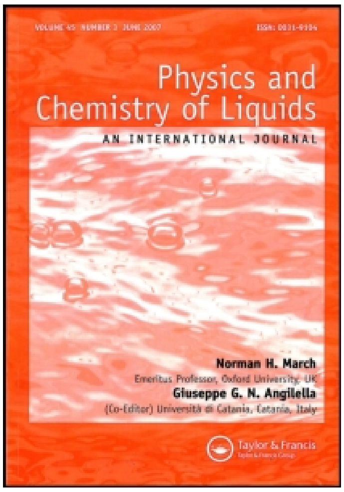

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Calculations of Two and Three-Body Correlation Entropies at the Freezing Points of Soft-Core Fluids: Effect of the Softness on the Correlation Entropy

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CALCULATIONS OF TWO AND THREE-BODY CORRELATION ENTROPIES AT THE FREEZING POINTS OF SOFT-CORE FLUIDS: EFFECT OF THE SOFTNESS ON THE CORRELATION ENTROPY

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Two and three-body correlation entropies of model fluids, in which particles interact each other through the 4th, 6th, 9th and 12th-inverse-power potentials, were calculated from their atomic configurations obtained by molecular dynamics simulations at their freezing points. Besides the soft-core fluid model with the inverse-power potentials, hard-sphere and classical one-component plasma models were employed to provide a comparison with the entropies of the soft-core model. The correlation entropies were plotted as a function of the softness of the potential. These values were also compared with the excess entropies of the hard-sphere and the one-component plasma models at their freezing points.

Keywords: Soft-core; Inverse-power potential; Correlation entropy; Excess entropy

1. INTRODUCTION

The statistical mechanical theory for the correlation entropy of classical liquids at equilibrium has been rederived [1–4]. The theory is based on a systematic expansion of the entropy in terms of the partial N-particle distribution functions originally developed by Green [5] for the canonical ensemble and by Nettleton and Green [6] for grand canonical ensemble. The formulae of the correlation entropies for grand canonical ensemble proposed by Baranyai and Evanse (BE), work well for simple liquid metals. On the basis of this theory, two and three-body correlation entropies of hard-sphere fluids have been calculated for a system generated by Monte Carlo (MC) simulation [7]. Both correlation entropies have also been estimated by Percus-Yevick (PY) and generalized mean spherical (GMS) approximations using Yokoyama-Arai (YA) approximation for three-body correlation entropies [8]. The difference between the sums of the two and three-body correlation entropies calculated with these two methods (MC and GMS) is at most 20% near the freezing point.

On the other hand, the excess entropy of model liquids has been estimated from the thermodynamic functions of some simple systems [9,10]. The excess entropy of a liquid

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is, in general, defined as a difference from the entropy of a perfect gas reference system. Therefore, the sum of the correlation entropies of the model liquid, which can be calculated from the atomic configuration, should be equal to the estimated excess entropy of the model in a thermodynamic way. The purpose of this article is to show the two and three-body correlation entropies of the soft-core (SC) fluids at their freezing points interacting through the inverse-power potentials, $\phi(r) = \varepsilon(\sigma/r)^n$. In this system, in infinite limit of n, the system becomes a hard-sphere (HS) model; it becomes a classical one-component plasma (OCP) model at $n = 1$. Therefore, two and three-body correlation entropies of HS and OCP models at their freezing points were also calculated in order to study the effect of the softness of the inverse-power potentials on the correlation entropies. It is also interesting to observe how the correlation entropies and the excess entropy change with the softness parameter $1/n$.

One can estimate the total entropy by adding the perfect gas entropy and electron contributions to the correlation entropy. This kind of study is important in order to reveal the relation between structural and physical properties of liquids as well as disordered materials.

2. FORMALISM

2.1. Entropy Expression

Two and three-body correlation entropies were calculated within the framework of the configurational entropy formalism by BE, which is summarized as follows: the configurational entropy per particle, that is, the ion motional entropy, s_I, is defined as

$$s_\mathrm{I} = s_\mathrm{PG} + s^{(2)} + s^{(3)} + \cdots, \tag{1}$$

where s_PG is the perfect gas entropy, $s^{(2)}$ the pair correlation entropy, $s^{(3)}$ the triplet correlation entropy per particle and so on. The units of the entropies here are k_B where k_B is the Boltzmann constant. The pair correlation entropy can be written as

$$s^{(2)} = \frac{1}{2}\rho \int g^{(2)}(r) \ln g^{(2)}(r)\, dr + \frac{1}{2}\rho \int (g^{(2)}(r) - 1)\, dr, \tag{2}$$

