Note

The specific heat of linear tangent hard sphere chains

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stract The specific heat (C_p) of linear tangent hard sphere chains of varying length is determined by employing Wertheim's first order turbation theory It is shown that the equation of state obtained by Wertheim's first order perturbation theory predicts the same values of specific as those obtained through the equation of state obtained by Monte Carlo computer simulation

ell-established model to study chain-like molecular system
ne in which the molecules are modeled as chains formed by
nnected spherical segments This model is commonly used
represent polymer's thermodynamics properties and their
use behavior Chain molecules of tangent segments can be
sidered fully flexible unless bending and torsional potentials
explicitly incorporated In these models, the pair potential
ween monomers that form this chain is given by a spherical
tential Wertheim [1-4] and Chapman, Jackson and Gubbins
presented independently a very successful theory to study
thermodynamic properties of hard core fluids interacting
short range attractive forces Wertheim's formulation also
lds quite good description for Lennard Jone (LJ) chains [6-
square well chains [8], Yukawa chains [9], vapour – liquid
uilibrium [10], critical properties [11] and fluid – solid
existence [12-14] Thus, it is possible to derive an equation of
ate for a chain of freely joined tangent hard segments using
ly thermodynamic information of monomer reference fluid,
s theory is commonly known as the first order thermodynamic
rturbation theory (TPT 1) By employing TPT 1, the
proximate equation of state of the chain fluid can be derived
knowing the equation of state of the monomer fluid and its
correlation function at contact As we have considered the
erical segments of the chain, hard sphere reference system
be quite useful

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Despite the extensive number of studies devoted to the Wertheim's theory, relatively little attention has been paid to the thermodynamic properties such as specific heat of the chain molecules To the best of our knowledge, no work has been done in this direction In the present work, we have carried out a simple numerical calculations by employing a simple formula of specific heat depending upon the equation of state We have also carried out the numerical calculations of the specific heat from equation of state obtained by Monte Carlo simulations and compared both theoretical results and those obtained from Monte Carlo results We find a good agreement between the two values

Let us consider the spherical monomer particles N^{ref} within a certain volume V at temperature T These spherical particles interact through a spherical pair potential $u(r)$ We shall denote this fluid as the reference fluid and labeled by superscript reference Let us also consider a fully flexible chains of m monomers such that $N = N^{ref}/m$ The Helmholtz free energy of the reference fluid A^{ref} can be divided into an ideal and a residual part as follows [12] ·

$$\frac{A^{ref}}{N^{ref} KT} = \frac{A^{ref}_{ideal}}{N^{ref} KT} + \frac{A^{ref}_{residual}}{N^{ref} KT} = \ln\left(\rho^{ref}\sigma^3\right) - 1 + \frac{A^{ref}_{residual}}{N^{ref} KT},$$

(1)

where ρ^{ref} is the number density of the reference fluid and σ is the thermal de Broglie wavelength

From the Helmholtz free energy, we can derive the expression of the equation of state as

$$Z^{chain} = Z(\eta) = mZ^{ref} - (m-1)\frac{1+\eta-0.5\eta^2}{(1-\eta)(1-0.5\eta)} \quad (2)$$

For flexible chain molecules, the reference fluid is that of hard spheres in the fluid phase and described by Carnahan-Starling Equation of state [15] as

$$Z^{ref} = \frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3} \quad (3)$$

where η is the volume fraction of the hard sphere defined as $\eta = (\pi/6)\rho^{ref}\sigma^3$, the $g^{ref}(\sigma)$ can be obtained by employing Virial route to the pressure as [16]

$$Z^{ref} = 1 + 4\eta g^{ref}(\sigma) \quad (4)$$

Now, we know that the specific heat C_p of a system of hard spheres of diameter σ can be expressed as [17, 18]

$$\frac{C_p}{K_B} = \frac{D}{2} + \frac{|Z(\eta)|^2}{\frac{\partial}{\partial\eta}[\eta Z(\eta)]}, \quad (5)$$

where D is the dimension (in the present case $D=3$) and $Z(\eta)$ is the equation of state of the hard sphere system We consider $Z(\eta)$ is the equation of state of chain system which can be obtained by employing Wertheim's first order theory

