MOLECULAR PHYSICS, 20 JULY 2003, VOL. 101, NO. 14, 2241–2255

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The properties of fully flexible Lennard-Jones chains in the solid phase: Wertheim theory and simulation

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(*Received 6 January 2003; revised version accepted 11 March 2003*)

NpT ensemble Monte Carlo simulations were performed for fully flexible Lennard-Jones (LJ) chains in the solid phase. The bond length between monomers within the chains is fixed to $L = \sigma$ and the molecule is free to adopt any configuration. The solid structure of fully flexible chains is obtained by randomly locating the bonds of the chain within a face-centred cubic close-packed arrangement of atoms. For fully flexible chains it is believed that the stable solid phase is disordered. Such a solid is considered in this work. Computer simulations were performed for chains with $m = 3$, 4 and 5 monomer units, and results were obtained for the equation of state and internal energy of the chains. An extension of Wertheim's first-order thermodynamic perturbation theory (TPT1) to the solid phase of LJ chains has been proposed recently [1]. The simulation results of this work provide a check on the performance of this theory. It is found that Wertheim's TPT1 successfully predicts the equation of state and internal energies of fully flexible LJ chains in the solid phase. Linear rigid LJ chains have also been considered. Computer simulations were performed for linear rigid chains in an ordered solid structure. It is found that fully flexible and linear rigid chains present quite different equations of state and different thermodynamic properties in the solid phase.

1. Introduction

One of the simplest molecular models that one can conceive for flexible chains is that formed by tangent Lennard-Jones (LJ) monomers. The pair potential between two monomers (belonging either to the same molecule or to different molecules) is given by the Lennard-Jones potential with potential parameters ε and σ. The reduced bond length L between bonded monomers is fixed to the value $L^* = L/\sigma = 1$ so that, in some respects, one may say that the chain is formed by 'tangent' monomers. There is neither a bending potential constraining the angle between three contiguous monomers of the chain, nor a torsional potential between four contiguous monomers. We shall denote this model as the fully flexible tangent LJ chain model, or, more succinctly, as the LJ chain model. The LJ chain model provides an ideal starting point for the computational and theoretical study of simple polymer chains. One of the attractive features of the LJ chain model in such a study is the large and ever-growing body of theoretical and simulation work published over the past decade or so.

A great inroad to the theoretical treatment of molecular fluids was provided by Wertheim. In the 1980s Wertheim developed a theory for associating fluids [2–5]. When the association strength becomes infinitely strong, then chains are formed from a fluid of associating monomers [6, 7]. In this way it was possible to derive an equation of state for a chain of freely jointed tangent monomers by using thermodynamic information of the monomer reference fluid only. In the simplest implementation of the theory, known as first-order thermodynamic perturbation theory (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. Although Wertheim's formalism was originally conceived for hard chains, it was soon realized that it could also be applied to LJ chains [8–13]. It has been shown that Wertheim's TPT1 provides a good description of the thermodynamic properties of the LJ chains in the fluid phase (including the description of vapour–liquid equilibria).

Although a lot of work has been devoted to the study of LJ chains in the fluid phase [14, 15], studies of LJ chains in the solid phase are rather scarce [16]. The solid phase of diatomic LJ models has been considered by

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Molecular Physics ISSN 0026–8976 print/ISSN 1362–3028 online
http://www.tandf.co.uk/journals
DOI: 10.1080/0026897031000112424

Lisal and Vacek [17] (for $L^* = L/\sigma = 0.67$) and by Vega, Blas and Galindo [1] (for $L^* = 1$). Semi-flexible LJ chains (with $m = 6$ and a bending potential favouring the linear configuration) have been considered by Polson and Frenkel [18]. A natural question that arises is the possibility of extending Wertheim's TPT1 to the solid phase. Recently we have shown that such an extension is indeed possible. Vega and MacDowell [19] have shown that Wertheim's TPT1 can be extended to the solid phase of freely jointed hard spheres, obtaining excellent agreement with the simulation results of Malanoski and Monson [20]. Similar results were obtained in two dimensions [21]. Encouraged by these results, Vega *et al.* extended Wertheim's TPT1 to LJ chains in the solid phase [1]. It has been shown that Wertheim's TPT1 provides a good description of the equation of state and internal energy of the LJ dimer in the solid phase.

Theoretical predictions for longer LJ chains in the solid phase (formed by $m = 3$, 4, 5, 6 monomers) have been published [1] but, owing to the lack of simulation results for LJ chains in the solid phase, direct comparison with numerical results was not possible. The goal of this paper is to perform computer simulations of LJ chains in the solid phase and to compare the theoretical predictions of Wertheim's TPT1 to the numerical results.

Let us briefly discuss the solid structure of LJ chains. Lennard-Jones monomers freeze [22, 23] into a close-packed structure (face-centred cubic, fcc). In principle one may suspect that the solid structure of LJ chains should be related to the close-packed structure of the LJ monomer. One possibility for the solid structure of LJ chains is to form layers of molecules with the chains adopting a linear configuration, with all the molecules within the same layer pointing in the same direction. Examples of such structures were presented in earlier work for hard diatomic fluids (hard dumbbells) by Vega *et al.* [24] and for LJ chains (with bending potential favouring linear configurations) by Polson and Frenkel [18]. In the particular case of the so-called CP1 structure (see [24] for details) the molecular axis of all the molecules of the solid points in the same direction. There is no doubt that this should indeed be the stable solid structure when a 'bending' potential between contiguous monomers of the chain exists, as is the case in the study by Polson and Frenkel, or for a linear rigid chain.

However, it is likely that ordered structures (those formed by layers of oriented molecules) are not the stable solid phase for fully flexible LJ chains (i.e. chains with no bending potential). It is possible to build a solid structure where the atoms follow an fcc close packing but where the bonds between monomers are located randomly within the solid, with no long-range orientational order between the bond vectors of the chains. Wojciechowski *et al.* [25, 26] were the first to realize this important feature. We shall denote this structure as the disordered solid. In fact Wojciechowski *et al.* [25, 26] showed 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. The same idea holds for hard chains in three dimensions [20] and one may expect that the same would occur for a three-dimensional LJ fully flexible chain.

In a sense this is one of nature's clever solutions. The molecules may achieve the close packing structure of the monomers, leading to an optimally high density. At the same time the bond structure of the system is disordered. The great beauty of such a system is the stabilizing effect of an additional contribution to the entropy of the system arising from the degeneracy of the solid structure (i.e. there are a number of ways of forming the disordered solid whereas there is only one way of forming the ordered solid). For $m = 2$ this degeneracy has been estimated by Nagle [27], and for longer chains Malanoski and Monson [20] have shown that it can be estimated quite accurately from the Flory–Huggins lattice theory of chains [28, 29].

The scheme of this paper is as follows. In § 2 the extension of Wertheim's theory to the solid phase of LJ chains will be described. In § 3 we shall provide details of the simulations performed in this work. In § 4 the results of this work will be presented, and in § 5 the conclusions will be presented.

2. Brief description of Wertheim's perturbation theory

Since details of the extension of Wertheim's TPT1 to the solid phase for LJ chains has been published previously [1, 19], the following forms only an outline description of the technique.

