1984, *Polymer Chemistry* (New York: Marcel Dekker, Inc.).
[16] Sear, R. P., and Jackson, G., 1995, *J. chem. Phys.*, **102,** 939.
[17] Malanoski, A. P., and Monson, P. A., 1997, *J. chem. Phys.*, **107,** 6899.
[18] Malanoski, A. P., and Monson, P. A., 1999, *J. chem. Phys.*, **110,** 664.
[19] Malanoski, A. P., Vega, C., and Monson, P. A., 2000, *Molec. Phys.*, **98,** 363.
[20] Polson, J. M., and Frenkel, D., 1998, *J. chem. Phys.*, **109,** 318.
[21] Polson, J. M., and Frenkel, D., 1999, *J. chem. Phys.*, **111,** 1501.
[22] Monson, P. A., and Kofke, D. A., 2000, *Adv. Chem. Phys.*, **115,** 113.
[23] Vega, C., and MacDowell, L. G., 2001, *J. chem. Phys.*, **114,** 10411.
[24] McBride, C., and Vega, C., 2002, *J. chem. Phys.*, **117,** 1757.
[25] Vega, C., Blas, F. J., and Galindo, A., 2002, *J. chem. Phys.*, **116,** 7645.
[26] Elvassore, N., and Prausnitz, J. M., 2002, *Fluid Phase Equilib.*, **194–197,** 567.
[27] Dickman, R., and Hall, C. K., 1986, *J. chem. Phys.*, **85,** 4108.
[28] Wojciechowski, K. W., Frenkel, D., and Branka, A. C., 1991, *Phys. Rev. Lett.*, **66,** 3168.
[29] Wojciechowski, K. W., Branka, A. C., and Frenkel, D., 1993, *Physica A*, **196,** 519.
[30] Wojciechowski, K. W., 1987, *Phys. Lett.* A, **122,** 377.
[31] Longuet-Higgins, H. C., and Widom, B., 1964, *Molec. Phys.*, **8,** 549.
[32] Longuet-Higgins, H. C., and Widom, B., 2002, *Molec. Phys.*, **100,** 23.
[33] Paras, E. P. A., Vega, C., and Monson, P. A., 1993, *Molec. Phys.*, **79,** 1063.
[34] Vega, C., and Monson, P. A., 1995, *Molec. Phys.*, **85,** 413.
[35] Jackson, G., and Gubbins, K. E., 1989, *Pure appl. Chem.*, **61,** 1021.
[36] Archer, A. L., Amos, M. D., Jackson, G., and McLure, I. A., 1996, *Int. J. Thermophys.*, **17,** 201.
[37] Galindo, A., Whitehead, J. P., Jackson, G., and Burgess, A. N., 1997, *J. phys. Chem.* B, **101,** 2082.
[38] Galindo, A., Whitehead, J. P., Jackson, G., and Burgess, A. N., 1996, *J. phys. Chem.*, **100,** 6781.
[39] García-Lisbona, M. N., Galindo, A., Jackson, G., and Burgess, A. N., 1998, *Molec. Phys.*, **93,** 57.
[40] García-Lisbona, M. N., Galindo, A., Jackson, G., and Burgess, A. N., 1998, *J. Am. chem. Soc.*, **120,** 4191.
[41] McQuarrie, D. A., 1976, *Statistical Mechanics* (New York: Harper and Row).
[42] Carnahan, N. F., and Starling, K. E., 1969, *J. chem. Phys.,* **51,** 635.
[43] Hall, K. R., 1972, *J. chem. Phys.*, **57,** 2252.
[44] Polson, J. M., Trizac, E., Pronk, S., and Frenkel, D., 2000, *J. chem. Phys.*, **112,** 5339.
[45] Vega, C., and MacDowell, L. G., 2000, *Molec. Phys.*, **98,** 1295.
[46] Flory, P. J., 1954, *Principles of Polymer Chemistry* (Ithaca: Cornell University Press).

[47] Maple is a registered trademark of Waterloo Maple Software, Waterloo, Ontario, Canada.

[48] Allen, M. P., and Tisdesley, D. J., 1987, *Computer Simulation of Liquids*, 2nd Edn (Oxford: Clarendon Press).

[49] Vega, C., and MacDowell, L. G., 1996, *Molec. Phys.*, **88,** 1575.

[50] Lue, L., Friend, D. G., and Elliot Jr, J. R. E., 2000, *Molec. Phys.*, **98,** 1473.

[51] Nikitin, E. D., 1998, *High Temp.*, **36,** 305.

[52] Schultz, A. R., and Flory, P. J., 1952, *J. Am. chem. Soc.*, **74,** 4760.

[53] Sheng, Y.-J., Panagiotopoulos, A. Z., and Kumar, S. K., 1994, *Macromolecules*, **27,** 400.

[54] Morgan, D. L., and Kobayashi, R., 1991, *Fluid Phase Equilib.*, **63,** 317.