PHYSICAL REVIEW E, VOLUME 65, 052501

Scaling laws for the equation of state of flexible and linear tangent hard sphere chains

Carlos Vega and Carl McBride
Departamento de Química Física, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, Ciudad Universitaria, 28040 Madrid, Spain

(Received 19 November 2001; published 3 May 2002)

The influence that molecular flexibility has on the phase diagram and equation of state of hard sphere chains is examined. In the isotropic phase the equation of state is insensitive to flexibility; rigid chains display the same equation of state as flexible chains. However, with the onset of liquid crystalline phases for rigid molecules this similarity disappears. Differences are also apparent between the rigid and flexible models in the solid phase. Wertheim's thermodynamic perturbation theory has been extended to describe the solid phase of fully flexible chains and excellent agreement with simulation results is seen. A scaling is proposed that, when applied to the fully flexible model, reproduces simulation results for a linear rigid model. It is shown that for the fully flexible model the compressibility factor for the fluid and solid phases scale with the number of monomers *m*. The compressibility factor for the linear model scales with *m* in the isotropic fluid, and becomes independent of *m* in the nematic, smectic, and solid phases.

DOI: 10.1103/PhysRevE.65.052501 PACS number(s): 61.25.Em, 89.75.Da, 64.70.Md, 83.80.Xz

In the 1980s Wertheim developed a theory, known as the first-order thermodynamic perturbation theory (TPT1) [1–4], to describe the equation of state (EOS) of associating fluids. It was soon realized [5–8] that if the association forces became infinitely strong then chains would form. The TPT1 EOS for a fluid of monodisperse hard sphere chains built up from m tangent hard spheres of diameter σ can be written as

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

where Z is the compressibility factor, ρ is the number density of chains, p is the pressure, and $y=(\rho\pi/6)m\sigma^3$ is the packing fraction. Z^{ref} is the EOS of the reference monomer system (i.e., hard spheres) and $g^{ref}(\sigma,y)$ is the contact value of the pair correlation function for this system. Equation (1) can be rewritten in the form

$$Z(y)=Z_1(y)+mZ_2(y), \tag{2}$$

where Z_1 and Z_2 are functions that only depend on the packing fraction.

Two interesting observations can be gleaned from Eqs. (1) and (2). First, that the compressibility factor is a linear function of the degree of polymerization of the chain m. Simulation results are consistent with this prediction [9]. Second, that according to TPT1 the presence or absence of flexibility in the chain does not affect its EOS. In this work, we shall consider two different models; a linear tangent hard sphere (LTHS) chain and the so called pearl-necklace (PN) chain. The LTHS model is composed of m tangent hard spheres in a rigid linear configuration. The PN is also composed of tangent hard spheres, however, the monomers are able to adopt any configuration that is free of intermolecular and intramolecular overlap. Computer simulation results for short chains support the prediction that in the fluid phase the LTHS and the PN models have the same EOS [10]. If one defines a reduced pressure as $p^*=p\sigma^3/kT$, then from Eq. (2) we have

$$p^*=\frac{p_1(y)}{m}+p_2(y). \tag{3}$$

Thus, for a given packing fraction the reduced pressure becomes independent of m for sufficiently long chains.

In this paper, we wish to address two simple yet interesting questions. The first is, are the similarities between the EOS of the LTHS and the PN models in the isotropic fluid phase also seen for the solid phase? We shall see that this is not the case. Second, can Wertheim's TPT1 be adapted to the solid phase? We will show that such an extension is possible. Let us focus on the first question. In Figs. 1 and 2, equations of state obtained by computer simulation are presented for

