

Fluid solid equilibrium for two dimensional tangent hard disk chains from Wertheim's perturbation theory

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Wertheim's first order thermodynamic perturbation theory [M. S. Wertheim, *J. Chem. Phys.* **87**, 7323 (1987)] has been extended to the two-dimensional tangent hard disk dimer for both the solid and the fluid phases. This extension utilizes pre-existing equations of state for the fluid [C. F. Tejero and J. A. Cuesta, *Phys. Rev. E* **47**, 490 (1993)] and for the solid phases [B. J. Alder, W. G. Hoover, and D. A. Young, *J. Chem. Phys.* **49**, 3688 (1968)], of the two-dimensional hard disk monomer system. The theory has been compared to simulation results and a good agreement has been found between them. Results are also presented for the fluid–solid tie line for $m=2$ up to $m=30$. The results of this work may be of interest to those involved in the study of chainlike systems adsorbed on a two-dimensional surface. © 2002 American Institute of Physics. [DOI: 10.1063/1.1446842]

I. INTRODUCTION

The first order thermodynamic perturbation theory of Wertheim (TPT1)^{1–4} was designed for use with associating fluids. Soon after its conception it was extended to the treatment of chain molecules by Wertheim himself and by Chapman, Jackson, and Gubbins.^{5,6} Wertheim's TPT1 has since been applied to chains in the fluid phase composed of Lennard-Jones sites.^{7,8}

Recently Wertheim's theory has been extended to the solid phase of the fully flexible tangent hard sphere chain model by Vega and MacDowell.⁹ With this extension it is now possible to study the fluid–solid equilibrium conditions of fully flexible chains, demonstrating a good agreement with the simulation results of Malanoski and Monson.¹⁰

In this paper the focus is on the two-dimensional flexible chain tangent hard disk system.^{11–15} The case of the monomer fluid was the subject of the very first computer simulation studies, most famously by Metropolis *et al.*,¹⁶ but also by Alder and Wainwright,¹⁷ Wood,^{18,19} and Rotenberg.²⁰ As well as the monomer fluid, the dimer fluid has been the subject of interest. Wojciechowski and co-workers have shown that the dimer fluid freezes into an orientationally disordered solid.^{21–23} Similar results for other systems have since been found by a number of other authors.^{24–26} By means of computer simulation Wojciechowski *et al.* have also located the fluid–solid equilibrium point for the dimer fluid.^{21,22} The possibility of extending Wertheim's theory to hard disk chains in the fluid phase has been recently proposed.^{11,27}

In this paper Wertheim's TPT1 is extended to the solid phase of tangent hard disk chains. The fluid–solid equilibrium for chains consisting of a number of tangent hard disks is also obtained. Such chains provide an analog to chain like molecular systems adsorbed on planar surfaces.

II. WERTHEIM'S FIRST ORDER THERMODYNAMIC PERTURBATION THEORY

A. Equation of state

Given the equation of state (EOS) and the pair correlation function for a monomer fluid Wertheim's TPT1 can be used to provide an equation of state for a chain fluid composed of m monomers. This applies similarly to the solid phase. This approach has been recently applied to the three-dimensional case (the pearl-necklace model) by Vega and MacDowell.⁹ More details being given in the aforementioned paper. Wertheim's TPT1 EOS for a flexible chain composed of m monomer units is given by^{5,6}

$$Z_{TPT1} = \frac{p}{\rho kT} = m Z_{\text{monomer}}^{\text{fluid/solid}} - (m-1) \left(1 + \rho^{\text{ref}} \frac{\partial \ln g(\sigma)}{\partial \rho^{\text{ref}}} \right), \quad (1)$$

where $Z_{\text{monomer}}^{\text{fluid/solid}}$ is the reference EOS for the monomer hard disks in either the fluid or the solid phase, $\rho = N/A$ where N is the number of chains, A is the area of the system, m is the number of monomers in the hard disk molecule, and ρ^{ref} is the monomer number density. In the fluid phase an EOS proposed by Tejero and Cuesta^{28,29} is used as the reference EOS

$$Z_{\text{monomer}}^{\text{fluid}} = \frac{1 + \sum_{n=1}^6 C_n y^n}{(1-y)^2}, \quad (2)$$

where $C_1=0$, $C_2=0.128\,018$, $C_3=0.001\,818\,8$, $C_4=-0.725\,53$, $C_5=2.527\,83$, and $C_6=-2.4945$. y is the packing fraction which, in two dimensions, is given by

$$y = \frac{\pi}{4} \rho^{\text{ref}} \sigma^2, \quad (3)$$

where σ is the hard disk diameter. Equation (2) was proposed by Baus and Colot²⁹ as a rescaled and truncated virial series “inspired” by the results of scaled particle theory. The coefficients C_1 , C_2 , and C_3 are chosen to reproduce the results for B_2 , B_3 , and B_4 for the hard disk fluid. The coefficients C_4 , C_5 , and C_6 were obtained by a fit to simulation data.³⁰