where $g^{(2)}$ is the two-body correlation function and ρ the average number density of the liquid. The three-body correlation entropy can be written as

$$\begin{aligned} s^{(3)} = {} & \frac{1}{6}\rho^2 \iint g^{(3)}(r, s, t) \ln \delta g^{(3)}(r, s, t)\, dr\, ds \\ & + \frac{1}{6}\rho^2 \iint [g^{(3)}(r, s, t) - g^{(2)}(r) g^{(2)}(s) - g^{(2)}(s) g^{(2)}(t) \\ & - g^{(2)}(t) g^{(2)}(r) + g^{(2)}(r) + g^{(2)}(s) + g^{(2)}(t) - 1]\, dr\, ds, \end{aligned} \tag{3}$$

where $g^{(3)}$ is the triplet correlation function and $r = |\boldsymbol{r}|$, $s = |\boldsymbol{s}|$, and $t = |\boldsymbol{s} - \boldsymbol{r}|$. The irreducible part of the triplet correlation function is defined by $\delta g^{(3)}(r, s, t) = g^{(3)}(r, s, t)/(g^{(2)}(r) g^{(2)}(s) g^{(2)}(t))$.

Although $s^{(2)}$ can be estimated from some diffraction measurements it is difficult to determine $g^{(3)}(r, s, t)$ experimentally. Yokoyana and Arai developed an approximation method for the estimation of $s^{(3)}$ instead of direct calculation by Eq. (3). Details are given in [8] and are summarized briefly here. We define the function, $H(r, s, t)$, in the same way as the work of Egelstaff *et al.* [11], as follows:

$$H(r, s, t) = g^{(3)}(r, s, t) - g^{(2)}(r)g^{(2)}(s)g^{(2)}(t), \tag{4}$$

where $g^{(2)}(r)g^{(2)}(s)g^{(2)}(t)$ is the superposition approximation for $g^{(3)}(r, s, t)$ proposed by Kirkwood [12]. If we rewrite $\delta g^{(3)}(r, s, t)$ as $H(r, s, t) - g(r)g(s)g(t)/g(r)g(s)g(t)$ using the function $H(r, s, t)$ and substitute it for $\delta g^{(3)}(r, s, t)$ of Eq. (3), the first term of (3) can be approximated, under the assumption $g^{(3)}(r, s, t) \ll 2g^{(2)}(r)g^{(2)}(s)g^{(2)}(t)$, as follows:

$$-\frac{1}{6}\rho^2 \iint g^{(3)}(r, s, t) \ln \delta g^{(3)}(r, s, t)\, dr\, ds \approx -\frac{1}{6}\rho^2 \iint H(r, s, t)\, dr\, ds. \tag{5}$$

With the Fourier transformation of $H(r, s, t)$ denoted as $\tilde{H}(Q), \tilde{H}(Q)$ can be separated into three expressions [2]:

$$\tilde{H}(Q) = H_1(Q) + H_2(Q) + H_3(Q), \tag{6}$$

where

$$H_1(Q) = \frac{1}{(2\pi)^3 \rho}[S(Q) - 1] * [S(Q) - 1]^2, \tag{7}$$

$$H_2(Q) = (S(Q) - 1)(S(0) + S(Q) - 1), \tag{8}$$

and

$$\mathrm{H}_3(Q) = -S(0)\rho\left(\frac{\partial S(Q)}{\partial \rho}\right)_T. \tag{9}$$

In the above equations Q is the wavenumber, $S(Q)$ the liquid structure factor and * represents the convolution between $[S(Q)-1]$ and $[S(Q)-1]^2$. $S(0)$ is the structure factor at $Q = 0$. The second term of Eq. (3) can be also expressed by $\tilde{H}(Q)$ using the relation in the appendix of the paper of Mountain and Raveché [2]. Therefore $s^{(3)}$ is approximated by

$$s^{(3)} \approx \tfrac{1}{6}H_1(0) - \tfrac{1}{3}(H_1(0) + H_2(0) + H_3(0)) \tag{10}$$

When the second term, i.e., the three terms in the round brackets of Eq. (10) is omitted, this gives the Kirkwood superposition approximation form for $s^{(3)}$. The YA approximation for $s^{(3)}$ gives good results with regard to the experimental data of the total entropy of the actual liquid metals near the melting points [8]. In a simple liquid at high density near the freezing point the term $H_3(0)$ in Eq. (10) is negligible.