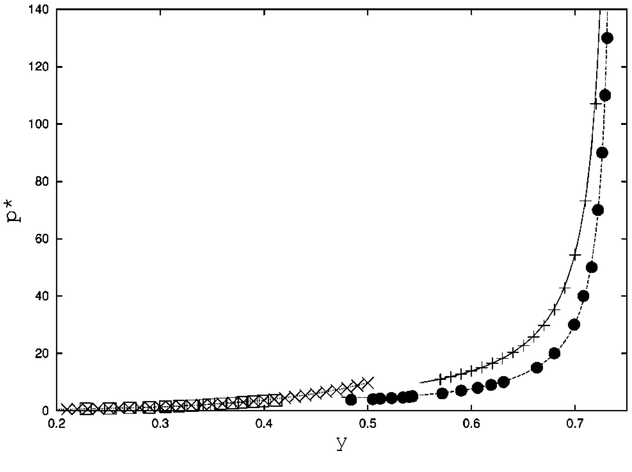

FIG. 1. Equation of state for flexible and rigid tangent hard sphere models with $m=4$. × and + are simulation points for the PN model from Malanoski and Monson [13] in the isotropic fluid and solid phases, respectively. □ and ● are MC simulation results for the LTHS model from Vega *et al.* [12] for the isotropic and solid phases, respectively. The dotted line is TPT1 for the isotropic fluid. The solid line is TPT1 for the disordered solid and the dashed line is the aforementioned theory with the application of the scaling given by Eq. (5). y is the packing fraction, $p^*=p\sigma^3/kT$.

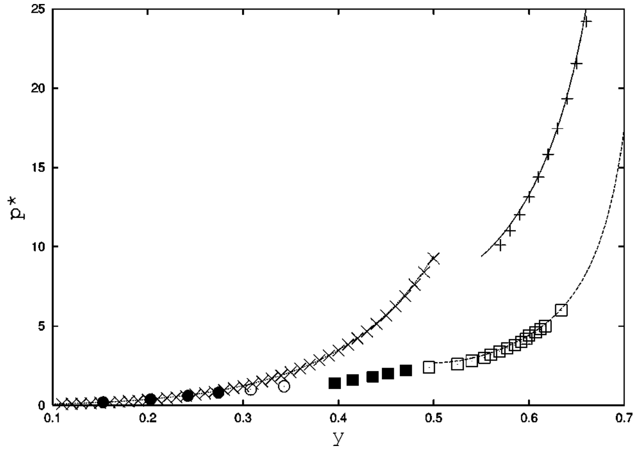

FIG. 2. Equation of state for flexible and rigid tangent hard sphere models with $m=7$. × and + are simulation points for the PN model from Malanoski and Monson [13] in the isotropic fluid and solid phases, respectively. Monte Carlo simulation results for the LTHS model [11,12] are given by ● isotropic, ⊙ nematic, ■ smectic, and □ solid state points. The dotted line is TPT1 for the isotropic fluid. Solid line is TPT1 for the disordered solid and the dashed line is the aforementioned theory with the application of the scaling given by Eq. (5). y is the packing fraction, $p^*=p\sigma^3/kT$.

both the PN model and the LTHS model with $m=4$ (Fig. 1) and $m=7$ (Fig. 2). For both $m=4$ and 7 it can be seen that in the isotropic fluid, in accordance with TPT1, there is very little difference between the EOS of the flexible PN model and that of the rigid LTHS models. However, at higher packing fractions dramatic differences are observed; first with the onset of liquid crystalline phases for the LTHS $m=7$ model (nematic and smectic A) [11,12] and, at even higher packing fractions, between the solid phases of the two models [12,13]. The structure of the solid phases of the LTHS and PN models has been described in detail in Refs. [12] and [13], respectively. In both cases the structure is based on the face centered cubic (fcc) structure of hard spheres. The difference between the structures lies in the topology of the bonds; in the PN model there is no long range orientation order between the bond vectors of the chain [14–16], whereas in the LTHS solid bonds are orientationally ordered. It would be highly desirable to have an implementation of Wertheim's theory for the solid phase. It is clear from the previous results that such an implementation should take into account the fact that PN and LTHS present different EOS in the solid phase. Let us start with the solid phase of the PN model. In the solid phase of the PN model the molecular bonds are located randomly, thus forming an isotropic distribution of bonds within a fcc structure of hard spheres. Similarly, there is an isotropic distribution of bonds in the isotropic fluid phases of both the PN and the LTHS models. A starting point for such a theory is to apply Eq. (1) to the solid phase. Notice that the only input required in Eq. (1) is the equation of state of the hard sphere monomer in the solid phase. Such an EOS is provided by Hall [17]. The contact value $g^{ref}(\sigma,y)$ required by the theory can be obtained from the virial theorem, $Z^{ref}=1+4yg^{ref}(\sigma,y)$. The original idea for such an extension was given by Sear and Jackson [18] for $m=2$. In Figs. 1 and 2 simulation results of Malanoski and Monson [13] for the PN model with $m=4$ and 7 are compared with the solid phase extension for TPT1. As can be seen the agreement between theory and simulation is excellent. The TPT1 solid phase extension has been shown to work well for other systems and properties, such as two-dimensional chains, Lennard-Jones chains, and for free energies [16,19,20]. It is worth mentioning that the expressions for TPT1 in the solid phase are also of the form given by Eqs. (2) and (3), although the precise expressions for Z_1, p_1, Z_2, and p_2 differ from those of the fluid phase. Is it possible to derive a Wertheim-like theory for the solid phase of the LTHS? It is clear from the isotropic results that TPT1 does not take into account intramolecular flexibility. Since the solid phase EOS of the PN and the LTHS models differ, and that TPT1 reproduces the PN EOS, then we do not expect TPT1 to be successful in describing the LTHS solid phase. Given that the distribution of bonds in the LTHS solid is anisotropic then one may suspect that such an implementation would require knowledge of the three- or four-body distribution functions for the hard sphere monomer solid (i.e., Wertheim's theory should be extended to the second or third order for the solid phase) thereby allowing differences between flexible and rigid chains to appear naturally. Since little is known about the three- or four-body correlation functions for the hard sphere monomer solid then such an extension is not possible at the moment. However, we shall show that a simple scaling argument is successful in describing the simulation results for the LTHS in the solid phase. The quality of the result is so good that it strongly suggests that such an extension of Wertheim's theory for the LTHS solid may indeed be possible. The approach we shall use is to relate the reduced pressure p^* of the LTHS model to that of the PN model at the same packing fraction y by the scaling