Let us assume that there are a certain number, N^{ref}, of spherical monomer particles within a certain volume V at temperature T. These spherical particles interact with each other via a spherical pair potential $u^{\text{ref}}(r)$. In this work the pair potential $u^{\text{ref}}(r)$ will be the Lennard-Jones potential with parameters σ and ε. We shall denote this fluid as the reference fluid and the properties of this reference fluid will be labelled by the superscript 'ref'. Let us also assume that in another container of volume V and temperature T, we have $N = N^{\text{ref}}/m$ 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 angles 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 only exception being the monomer(s) to which it is bonded) with the pair potential $u^{\text{ref}}(r)$. The chain system described so far will be denoted as the chain fluid. It follows from Wertheim's TPT1 that the free energy of the chain model is given by

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

The above equation shows that the free energy of the chain may be obtained from knowledge of the residual free energy of the reference fluid and the pair background correlation function $y(\sigma)$ of the reference fluid at the bonding distance of the chain [30, 31]. Notice that in equation (1) we have set the thermal de Broglie wavelength to σ and $\rho = N/V$ is the number density of chains. It is worth recalling that Wertheim's TPT1 is normally used to describe chains formed by 'tangent' spheres (i.e. those with reduced bond length between monomers $L^* = 1$). Since for the LJ potential model the pair potential is zero for $r = \sigma$, it turns out that for this particular choice of bond length, $y(\sigma)$ is equal to $g(\sigma)$, so that one is able to replace $y(\sigma)$ by $g(\sigma)$ in equation (1).

The equation of state that follows from equation (1) is given by

$$Z = mZ^{\text{ref}} - (m-1)\left(1 + \rho^{\text{ref}}\frac{\partial \ln g^{\text{ref}}(\sigma)}{\partial \rho^{\text{ref}}}\right), \quad (2)$$

where we have defined Z^{ref} as $Z^{\text{ref}} = p^{\text{ref}}/(\rho^{\text{ref}}kT)$. The residual part of the internal energy U is given by

$$\frac{U}{NkT} = m\frac{U^{\text{ref}}}{N^{\text{ref}}kT} + (m-1)T\frac{\partial \ln g^{\text{ref}}(\sigma)}{\partial T}. \quad (3)$$

We shall denote equations (1)–(3) as Wertheim's TPT1 theory. We note that the arguments used to arrive at equations (1) and (2) make no special mention of the actual nature of the phase considered [19, 32, 33]. Therefore the equations can be applied to both the fluid and the solid phases. The possibility of extending Wertheim's TPT1 to the solid phase has been explored only in the past three years [1, 19, 21]. All that is required in order 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 for both the fluid and solid phases. For the fluid phase, Johnson *et al.* [9, 10] have provided values of the free energy and structural properties (i.e. $g^{\text{ref}}(\sigma)$) of the monomer LJ fluid. Therefore, for the fluid phase we shall use the implementation of TPT1 provided by Johnson *et al.* [9, 10]. For the solid phase, van der Hoef [34] has recently proposed an analytical expression for the free energy of the LJ monomer solid. This analytical expression is essentially a fit to the most recent simulation results for the solid phase of this model. Therefore we shall simply adopt the expression provided by van der Hoef for the free energy of the LJ monomer solid. The other piece of information required by the theory is the value of $g^{\text{ref}}(\sigma)$ for the LJ monomer solid. In [1] we have performed computer simulations of the LJ monomer in the solid phase to obtain $g^{\text{ref}}(\sigma)$ for a number of temperatures and densities. The simulation results for $g^{\text{ref}}(\sigma)$ were fitted to an empirical expression similar to that proposed by Johnson *et al.* [10] for the fluid phase. In this work we shall use the expression given by us in [1] for $g^{\text{ref}}(\sigma)$ of the solid phase, which is essentially a fit to the structural results from simulations of the LJ monomer solid.

3. Simulation details

The model considered in this work consists of a chain formed by m identical LJ sites. The bond distance between contiguous monomer units is given by $L = \sigma$. The interaction between a pair of molecules is given by

$$u(1,2) = \sum_{i=1}^{i=m}\sum_{j=1}^{j=m} 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right], \quad (4)$$

where r_{ij} is the distance between site i of molecule 1 and site j of molecule 2. We also used the LJ potential to describe the interaction between monomers of the same chain separated by at least two molecular bonds (i.e. a LJ potential was not included between contiguous bonded monomers of the same chain).

In order to describe a disordered structure, we generated a close-packed arrangement (fcc) of atoms with the molecular bonds randomly distributed. A trial-and-error algorithm was used to generate the initial disordered structures. The algorithm starts at one corner of an fcc lattice with sufficient number of lattice points to contain an integer number of molecules. Bonds are made to unoccupied randomly chosen adjacent lattice points until a molecule is placed. The algorithm then 'looks' for the next vacant space in order to place the first atom of the second molecule. Once placed, bonds are once again made by randomly selecting one of the unoccupied adjacent lattice points. If none of the adjacent lattice points are unoccupied, then the algorithm restarts from the beginning. This algorithm only works well for short chains with a modest number of lattice points. Once a randomly ordered configuration has been generated, then the structure can be copied, rotated and translated. In this work the initial structures were as follows: for $m = 3$, 64 molecules were randomly packed; for $m = 4$, 27 molecules were randomly packed; and for $m = 5$, 18 molecules were randomly placed. These initial structures were then replicated 12 times for $m = 3$, thus resulting in a system with $N_{\text{m}} = 2304$; eight times for $m = 4$, thus resulting in a system with $N_{\mathrm{m}} = 864$; and eight times for $m = 5$, thus resulting in a system with $N_{\mathrm{m}} = 720$. We have defined N_{m} as the total number of monomer units of the system.

For a number of systems a second disordered configuration was generated in order to check for differences in the thermodynamic properties. Upon analysis, such differences were found to be minimal. Simulations were initiated at very high pressures where the density is close to the close-packing limit. (Note that there is no true close-packing density for a soft potential such as the LJ. However, the reduced monomer number density of hard spheres at close-packing, $\sqrt{2}$, proved to be a good starting point.) After generating the initial structure at the close packing density (i.e. the reduced number density of LJ monomers was $\sqrt{2}$), this structure was expanded to lower densities by performing NpT Monte Carlo simulations [35] at successively lower pressures. Since the distribution of bonds in the solid phase was isotropic, changes in the volume of the simulation box were made isotropically.

For all of the simulations performed in this work, the site–site LJ pair potential was truncated at $r_{\mathrm{c}} = 2.5\sigma$ and long-range interactions were added to all the computed thermodynamic properties (internal energy, pressure) by assuming that the site–site pair correlation function is unity beyond the cutoff [35]. A cycle will be defined as a trial move per particle, plus a trial volume change. Three different kinds of trial moves were used: translation of the whole molecule, rotation of the whole molecule, and configurational bias move. The aforementioned trial moves were performed with the following probabilities: 40%, 40% and 20%, respectively. In the configurational bias move a segment of the chain was chosen randomly and the chains were regrown in a random direction. Typically eight trial orientations were used for regrowing each segment of the chain. Since configurational bias is now a standard technique, we refer the reader to [36] for further details. Throughout this work reduced units will be used, so that $T^* = T/(\varepsilon/k)$, $\rho^* = \rho\sigma^3 = (N/V)\sigma^3$ and $p^* = p/(\varepsilon/\sigma^3)$. A typical run of the solid phase involved 70 000 cycles of equilibration followed by 70 000 cycles for obtaining equilibrium properties.

In summary, an isotropic NpT ensemble was applied to an fcc arrangement of atoms with randomly assigned bond vectors, using translation, rotation and configurational bias moves.