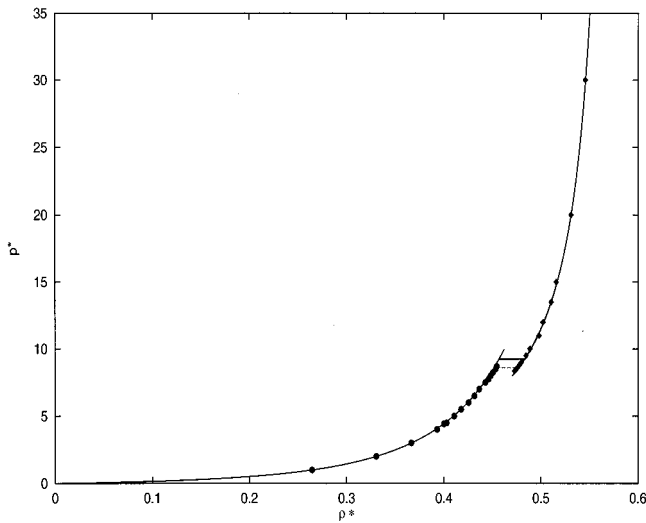


FIG. 1. Equation of state for the fluid and solid phases of the 2D hard disk dimer. The solid lines are Wertheim's TPT1 for the fluid phase and solid phase. The solid points are simulation results for the fluid and disordered solid phases (Ref. 22). The solid tie line is that from this work. The dashed tie line is that of Wojciechowski *et al.* (Refs. 21 and 22). $p^* = \rho\sigma^2$, $p^* = \rho\sigma^2/kT$.

In the solid phase the reference EOS used in this study is that proposed by Alder *et al.*³¹

$$Z_{\text{monomer}}^{\text{solid}} = \frac{D}{\alpha} + c_0 + c_1\alpha, \quad (4)$$

where $c_0 = 1.90$, $c_1 = 0.67$, and D is the dimensionality of the system (in this case $D = 2$) and $\alpha = (\rho_0^{\text{ref}} - \rho^{\text{ref}})/\rho^{\text{ref}}$ with the monomer close packing value being given by

$$\rho_0^{\text{ref}} = \frac{2}{\sigma^2\sqrt{3}}. \quad (5)$$

From the two-dimensional virial equation^{32,33}

$$Z = \frac{p^{\text{ref}}}{\rho^{\text{ref}}kT} = 1 + \frac{\pi}{2}\rho^{\text{ref}}\sigma^2g(\sigma) \quad (6)$$

giving

$$g(\sigma) = \frac{Z_{\text{monomer}}^{\text{fluid/solid}} - 1}{\frac{\pi}{2}\rho^{\text{ref}}\sigma^2}. \quad (7)$$

The substitution of Eq. (7) into Eq. (1) with $Z_{\text{monomer}}^{\text{fluid/solid}}$ being either Eq. (2) in the fluid phase or Eq. (4) in the solid phase provides us with an EOS for 2D flexible chain molecules composed of m hard disks. By means of an analytical mathematics package expressions and values for the EOS can be readily generated. This procedure has been performed previously for the fluid phase by Zhou and co-workers.²⁷

B. Free energy

In general the Helmholtz free energy can be divided into two components, the ideal component and a residual component

$$\frac{F^{\text{total}}}{NkT} = \frac{F^{\text{ideal}}}{NkT} + \frac{F^{\text{residual}}}{NkT}. \quad (8)$$

TABLE I. Fluid–solid phase transition for two-dimensional hard chains.

m	γ_{fluid}	γ_{solid}	p^*	μ/kT
1	0.690	0.727	9.365	Hoover and Ree ³⁵
1	0.691	0.716	8.914	Alder <i>et al.</i> ¹⁷
1	0.682	0.717	8.779	12.35
2	0.714	0.747	8.6(2)	Wojciechowski <i>et al.</i> ²²
2	0.718	0.759	9.236	24.15
3	0.728	0.773	9.298	35.85
4	0.733	0.780	9.297	47.50
5	0.735	0.784	9.284	59.14
6	0.737	0.786	9.270	70.80
7	0.738	0.788	9.256	82.45
8	0.739	0.789	9.245	94.10
9	0.740	0.790	9.235	105.77
10	0.741	0.791	9.227	117.43
16	0.742	0.794	9.194	187.54
20	0.743	0.795	9.181	234.33
30	0.744	0.796	9.164	351.43