$$p^*_{\mathrm{LTHS}}(m,y)=\left(\frac{f_{\mathrm{LTHS}}}{f_{\mathrm{PN}}}\right)p^*_{\mathrm{PN}}(m,y), \tag{4}$$

where p^*_{LTHS} is the reduced pressure of the LTHS in the solid phase and p^*_{PN} is the reduced pressure of the pearl-necklace model in the solid phase. p^*_{PN} is provided by the solid phase PN extension to TPT1 described previously. The number of degrees of freedom of the LTHS molecule, f_{LTHS}, is equal to 5, and the number of degrees of freedom of the PN model, f_{PN}, is obtained by adding the three degrees of freedom of an arbitrary atom in the model and the two degrees of freedom for each of the bonds (note that in this model the bond length is fixed). This results in the formula

$$p^*_{\mathrm{LTHS}}(m,y)=\left(\frac{5}{3+2(m-1)}\right)p^*_{\mathrm{PN}}(m,y). \tag{5}$$

Cell theory [21] can be used to provide a heuristic argument as to why Eq. (5) holds. In cell theory, a theory successful in describing solid phases (although not quite so for liquids) [21], the configurational free energy can be expressed as

$$\frac{A}{NkT}=-\ln(v)=-\ln\left[\int\exp\left(\frac{-U(1)}{kT}\right)dq_1\right], \tag{6}$$

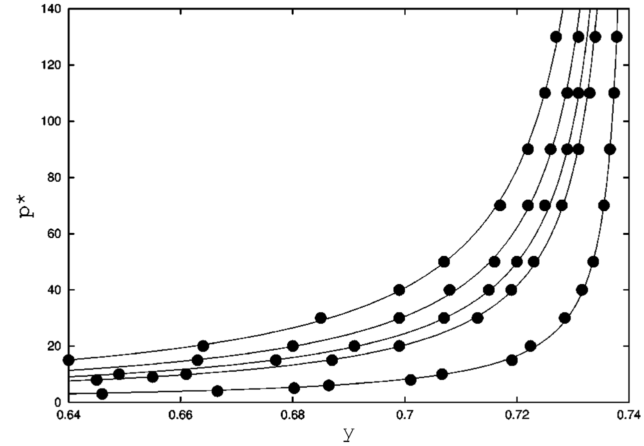

FIG. 3. Plot of the EOS for the LTHS model in the solid phase for, from top to bottom, $m=3$, 4, 5, 6, and 15. ● represents MC simulation points from this work ($m=15$), and data from Ref. [12]. The solid curve is the EOS obtained from Eq. (5) using TPT1 for the PN solid. $p^*=p/(kT)\sigma^3$.