4. Results

As an initial check of the simulation code and the structure generation algorithm, a system of fully flexible hard sphere chains with $m = 4$ monomers was simulated. The results of this simulation were compared to the work of Malanoski and Monson [20]. The results of this benchmark are presented in figure 1. As can be seen,

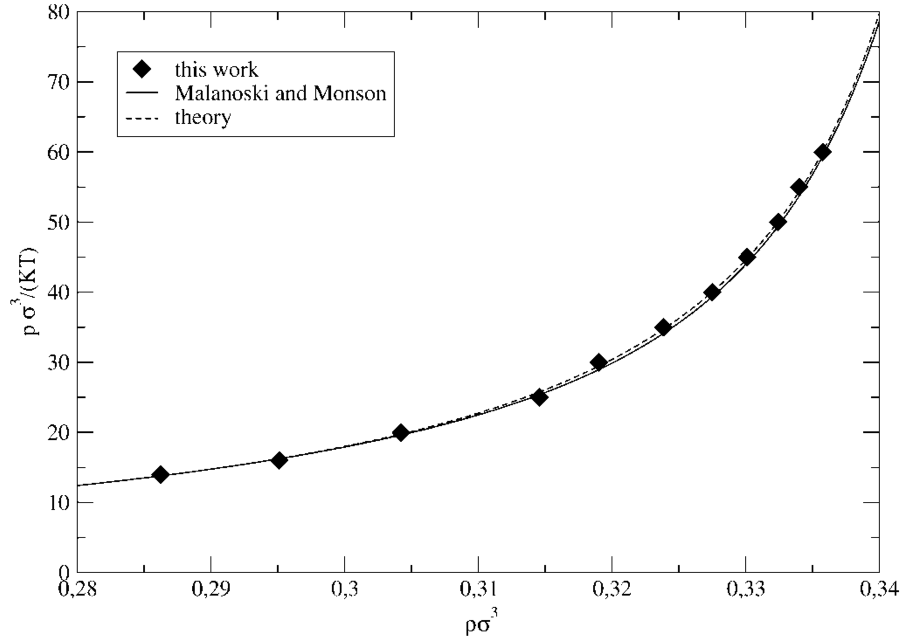

Figure 1. The EOS of fully flexible hard sphere chains with $m = 4$ in the solid phase as a function of the reduced number density of chains $\rho^* = \rho\sigma^3 = (N/V)\sigma^3$. Computer simulations of this work (diamonds), computer simulations of Malanoski and Monson (full line) and Wertheim's TPT1 (dashed line) as proposed and implemented in [19]. The solid structure is that of an fcc arrangement of atoms with a random assignment of bonds.

Table 1. Simulation results for fully flexible LJ chains with $m=3$ in the disordered solid phase. The solid structure is that of an fcc arrangement of atoms with a random assignment of bonds. Results were obtained from expansion runs (starting at high pressures and decreasing its value from one run to the next). The dotted lines separate the results for the solid phase from those for the fluid phase. The solid line separates the results for temperature $T^* = 1$ from those for $T^* = 2$. Reduced units were defined as follows $T^* = T/(\varepsilon/k)$, $\rho^* = \rho\sigma^3 = (N/V)\sigma^3$ and $p^* = p/(\varepsilon/\sigma^3)$

T^*	p^*	ρ^*	$U/(N\varepsilon)$
1	60.0	0.4667	−11.584
1	50.0	0.4571	−13.638
1	40.0	0.4455	−15.686
1	30.0	0.4312	−17.642
1	20.0	0.4127	−19.379
1	10.0	0.3867	−20.571
1	8.0	0.3795	−20.640
1	6.0	0.3710	−20.636
1	4.0	0.3597	−20.427
1	2.0	0.3425	−19.821
1	1.0	0.2979	−16.881
1	0.6	0.2921	−16.579
1	0.2	0.2855	−16.223
2	60.0	0.4584	−10.151
2	50.0	0.4474	−12.191
2	40.0	0.4343	−14.163
2	30.0	0.4176	−15.935
2	20.0	0.3951	−17.287
2	10.0	0.3252	−15.238
2	6.0	0.3004	−14.782
2	0.2	0.1880	−9.511

Table 2. Simulation results for fully flexible LJ chains with $m=4$. The rest of the notation is as in table 1.

T^*	p^*	ρ^*	$U/(N\varepsilon)$
1	60.0	0.3501	−15.532
1	50.0	0.3432	−18.184
1	40.0	0.3350	−20.821
1	30.0	0.3240	−23.439
1	20.0	0.3105	−25.818
1	10.0	0.2915	−27.348
1	8.0	0.2863	−27.432
1	6.0	0.2797	−27.402
1	4.0	0.2722	−27.222
1	2.0	0.2609	−26.591
1	1.0	0.2497	−25.582
1	0.8	0.2459	−25.151
1	0.7	0.2259	−22.626
1	0.4	0.2201	−21.965
1	0.2	0.2178	−21.774
2	60.0	0.3443	−13.767
2	50.0	0.3364	−16.376
2	40.0	0.3268	−18.936
2	30.0	0.3145	−21.287
2	20.0	0.2974	−22.979
2	10.0	0.2616	−22.462
2	8.0	0.2376	−20.127
2	4.0	0.2150	−19.009
2	1.0	0.1798	−16.129
2	0.2	0.1531	−13.627

the simulation results of this work agree rather nicely with those of Malanoski and Monson. Along with the simulation results, the predictions from Wertheim's TPT1 for hard sphere chains [19] in the solid phase are also presented. The agreement is again quite good. We shall not comment further on this point, since extensive comparison between simulation and theory for hard sphere chains exists in the published literature [19].

In tables 1, 2 and 3, simulation results for LJ chains with $m = 3$, 4 and 5 monomer units, respectively, are presented. Results correspond to two isotherms, namely $T^* = 1$ and $T^* = 2$.

In figure 2, a comparison is made between simulation and theoretical predictions from Wertheim's TPT1 for LJ chains with $m = 3$. In figure 2(*a*) results are presented for the equation of state (EOS) and in figure 2(*b*) for the internal energy. As can be seen, the theory describes quite accurately the simulation results both for the EOS and for the internal energies. When expanding the solid it was found that the solid melts at a certain pressure. We observed this spontaneous melting for the two considered temperatures ($T^* = 1$ and $T^* = 2$). The lines of figure 2 correspond to Wertheim's TPT1 theory. Figure 2 illustrates that Wertheim's TPT1 works quite well not only for the fluid phase, but also for the solid phase.

In figure 3, a comparison is made between simulation and theoretical results for LJ chains with $m = 4$. In figure 3(*a*) results are presented for the equation of state (EOS) and in figure 3(*b*) for the internal energy. Again the theory performs very well for both properties. For the two considered temperatures the solid phase melted into an isotropic fluid when decreasing the pressure. Finally in figure 4, a comparison is made between simulation and theoretical results for LJ chains in the solid phase with $m = 5$. In figure 4(*a*) results are presented for the equation of state (EOS) and in figure 4(*b*) for the internal energy. The theory once again is successful in describing the simulation results. For the two considered temperatures the solid phase melted into an isotropic fluid when decreasing the pressure.

Table 3. Simulation results for fully flexible LJ chains with $m = 5$. The rest of the notation is as in table 1.

T^*	p^*	ρ^*	$U/(N\varepsilon)$
1	60.0	0.2806	−19.571
1	50.0	0.2751	−22.840
1	40.0	0.2688	−26.007
1	30.0	0.2605	−29.074
1	20.0	0.2495	−32.020
1	10.0	0.2342	−34.033
1	8.0	0.2297	−34.258
1	6.0	0.2247	−34.262
1	4.0	0.2189	−34.112
1	2.0	0.2098	−33.269
1	1.0	0.2020	−32.151
1	0.8	0.1987	−31.680
1	0.4	0.1776	−27.543
1	0.2	0.1762	−27.354
2	60.0	0.2760	−17.281
2	50.0	0.2694	−20.552
2	40.0	0.2620	−23.539
2	30.0	0.2520	−26.545
2	20.0	0.2393	−28.949
2	10.0	0.2160	−29.202
2	8.0	0.1913	−25.250
2	2.0	0.1586	−22.056
2	0.2	0.1280	−17.691

For each of the chains considered in this work, the agreement between theory and simulation for $T^* = 1$ is as good as that for $T^* = 2$, thus indicating that the theory does not deteriorate with respect to variations in the temperature (at least for the range of temperatures considered here).

Good agreement between theory and simulation has previously been seen for the LJ dimer ($m = 2$) in the solid phase [1]. However, it is certainly gratifying to observe that the theory continues to perform well with increasing chain length. The message of figures 2–4 is that Wertheim's TPT1 theory can be used with confidence to predict the thermodynamic properties, for both the EOS and the internal energies of LJ chains in the solid phase.