2.2. Molecular Dynamics Simulation

In order to calculate $s^{(2)}$ and $s^{(3)}$ using Eqs. (2), (7–10) of the SC fluids interacting through the inverse-power potentials, we need to estimate values of $g(r)$ and $S(Q)$. Hansen and Schiff [13] evaluated the structure factors and the radial distribution functions for the inverse-power potentials $\phi(r) = \varepsilon(\sigma/r)^n$ $(n = 12, 9, 6, 4, 1)$ at the freezing point by means of MC method. Although they provide the numerical tables of the $g(r)$ and $S(Q)$ in the article, the tables do not contain enough data for integration. Therefore, we carried out molecular dynamics (MD) simulations with the non-dimensional equations of motion using scaled inverse-power potentials to obtain the pair correlation function, $g(r^*)$, where r^* denotes the length scaled by $l = \rho^{-1/3}$. In the equations of motion, the unit of time is scaled by τ:

$$\tau = l\left(\frac{m}{\varepsilon}\right)^{1/2}\left(\frac{l}{\sigma}\right)^{n/2},$$

where m is mass of the particle but this does not appear in the non-dimensional equations of motion. Although the inverse-power potential has the two parameters ε and σ, the thermodynamic state can be simply characterized by one parameter. We choose for the parameter, $\Gamma_{\mathrm{INV}} = \rho\sigma^3(\varepsilon/(k_{\mathrm{B}}T))^{3/n}$, where T is the temperature. We employed 5.54, 2.18,1.33 and 1.15 as the values of Γ_{INV} at the freezing conditions [14] for the 4th, 6th, 9th, and 12th-inverse-power potentials, respectively.

All systems studied in this present work had the number of particles $N = 1000$. In the case of the 4th-inverse-power system we also performed MC simulation with $N = 32\,000$ to estimate the error of the entropies. Next we calculated the $s^{(2)}$ in terms of the following equation instead of Eq. (2):

$$s^{(2)} = -2\pi\int [g(r^*)\ln g(r^*) - \{g(r^*) - 1\}]r^{*2}dr^*. \tag{11}$$

$H_1(0)$ in Eq. (10) can be written in non-dimension form as follows:

$$H_1(0) = \frac{1}{2\pi^2}\int (S(Q^*) - 1)^3 Q^{*2} dQ^*, \tag{12}$$

where Q^* is the reduced wavenumber scaled by l^{-1}. $S(Q^*)$ is the corresponding structure factor which was calculated directly by the atomic configurations obtained from the MD simulations, in the method based on the definition instead of the Fourier transformation of $g(r) - 1$.

3. RESULTS

3.1. Soft-core Model

The typical features of Eqs. (11) and (7) for the SC fluids obtained from the MD simulations are shown in Figs. 1 and 2. Calculated values of $s^{(2)}$ and $s^{(3)}$ are shown in Table I. The error in $s^{(2)}$ was found to be at most 1%. The error for $s^{(3)}$ was less than 10%.

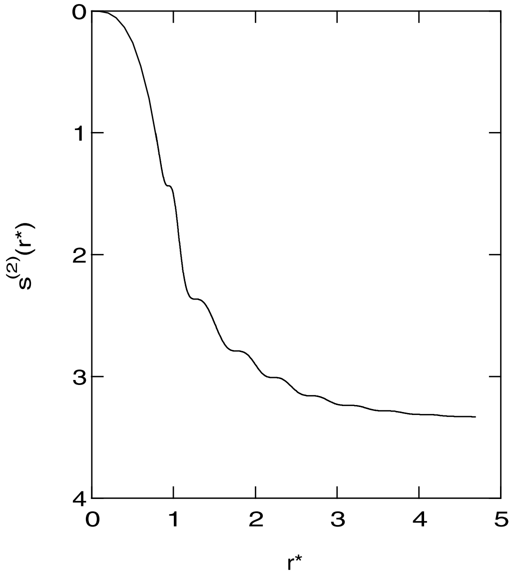

FIGURE 1 Typical behaviour of $s^{(2)}(r^*)$. $s^{(2)}(r^*)$ is expressed as a function of the upper limit of the integration of Eq. (11). The curve stands for the case of $n = 6$. We estimated $s^{(2)}$ as the value of $s^{(2)}(r^*)$ as the largest r^*.