where v is the free volume, q_1 describes the coordinates required to define the location, orientation, and configuration of an arbitrary molecule labeled as 1, and $U(1)$ is the energy of molecule 1 with respect to all other molecules in an equilibrium lattice. It is assumed that each degree of freedom contributes equally to the free volume. Thus, it follows that $v=(C)^f$, where f is the number of degrees of freedom of the molecule. By substituting the previous expression into Eq. (6) one is led to Eq. (5). In Figs. 1 and 2, it is shown that the scaling of Eq. (5) yields a good description of the EOS for the LTHS solid for $m=4$ and 7. In Fig. 3, Monte Carlo simulation results for $m=3,4,5,6$ (Ref. [12]) and for $m=15$ (this work) are compared with the predictions from Eq. (5). Again the agreement is seen to be excellent from $m=3$ to 15. For $m=2$ the prefactor of Eq. (5) is one, thus the LTHS and PN models have the same EOS for the dimer (the LTHS and PN models being identical models for $m=2$). It is worth noting that the only input information in the theoretical description of the EOS of the solid phases of the PN and LTHS models is the 30 year old solid phase monomer hard sphere EOS of Hall [17]. Let us now discuss the scaling laws for the EOS for the PN and LTHS models in the solid phase. Given that the PN solid can be described by TPT1 then Eqs. (2) and (3) also hold in the solid phase. Thus in both the solid and the fluid phases of the PN model Z scales as m, and p^* as m^0. For the LTHS model in the solid phase we can see from Eq. (5) that, for sufficiently large values of m, p^* scales as m^{-1} and Z scales as m^0. Scalings for the PN and the LTHS models are summarized in Table I for various phases for both the compressibility factor and the reduced pressure. It can be seen that the scaling is the same for both rigid and flexible molecules in the isotropic fluid, and differs in the solid. In the solid phase, orientational order precipitates this change in scaling. In order to see whether the solid phase scaling for the LTHS model also holds for the nematic and smectic-*A* phases, a plot is made of the compressibility factor with respect to the packing fraction (Fig. 4). For the nematic, smectic, and solid phase Monte Carlo simulation results are presented and curves for Wertheim's TPT1 represent the isotropic fluid. It can be seen that although in the isotropic phase the EOS is significantly different for each of the models, the results for the nematic, smectic, and solid phases are independent of m. Although not included in Table I, notice that at very low densities the compressibility factor goes to one; Z scales as m^0 for the PN and LTHS models in this region. At low densities the scaling of $Z-1$ is given by the scaling of the second virial coefficient of the models (see discussions in Refs. [22] and [23]).

TABLE I. Scaling laws for the compressibility factor Z, and the reduced pressure p^*.

	Isotropic fluid		Nematic		Smectic		Solid	
	Z	p^*	Z	p^*	Z	p^*	Z	p^*
PN	m	m^0					m	m^0
LTHS	m	m^0	m^0	m^{-1}	m^0	m^{-1}	m^0	m^{-1}

Given the remarkable performance of the scaling proposed here it is tempting to suggest that a similar scaling, for example $p^*_{\mathrm{LTHS,2D}}/p^*_{\mathrm{PN,2D}}=3/[2+(m-1)]$, may hold for two-dimensional hard chains in the solid phase [19]. We believe that the scaling proposed here for LTHS also holds also for other rigid linear hard bodies, for example hard spherocylinders [24–26]. All that is required is to replace m by $\gamma=(L/D+1)$, where L is the length and D is the diameter of the spherocylinder, in the scaling laws presented in Table I. Also notice that since the scaling of Z for the LTHS model is the same in the nematic, smectic-*A*, and solid phases, then the packing fraction at which the nematic–smectic-*A* and the smectic-*A*–solid phase transitions occur should be virtually

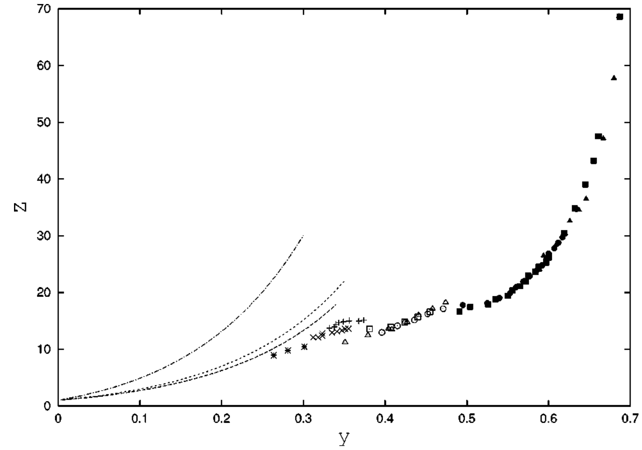

FIG. 4. Plot of the EOS for the LTHS model with $m=6$, 7, and 15. The dashed line is the TPT1 curve for $m=6$, the dotted line is the TPT1 curve for $m=7$, and the dot-dashed line is the TPT1 curve for $m=15$. $m=6$ solid phase simulation points are represented by ■, $m=7$ solid phase by ●, and $m=15$ solid phase by ▲. □ represents MC data points for $m=6$ in the smectic phase, ○ represents MC data points for $m=7$ in the smectic phase, △ represents MC data points for $m=15$ in the smectic phase, + represents MC data points for $m=6$ in the nematic phase, × represents MC data points for $m=7$ in the nematic phase (from Ref. [11]), and * represents MC data points for $m=15$ in the nematic phase.