It would be interesting to see if Wertheim's theory is also able to accurately predict the free energies of LJ chains in the solid phase. The determination of free energies of solid from computer simulation requires special techniques (Einstein crystal calculations [36–38]). At this point it is possible to mention that for $m = 2$ the comparison between free energies of the solid phase as obtained from Wertheim's TPT1 and from Einstein crystal calculations is quite good [39]. Free energy calculations of LJ chains would certainly present an interesting problem for future work.

One of the consequences of Wertheim's theory is the existence of asymptotic limits [1, 19] of the thermodynamic properties when plotted as a function of the number of monomer units per unit of volume (instead of plotting them as a function of the number of molecules per unit of volume). Let us define the monomer number density ρ_{m} as $\rho_{\mathrm{m}} = \rho m$. In Wertheim's formalism, the compressibility factor Z and residual internal energy $U/(NkT)$ can be written as [19]

$$X(\rho_{\mathrm{m}}, T, m) = X_1(\rho_{\mathrm{m}}, T) + mX_2(\rho_{\mathrm{m}}, T), \qquad (5)$$

where X stands for any of the thermodynamic properties (Z or $U/(NkT)$). For sufficiently large values of m, equation (5) can be written as

$$p^* = p/(\varepsilon/\sigma^3) = T^*\rho^* m Z_2(\rho_{\mathrm{m}}, T) = T^*\rho^*_{\mathrm{m}} Z_2(\rho_{\mathrm{m}}, T) \qquad (6)$$

and

$$U/(kT) = NmU_2(\rho_{\mathrm{m}}, T) = N_{\mathrm{m}} U_2(\rho_{\mathrm{m}}, T) \qquad (7)$$

$$U/(N_{\mathrm{m}}kT) = U_2(\rho_{\mathrm{m}}, T). \qquad (8)$$

According to equation (6) for very long chains (m sufficiently large), the reduced pressure is a function of the reduced temperature and of the reduced monomer number density only. In view of this a plot of p^* versus ρ_{m} for a certain temperature should yield a universal curve (regardless of the length of the chain m). Also according to equation (8) for very long chains (m sufficiently large), the residual internal energy per monomer unit depends only on the temperature and on the reduced monomer density. Therefore a plot of $U/(N_{\mathrm{m}}kT)$ versus ρ_{m} for a certain temperature should also yield a universal curve. Obviously the chains considered in this work are rather short ($m = 3, 4, 5$) and do not constitute large values of m. However, it is worth checking whether this prediction of Wertheim's TPT1 holds for the simulation results of this work. In figure 5(*a*) the reduced pressure is plotted as a function of the reduced monomer number density. In figure 5(*b*) the residual internal energy is plotted as a function of the reduced monomer number density. It can be seen that, although the results depend on the length of the chain, the presence of an asymptotic limit is clearly visible. The results of figure 5 support the prediction of TPT1 on the existence of an asymptotic limit and illustrate that even a chain of $m = 5$ monomer units is not too far from such a limit.

This work has been devoted to fully flexible linear LJ chains and all the results presented so far correspond to that model. We shall now present a different model that will be denoted as the 'linear rigid' chain. In the linear

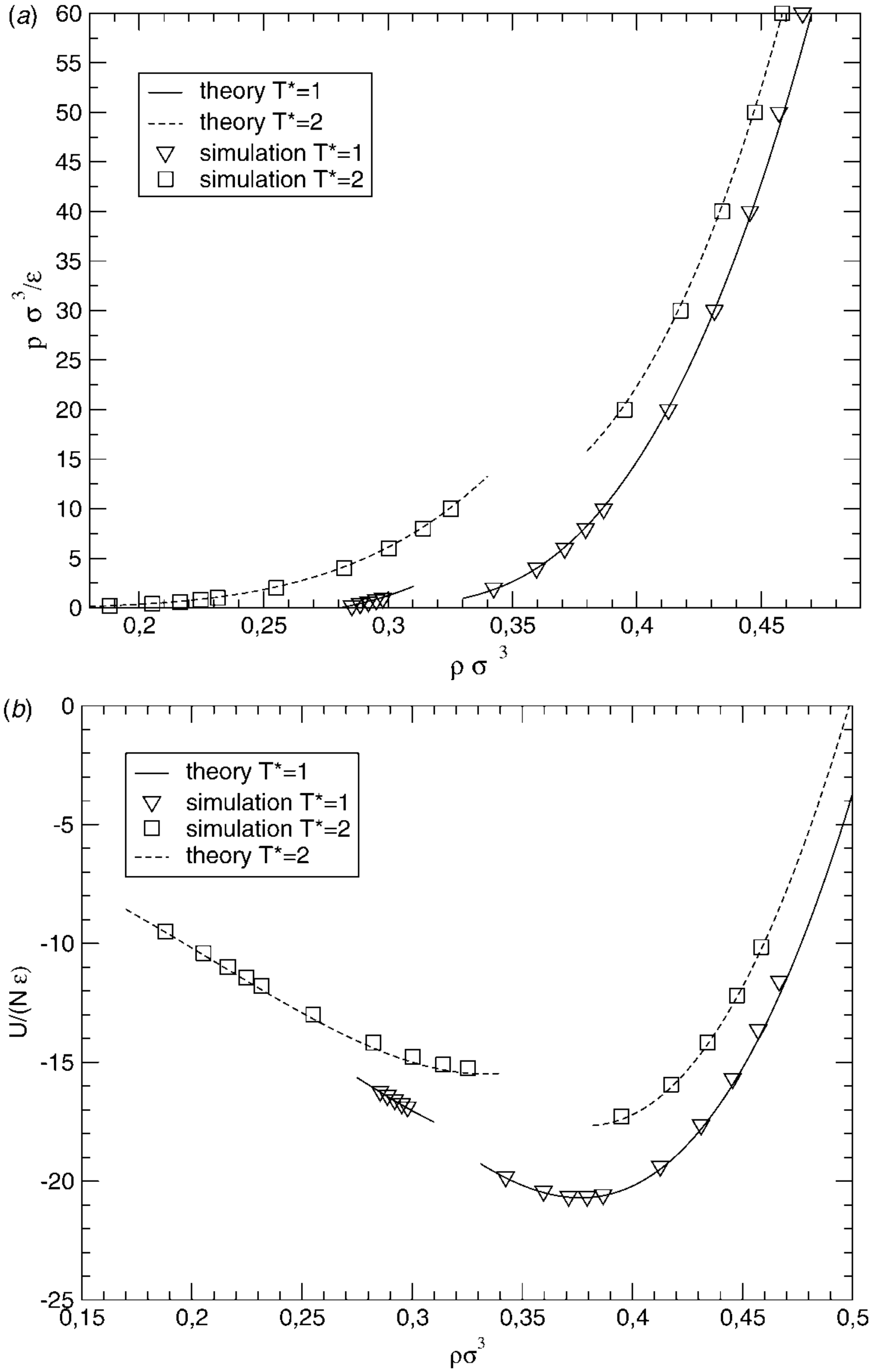

Figure 2. Properties of fully flexible LJ chains with $m = 3$ as obtained from computer simulations of this work (symbols) and from Wertheim's TPT1 for the fluid [10] and for the solid [1] phases (lines). Results were obtained for two reduced temperatures, $T^* = 1$ and $T^* = 2$. The solid structure is that of an fcc arrangement of atoms with a random assignment of bonds. (*a*) Results for the reduced pressure, $p^* = p/(\varepsilon/\sigma^3)$ as a function of the reduced number density of chains. (*b*) Results for the residual internal energy $U/(N\varepsilon)$ as a function of the reduced number density of chains.