Now, $\delta(\eta Z)/\delta\eta$ can be evaluated from eq (2) as

$$\frac{\partial}{\partial\eta}(\eta Z) = m\frac{\partial}{\partial\eta}\frac{\eta(1+\eta+\eta^2-\eta^3)}{(1-\eta)^3}$$

$$-(m-1)\frac{\partial}{\partial\eta}\left(\frac{\eta(1+\eta-0.5\eta^2)}{(1-\eta)(1-0.5\eta)}\right) \quad (6)$$

$$= ml_1 - (m-1)l_2$$

and

$$l_1 = \frac{(1-\eta)(1+2\eta+3\eta^2-4\eta^3)+3(\eta+\eta^2+\eta^3-\eta^4)}{(1-\eta)^4},$$

$$l_2 = \frac{(1-\eta)(1-0.5\eta)(1+2\eta-1.5\eta^2)+(\eta+\eta^2-0.5\eta^3)(1.5-\eta)}{(1-\eta)^2(1-0.5\eta)^2}$$

Thus, the C_p of the chain system can be determined by employing eqs (2) and (5)

Recently, Malanoski and Monson [19] have presented extensive calculations of the equation of state of freely joined chains of tangents hard spheres using Monte Carlo computer simulation, as

$$Z = \frac{p}{\rho KT}\frac{\left(C_0^3 + C_1\eta + C_2\eta^2 + C_3\eta^3 + C_4\eta^4\right)}{(C_0-\eta)^3}$$

where C_0, C_1 C_4 are the coefficients for the ratio function fits of the equations of state of the fluid at different density ranges and are given in Table 2 of the Ref [19] We can determine that

$$\frac{\partial}{\partial\eta}(\eta Z) = \left[(C_0-\eta)(C_0^3 + 2C_1\eta + 3C_2\eta^2 + 4C_3\eta^3 + 5C_4\eta^4)\right.$$

$$\left. +3(C_0^3 + C_1\eta^2 + C_2\eta^3 + C_3\eta^4 + C_4\eta^5)\right]/(C_0-\eta)^4$$

Thus, we can determine the values of C_p/K_B for chain fluids employing Monte Carlo equations of state (7) in eq (5)

In the present work, Wertheim's theory of the flexible chain molecules, called as pearl necklace model has been employed determine the specific heat (C_p) of the chain molecules of different chain lengths We assume that the simple formulation of the specific heat (C_p) of the system of hard spheres will remain valid for the chain molecules by approximating the equation of state of chain molecules instead of equation of state of hard spheres We shall compare the results obtained from the Wertheim's theory with the simulation results of Malanoski and Monson [19] for the pearl necklace model Malanoski and Monson [19] have provided empirical fits to their simulation results of the equation of state for the fluid phase of chain molecules with n ranging from $m = 3$ up to $m = 8$ Therefore, C_p obtained from these empirical fits are considered here as C_p simulation results A comparison between theoretical and simulation values of C_p/NK_B has been shown in table 1 for chain lengths $m=3,4,5$

Table 1 Specific heat (C_p/NK_B) of the pearl-necklace model in the fluid phase from Wertheim's theory and the simulation data

η	(C_p/NK_B)							
	$m=3$		$m=4$		$m=5$		$m=6$	
	TPT	MC	TPT	MC	TPT	MC	TPT	MC
0 20	1 06	1 04	0 86	0 84	0 74	0 68	0 65	0 66
0 25	1 186	1 14	0 98	0 97	0 86	0 81	0 77	
0 30	1 35	1 32	1 14	1 14	1 02	0 98	0 93	0 96
0 35	1 56	1 56	1 35	1 35	1 23	1 20	1 14	
0 40	1 85	1 86	1 63	1 62	1 50	1 48	1 41	
0 45	2 20	2 23	1 99	1 96	1 86	1 83	1 77	

6 We find a good agreement between the theoretical and ilations values However, the small discrepancy at low ues increases with increasing chain length This may be to the characteristic of the first order thermodynamic iriuion theory. More improved theories such as Dimei ence fluid theory [20] and Generalized Flory Dimer theory may improve the results for long chain molecules.

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