independent of the length of the chain m. Simulation results for hard spherocylinders are consistent with this suggestion [24]. Since Z scales with m for the LTHS chain in the isotropic phase and as m^0 in the nematic phase then one expects to see a shift in the location of the isotropic-nematic transition to lower densities as m increases. Similarly, the scaling of the reduced second virial coefficient of the LTHS model, $B_2^* = B_2/V_m$, where V_m is the molecular volume, goes as m in the isotropic phase and as m^0 in the nematic phase. These scalings have been well known since the work of Onsager [27]. Here we have shown that for the LTHS model Z scales as m^0 not only in the nematic phase but also in the smectic and solid phases.

Financial support is due to Project No. BFM2001-01420-C02-01 of the Spanish DGICYT (Dirección General de Investigación Científica y Técnica). One of the authors C.M. would like to acknowledge and thank the European Union FP5 Program for financial support through Contract No. HPMF-CT-1999-00163.

---

[1] M.S. Wertheim, J. Stat. Phys. **35**, 19 (1984).
[2] M.S. Wertheim, J. Stat. Phys. **35**, 35 (1984).
[3] M.S. Wertheim, J. Stat. Phys. **42**, 459 (1986).
[4] M.S. Wertheim, J. Stat. Phys. **42**, 477 (1986).
[5] M.S. Wertheim, J. Chem. Phys. **87**, 7323 (1987).
[6] W.G. Chapman, G. Jackson, and K.E. Gubbins, Mol. Phys. **65**, 1 (1988).
[7] Y. Zhou, C.K. Hall, and G. Stell, J. Chem. Phys. **103**, 2688 (1995).
[8] Y. Zhou and G. Stell, J. Chem. Phys. **96**, 1507 (1992).
[9] Y. Zhou, S.W. Smith, and C.K. Hall, Mol. Phys. **86**, 1157 (1995).
[10] T. Boublik, C. Vega, and M.D. Pena, J. Chem. Phys. **93**, 730 (1990).
[11] D.C. Williamson and G. Jackson, J. Chem. Phys. **108**, 10 294 (1998).
[12] C. Vega, C. McBride, and L. MacDowell, J. Chem. Phys. **115**, 4203 (2001).
[13] A.P. Malanoski and P.A. Monson, J. Chem. Phys. **107**, 6899 (1997).
[14] K.W. Wojciechowski, D. Frenkel, and A.C. Brańka, Phys. Rev. Lett. **66**, 3168 (1991).
[15] K.W. Wojciechowski, A.C. Brańka, and D. Frenkel, Physica A **196**, 519 (1993).
[16] C. Vega and L. MacDowell, J. Chem. Phys. **114**, 10411 (2001).
[17] K.R. Hall, J. Chem. Phys. **57**, 2252 (1972).
[18] R.P. Sear and G. Jackson, J. Chem. Phys. **102**, 939 (1995).
[19] C. McBride and C. Vega, J. Chem. Phys. **116**, 1757 (2002).
[20] C. Vega, F. J. Blas, and A. Galindo, J. Chem. Phys. (to be published).
[21] P. A. Monson and D. A. Kofke, in *Advances in Chemical Physics*, edited by I. Prigogine and S.A. Rice (Wiley, New York, 2000), Vol. 115, p. 113.
[22] C. Vega, J.M. Labaig, L.G. MacDowell, and E. Sanz, J. Chem. Phys. **113**, 10 398 (2000).
[23] D.C. Williamson and G. Jackson, Mol. Phys. **86**, 819 (1995).
[24] P. Bolhuis and D. Frenkel, J. Chem. Phys. **106**, 666 (1997).
[25] S.C. McGrother, D.C. Williamson, and G. Jackson, J. Chem. Phys. **104**, 6755 (1996).
[26] D. Frenkel, H.N.W. Lekkerkerker, and A. Stroobants, Nature (London) **332**, 822 (1988).
[27] L. Onsager, Ann. N.Y. Acad. Sci. **51**, 627 (1949).