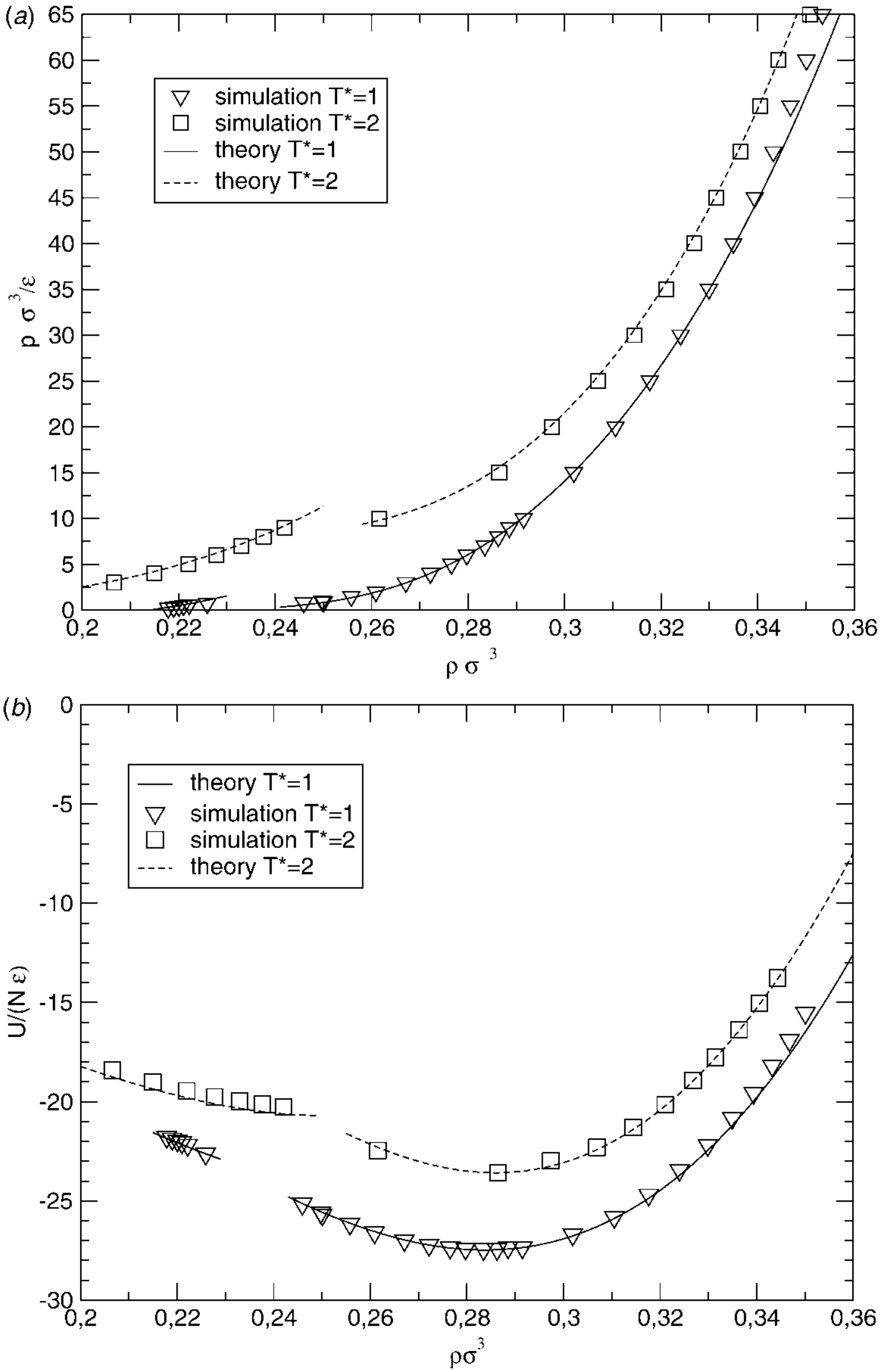

Figure 3. As in figure 2 for LJ chains with $m = 4$. (*a*) Results for the reduced pressure. (*b*) Results for the residual internal energy.

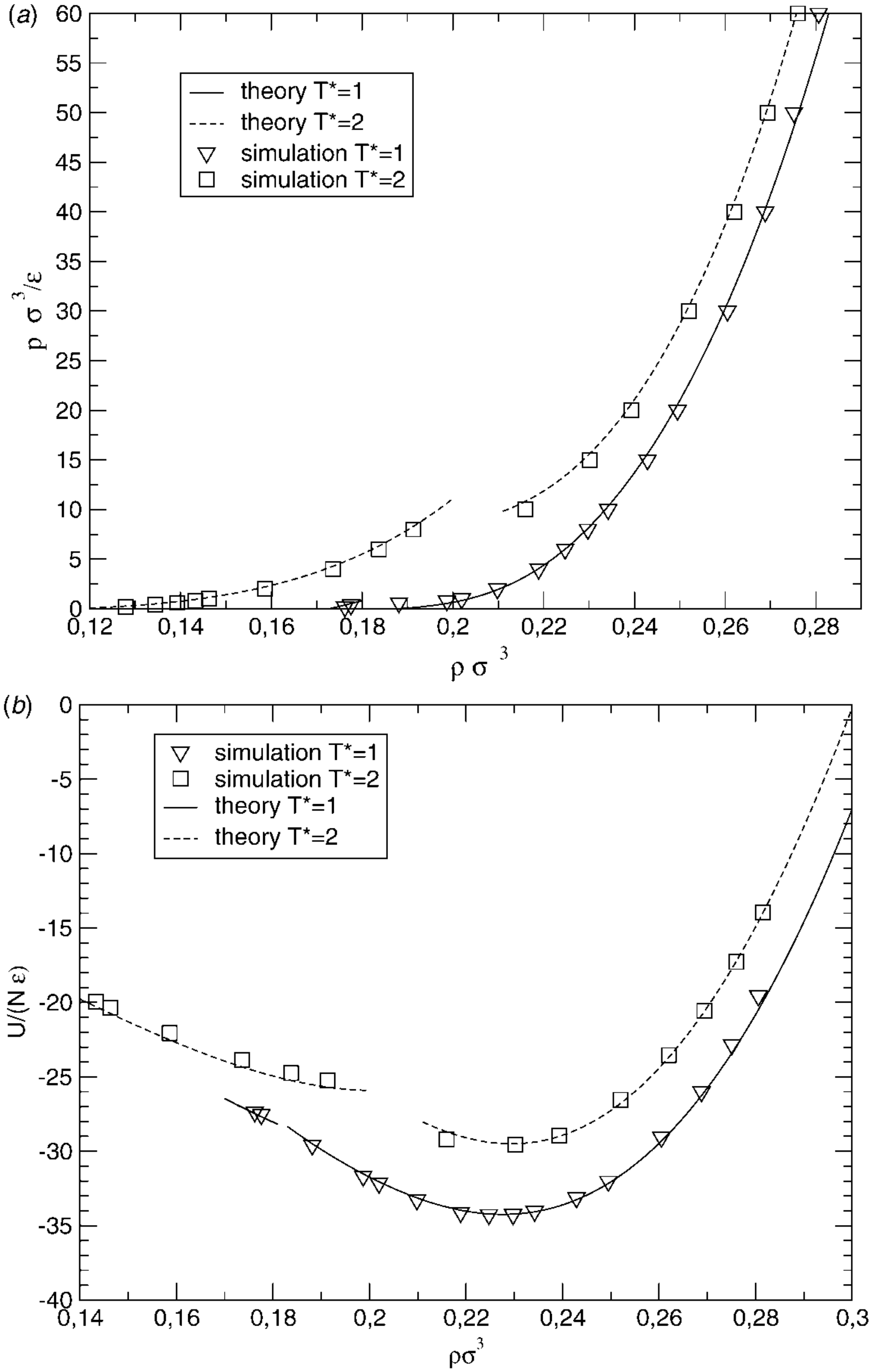

Figure 4. As in figure 2 for LJ chains with $m = 5$. (*a*) Results for the reduced pressure. (*b*) Results for the residual internal energy.