The chemical potential is given by

$$\frac{\mu}{kT} = \frac{F^{\text{ideal}}}{NkT} + \frac{F^{\text{residual}}}{NkT} + Z \quad (9)$$

with the ideal part of the Helmholtz free energy being

$$\frac{F^{\text{ideal}}}{NkT} = \ln(\rho\Lambda^2) - 1, \quad (10)$$

where Λ is the de Broglie thermal wavelength. We shall arbitrarily define Λ to be equal to σ . According to TPT1 the residual Helmholtz free energy for the chain is given by³⁴

$$\frac{F_{\text{chain}}^{\text{residual}}}{NkT} = m \frac{F_{\text{monomer}}^{\text{residual}}}{N_m kT} - (m-1) \ln g(\sigma), \quad (11)$$

where N_m is the number of monomers in the system. The residual Helmholtz free energy of the monomer fluid phase can be expressed as

$$\frac{F_{\text{monomer}}^{\text{residual}}}{N_m kT} = \int_0^\eta \frac{Z_{\text{monomer}}^{\text{fluid}} - 1}{\eta} d\eta. \quad (12)$$

The residual Helmholtz free energy of the monomer solid phase is given by⁹

$$\frac{F_{\text{monomer}}^{\text{residual}}}{N_m kT} = \frac{F_{\text{monomer}}^{\text{residual}}(\eta_0)}{N_m kT} + \int_{\eta_0}^\eta \frac{Z_{\text{monomer}}^{\text{solid}} - 1}{\eta} d\eta, \quad (13)$$

TABLE II. Comparison between values for the chemical potential from simulation results (Refs. 21 and 22) for $m = 2$, and the present work for the fluid (top) and solid phases (bottom).

p^*	$\mu_{\text{fluid}}^{\text{MC}}/kT$	$\mu_{\text{fluid}}^{\text{theory}}/kT$
8.35	22.18	22.19
8.70	22.95	22.97
p^*	$\mu_{\text{solid}}^{\text{MC}}/kT$	$\mu_{\text{solid}}^{\text{theory}}/kT$
8.35	22.20	22.30
8.70	22.94	23.04

where $F_{\text{monomer}}^{\text{residual}}(\eta_0)$ is the residual Helmholtz free energy of hard disks at the volume fraction η_0 .

For $\eta_0=0.71635$ Alder *et al.*³¹ have given a value of $F_{\text{monomer}}^{\text{residual}}(\eta_0)=3.818$ for the above equation. (See Table VIII in Ref. 31.)

III. RESULTS

In Fig. 1 a comparison is made between the TPT1 equation of state and Monte Carlo computer simulation results of Wojciechowski *et al.*²² The agreement between the simulation results and the theory is quite good for the EOS in both the fluid and the solid branches. However, it can be seen that the predicted location of the tie line is over estimated. It should be noted that the position of the tie line is highly sensitive to changes in the first term of Eq. (13). Simulation results also reflect this sensitivity in the spread of results for the location of the transition for the monomer system in the published literature.^{17,35,36} The two tie lines are those of Wojciechowski *et al.* and that derived from this work. Fluid–solid coexistence properties are given in Table I. We note from Table I that for $m=2$ the theory in this paper slightly overestimates the pressure at which the tie lines appear. In Table II we make a comparison of the chemical potential from simulation and that obtained from the theory in this paper. One can see that the estimates are in good agreement for the fluid phase, however, for the solid phase there is a discrepancy. The difference between the values of μ account for the overestimate of the pressure at the phase transition. Wojciechowski *et al.*²² have calculated the free energy of the solid dimer as being 5.20 at a packing fraction of $y=0.7685$. At the same packing fraction our calculations provide us with $F/NkT=5.28$. This higher value for the free energy in our theory delays the onset of freezing, thus placing our tie lines at slightly higher densities.

As well as for the monomer and dimer systems the solid–fluid equilibrium points are also calculated for a number of other chain lengths (see Table I). As can be seen the volume fraction at which both melting and freezing occurs increases with the number of monomers in the chain and reaches an asymptotic value. After peaking at $m=3$ the pressure at the transition also tends to an asymptotic limit. The reason for such asymptotic limits has been developed in a recent publication by Vega and MacDowell.⁹

IV. SUMMARY AND CONCLUSIONS

In this paper Wertheim's TPT1 has been extended to the two-dimensional tangent hard disk chain system for the fluid and solid branches. Good agreement has been found for the $m=2$ system between the theory and existing computer simulation results. Prediction of the location of the fluid–solid tie line shows fair agreement with that of simulation. The volume fraction at which melting and freezing occurs increases with increasing chain length and reaches an asymptotic value. This behavior is analogous to the three-dimensional situation.

For chains that contain more than two monomers it is conceivable that ordered phases could form between the isotropic fluid and the solid phase. If such phases form then

evidently the equation of state for these phases would differ from those of the isotropic fluid and the solid phase equations of state, and the equations of state described here would not hold in this regime.

In three dimensions it is possible to study intersecting hard sphere chains with TPT1 by means of a mapping to an equivalent number of monomer units (Zhou *et al.*²⁷). It is possible that a similarly designed scaling may be found to be applicable to two-dimensional 'fused' hard disks such as those studied by Wojciechowski.³⁷

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