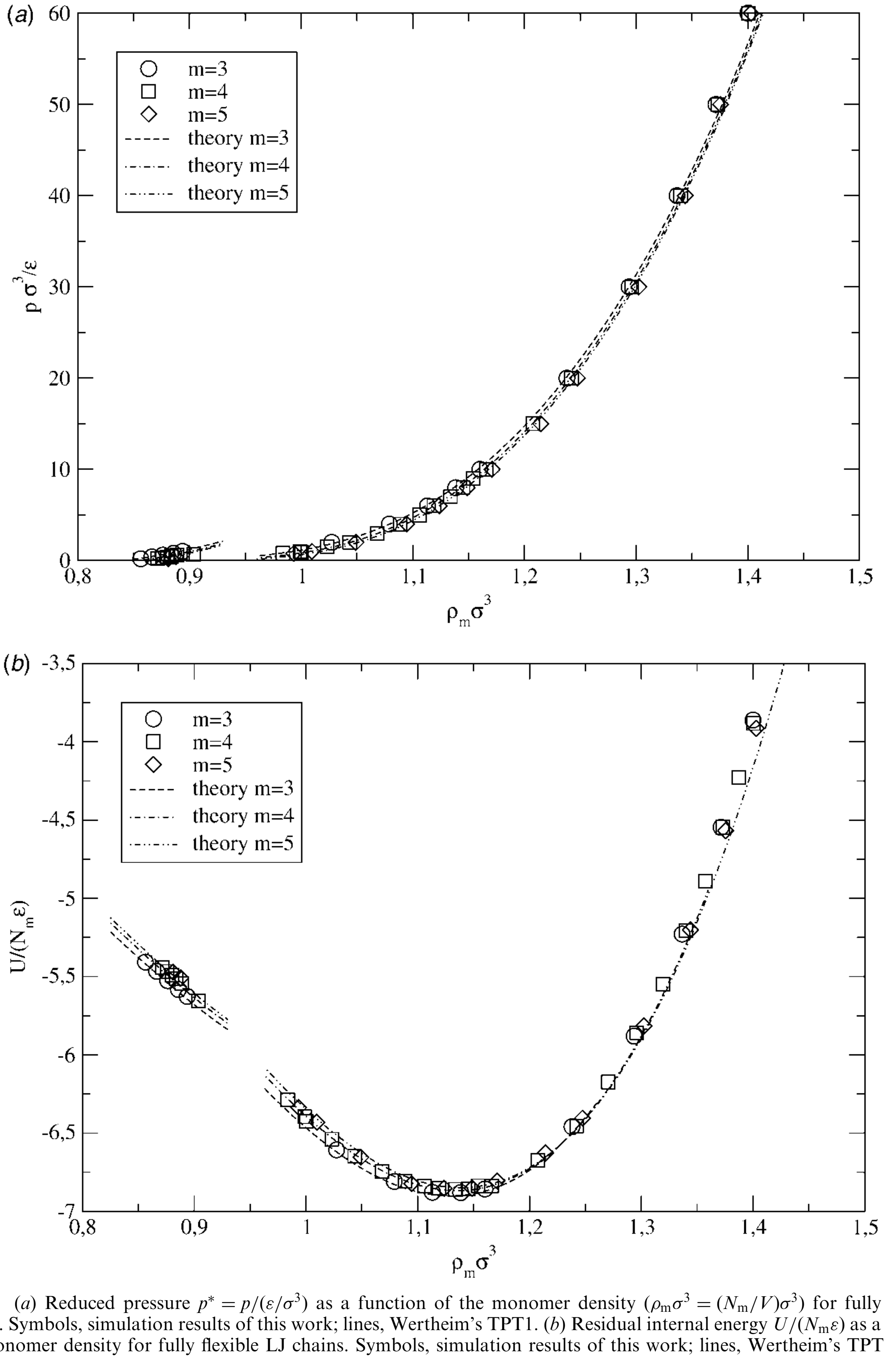

Figure 5. (*a*) Reduced pressure $p^* = p/(\varepsilon/\sigma^3)$ as a function of the monomer density ($\rho_m\sigma^3 = (N_m/V)\sigma^3$) for fully flexible LJ chains. Symbols, simulation results of this work; lines, Wertheim's TPT1. (*b*) Residual internal energy $U/(N_m\varepsilon)$ as a function of the monomer density for fully flexible LJ chains. Symbols, simulation results of this work; lines, Wertheim's TPT1.

rigid chain the bond length, bond angles and internal degrees of freedom are fixed. This linear rigid LJ chain is formed by m LJ monomer units with bond length $L = \sigma$ in a linear rigid configuration. Notice that the Hamiltonian of a system of fully flexible LJ chains and that of the linear rigid LJ chain are different. In fact, in the first model there are intramolecular interactions (between non-bonded monomer units) whereas these intramolecular interactions are missing in the 'linear rigid chain' (or one can say more generally that the intramolecular energy is simply a constant). Also in the first model the molecule can adopt any bond angle or torsional state reflecting the fact that the molecule is indeed flexible whereas these degrees of freedom are frozen in the 'linear rigid chain'. Wertheim's TPT1 theory does not distinguish between fully flexible and 'linear rigid' chains and therefore it predicts the same EOS for a fully flexible chain and for a fully rigid chain. This surprising result holds very well in the fluid phase, both for hard sphere chains [40] and for LJ chains. In fact in the fluid phase fully flexible and fully rigid chains present a quite similar (although not identical) EOS. Is this also true in the solid phase? It has been shown recently [41, 42] that the similarity between fully flexible and fully rigid linear chains does not hold in the solid phase. In fact in the case of hard sphere chains the EOS of fully flexible chains differs considerably from that of 'linear rigid' chains. Given that Wertheim's TPT1 describes very well the EOS of fully flexible hard sphere chains in the solid phase and fails completely in describing the EOS of 'linear rigid' chains in the solid phase, one may enquire as to the situation for LJ chains in the solid phase. To illustrate whether flexible and rigid LJ chains present the same or different EOS in the solid phase, we have performed NpT simulation for linear rigid LJ chains. Details are similar to those previously presented for flexible chains. Two differences are encountered. Firstly the initial configuration of the solid is not a random configuration but an ordered one. The ordered structure used is the one denoted as CP1 in [24]. This CP1 structure is similar to that proposed by Polson and Frenkel [18] for LJ semi-flexible chains. Secondly we used anisotropic NpT scaling in the way described in [43, 44]. This is important since our simulation box (and the symmetry of the unit cell) is no longer cubic.

In table 4 simulation results for 'linear rigid' LJ chains with $m = 3$ are presented. In figure 6(a) the EOS for $m = 3$ as obtained from Wertheim's TPT1 and from the Monte Carlo results of this work for fully flexible and linear rigid chains are presented. The conclusion is clear. Although at very high densities flexible and linear rigid chains present a quite similar equation of state, differences are clearly visible at smaller densities within the solid phase. The linear rigid chain tends to have a higher density for a certain pressure. A second significant difference was that for the linear rigid chain model the solid phase was mechanically stable up to zero pressure. That provides some evidence that the triple point temperature of linear rigid chains may appear at higher temperatures than that of flexible chains. Free energy calculations will be necessary to check this point. In figure 6(b) the internal energy for $m = 3$ is presented for both flexible and linear rigid chains. Again differences between flexible and linear rigid chains are clearly visible. For a certain density the internal energy of the linear rigid chain is lower than that of the flexible chain. To analyse in more detail whether differences between flexible and linear rigid chains increase with the length of the chain, we have performed simulations also for linear rigid chains with $m = 5$. Results are presented in table 5. In figure 7, a comparison is made between flexible chains in a disordered structure and linear rigid chains in an ordered structure with $m = 5$, in figure 7(a) for the EOS and in figure 7(b) for the internal energy. Differences between flexible and linear rigid chains are quite evident. Differences are larger than for the model with $m = 3$, indicating that the differences between flexible and linear rigid chains in the solid phase increase with the length of the chain. Only at very high densities (when approaching 'close packing') are differences found to be small.

In summary, we have found that, for LJ chains in the solid phase, fully flexible and fully rigid molecules present markedly different equations of state. This has

Table 4. Simulation results for linear rigid LJ chains with $m = 3$ in the solid phase. The solid structure considered is that denoted as CP1 in [24]. In reporting the internal energy it should be noted that only intermolecular contributions are considered since we have set to zero the intramolecular energy (the model is rigid).

T^*	p^*	ρ^*	$U/(N\varepsilon)$
1	60.0	0.4683	−12.072
1	40.0	0.4459	−16.650
1	30.0	0.4312	−18.799
1	20.0	0.4131	−20.695
1	10.0	0.3895	−21.998
1	8.0	0.3834	−22.134
1	6.0	0.3764	−22.196
1	5.0	0.3723	−22.190
1	4.0	0.3678	−22.154
1	3.0	0.3628	−22.080
1	2.0	0.3572	−21.950
1	1.0	0.3507	−21.753
1	0.6	0.3479	−21.648
1	0.1	0.3441	−21.498

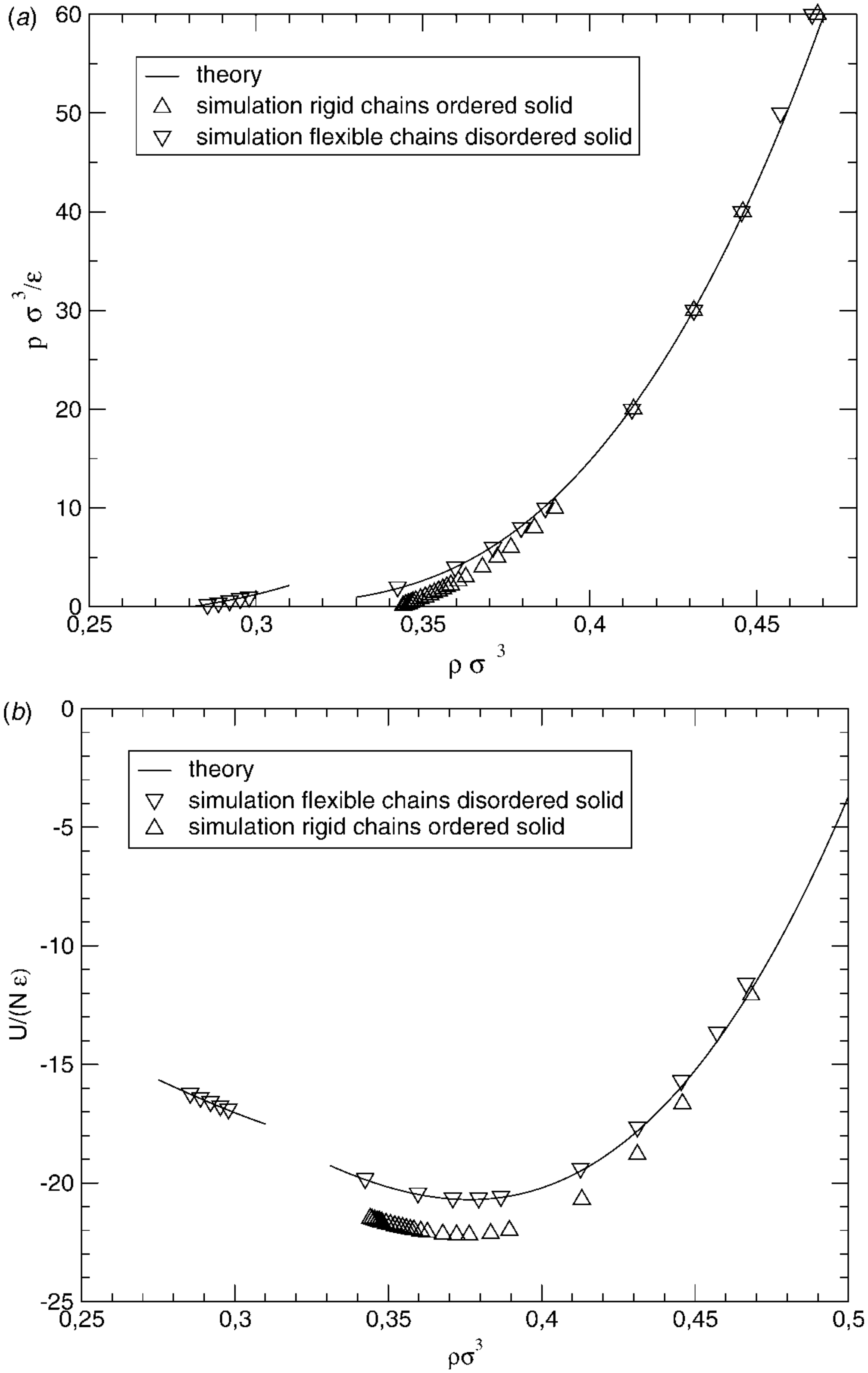

Figure 6. Properties of disordered solid formed by $m = 3$ LJ flexible chains (triangles down) and of ordered solid formed by $m = 3$ LJ rigid chains (triangles up) as a function of the reduced number density of chains. Theoretical prediction from Wertheim's TPT1 (solid line). (*a*) Results for the reduced pressure. (*b*) Results for the residual internal energy.

Table 5. Simulation results for linear rigid LJ chains with $m = 5$ in the solid phase. The solid structure considered is that denoted as CP1 in [24]. In reporting the internal energy it should be noted that only intermolecular contributions are considered since we have set to zero the intramolecular energy (the model is rigid).

T^*	p^*	ρ^*	$U/(N\varepsilon)$
1	60.0	0.2824	−20.672
1	40.0	0.2699	−28.128
1	30.0	0.2615	−31.729
1	20.0	0.2512	−34.979
1	10.0	0.2384	−37.335
1	8.0	0.2354	−37.624
1	6.0	0.2319	−37.827
1	5.0	0.2299	−37.893
1	4.0	0.2277	−37.917
1	3.0	0.2252	−37.903
1	2.0	0.2224	−37.835
1	1.0	0.2194	−37.708
1	0.8	0.2187	−37.671
1	0.1	0.2163	−37.521

already been observed for hard sphere chains, and the work here serves as a further illustration that the same occurs again for LJ chains. Wertheim's TPT1 describes very well the EOS of fully flexible chains but fails to describe the behaviour of linear rigid LJ chains. One may conclude that the similarity between fully flexible and 'linear rigid' chains is broken in the solid phase. Notice that the 'close-packed' density in the solid phase is the same for fully flexible and for linear rigid chains, so that a different packing density is not the reason for the differences found in figures 6 and 7.

Let us just finish by analysing an interesting issue. Although it is clear that for flexible chains the equilibrium solid structure is a disordered solid, and for linear rigid chains the equilibrium solid structure is an ordered one, one may ask what the properties of a flexible chain would be if it were arranged in an ordered solid. Malanoski and Monson [20] considered this aspect for flexible hard chains. They showed that the stable solid phase for hard flexible chains is a disordered solid [20]. They also analysed the behaviour of a flexible hard chain in an ordered solid. They found that, for hard flexible chains at a certain density, the ordered solid gave a higher pressure than the disordered one. To analyse whether this result also holds for LJ chains, we decided to perform NpT simulations (with anisotropic scaling) of flexible LJ chains in an ordered CP1 solid structure. Results for this flexible LJ chain in an ordered solid structure are presented in table 6. In figure 7 the results of these simulations are also presented (they are labelled as 'flexible chains ordered solid'). As can be seen in figure 7(*a*), for a certain density the pressure of the flexible chain in the ordered solid is slightly higher than that of the flexible chain in the disordered solid. Differences are not too large but are clearly visible. Our results agree with those of Malanoski and Monson [20] in the sense that they yield higher pressures for the ordered solid than the disordered solid. A simple summary of figure 7(*a*) would be to say that flexible and linear rigid chains present quite a different EOS in the solid phase and that differences between different solid structures of the flexible chains (disordered or ordered) are much smaller at least for the case considered here ($m = 5$). In figure 7(*b*) results are presented for the internal energy. It is seen that, for the flexible chain, the ordered solid presents a lower internal energy than the disordered solid. The reader should not take that as evidence of the greater stability of the ordered solid with respect to the disordered solid for flexible chains. Notice that the disordered solid has a significant stabilizing contribution to the free energy arising from the degeneracy entropy which is not present in the ordered solid. For the temperatures considered in this paper (the behaviour at very low temperatures should be considered in more detail) the slightly lower value of the internal energy of the ordered solid cannot compensate for the loss of the large value of the degeneracy entropy.

5. Conclusions

In this work, computer simulations were performed for fully flexible LJ chains in the solid phase. The solid structure considered is based on a face-centred cubic (fcc) close-packing arrangement of atoms. The initial configuration of the chains is obtained by randomly distributing the molecular bonds of the chains. The NpT simulations of this work provide values of the EOS and internal energy of the LJ chains in the solid phase. The chains considered here were formed by $m = 3, 4, 5$ monomer units. The performance of Wertheim's TPT1 theory as extended recently to the solid phase was analysed. It was found that Wertheim's TPT1 provides a very accurate description of the equation of state and residual internal energies of LJ chains. In previous work we found good agreement for the simplest case $m = 2$ and here it is shown that the agreement is also quite good for longer chains. The performance of the theory does not seem to deteriorate with the length of the chain (at least for the lengths considered here). The results of this work provide further evidence that Wertheim's TPT1 can be used with confidence for fully flexible LJ chains in the solid phase. It was also found that for a fixed temperature the EOS and internal energies of LJ chains tend to asymptotic limits when plotted as a function of the monomer number density. This behaviour

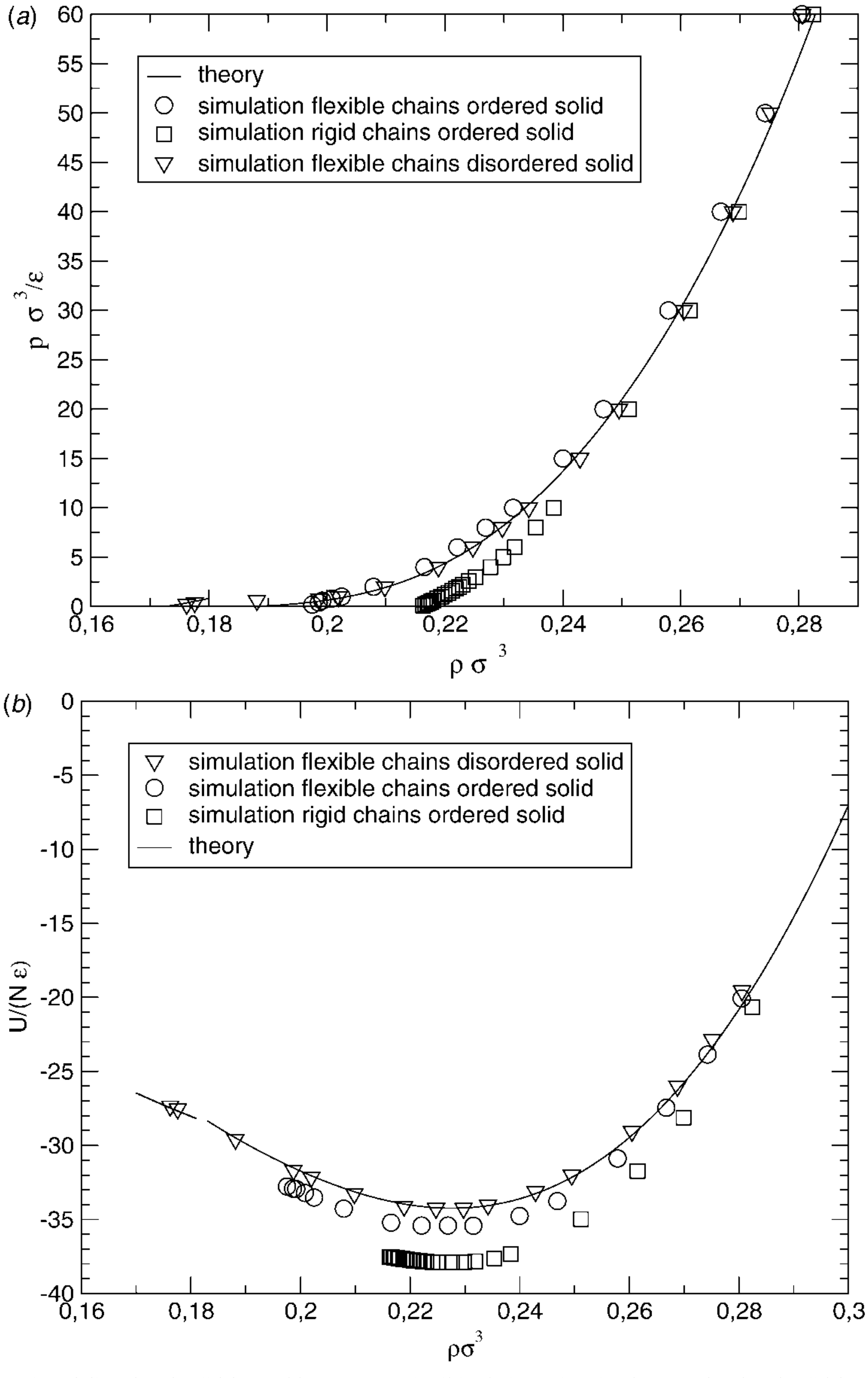

Figure 7. Properties of disordered solid formed by $m = 5$ LJ flexible chains (triangles down), of ordered solid formed by $m = 5$ LJ rigid chains (squares) and of ordered solid formed by $m = 5$ LJ flexible chains (circles) as a function of the reduced number density of chains. Theoretical predictions from Wertheim's TPT1 (solid line). (*a*) Results for the reduced pressure. (*b*) Results for the residual internal energy.

Table 6. Simulation results for fully flexible LJ chains with $m = 5$. The solid structure considered here is an ordered structure denoted as CP1 in [24].

T^*	p^*	ρ^*	$U/(N\varepsilon)$
1	60.0	0.2805	−20.077
1	50.0	0.2743	−23.866
1	40.0	0.2668	−27.457
1	30.0	0.2579	−30.880
1	20.0	0.2469	−33.762
1	15.0	0.2400	−34.768
1	10.0	0.2315	−35.427
1	8.0	0.2269	−35.414
1	6.0	0.2221	−35.409
1	4.0	0.2165	−35.218
1	2.0	0.2079	−34.272
1	1.0	0.2025	−33.523

is suggested by Wertheim's TPT1 and our simulation results are fully consistent with that behaviour. Finally some simulations were also performed for 'linear rigid' LJ chains in an ordered solid (CP1 structure). We found differences in the thermodynamic properties of fully flexible and 'linear rigid' chains in the solid phase. Therefore the similarity in thermodynamic properties between fully flexible and 'linear rigid' chains predicted by Wertheim's TPT1 does not hold in the solid phase (although it holds quite well in the fluid phase). This work shows that Wertheim's TPT1 can be used to accurately describe in the thermodynamic properties of fully flexible chains, both in the fluid and in the solid phase.

Financial support has been given by project number BFM-2001-1420-C02-01 of the Spanish DGICYT (Dirección General de Investigación Científica y Técnica). One of us (E.S.) would like to thank Ministerio de Educacion y Ciencia for the award of a PhD grant (FPU).

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