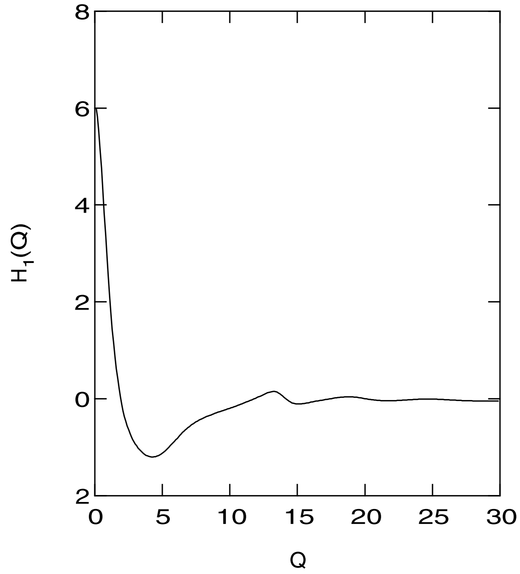

FIGURE 2 Typical behaviour of $H_1(Q)$ of Eq. (7). The curve stands for the case of $n = 6$. We estimated $H_1(Q)$ as the value of $H_1(Q)$ at $Q = 0$.

3.2. Hard-sphere Model

The SC model described with the inverse-power potential becomes the HS model in limit of infinite n. The two and three-body correlation entropies of the HS fluids have been calculated by MC simulation [7], PY and GMS approximations [15,16] with the various reduced densities $\rho\sigma_{\mathrm{HS}}^3$ except at the freezing points, where σ_{HS} is

TABLE I Correlation entropies of soft-core fluids at their freezing points. Numbers in round brackets denote the result of MC simulation with $N = 32000$. The remainder are the results of MD simulations with $N = 1000$

n	4	6	9	12
$s^{(2)}$	−3.33(−3.28)	−3.33	−3.34	−3.69
$s^{(3)}$	−1.45(−1.17)	−1.34	−1.24	−1.41
$s^{(2)} + s^{(3)}$	−4.78(−4.45)	−4.67	−4.58	−5.10

the hard-sphere diameter. It is important to compare the correlation entropies of the HS model with those of the SC model at the freezing point. As can be seen in Table I, $s^{(2)}$ is almost constant up to $n = 9$. The absolute value reaches a maximum at $n = 12$ in the inverse-power potential system. On the other hand, $s^{(2)} + s^{(3)}$ does not systematically vary at first glance.

In this article, we calculated values of $s^{(2)}$ and $s^{(3)}$ of the HS fluid at the freezing point in the same way as in [16], that is by means of the GMS approximation. The thermodynamic state of the HS model can also be described by one parameter. We choose the packing fraction, $\eta = \pi \rho \sigma_{\mathrm{HS}}^3/6$, as the parameter. In the HS model, using η, Eq. (2) can be rewritten a follows:

$$x \equiv r/\sigma_{\mathrm{HS}};$$
$$s^{(2)} = -12\eta \int [g(x) \ln g(x) - \{g(x) - 1\}] x^2 \, dx \tag{13}$$

$H_1(0)$ in the HS model can be expressed as follows:

$$H_1(0) = \frac{1}{12\pi\eta} \int (S(k^*) - 1)^3 k^{*2} \, dk^*, \tag{14}$$

where $k^* \equiv Q\sigma_{\mathrm{HS}}$.

The GMS approximation was introduced by Waisman [17] to obtain values of $g(r)$ so as to satisfy the Carnahan–Staring equation of state [18] for the HS model. Waisman emphasized that the equation of state reproduces very well the computer results up to the packing fraction $\eta = 0.49$, which is the freezing condition of the HS fluid. The solution of the GMS approximation gives the analytic form of $S(Q)$. The values of $g(r)$ obtained by inverse Fourier transformation of $S(Q) - 1$ reproduces the first peak height of the computer results of the HS model even at high densities better than the PY approximation, although the direct correlation function outside the core is assumed by the Yukawa form.

The direct correlation function derived from the GMS approximation is solved as follows:

$$c(x) = \begin{cases} K x^{-1} e^{-z(x-1)} & \text{for } x > 1 \\ a + bx + \dfrac{a\eta x^3}{2} + v\dfrac{1 - e^{-zx}}{zx} + v^2 \dfrac{(\cosh\ zx - 1)}{2Kz^2 x e^z} & \text{for } x < 1 \end{cases} \tag{15}$$

Here a, b, v, K and z can be found with the help of the method of Høye and Stell [19], by solving the following equations one by one:

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

$$y_0 = \frac{2-\eta}{2(1-\eta)^3},$$

$$A = (1-\eta)^2 a,$$

$$p = \frac{(1+2\eta)^2}{(1-\eta)^2},$$

$$U_0 = 6\eta y_0 - A + 1,$$

$$z = \frac{2}{p-A}\left[(U_0 + A - p)\sqrt{A} + \sqrt{(U_0 + A - p)U_{0p}}\right],$$

$$\sigma_z = \frac{1}{2z}\left[\frac{z-2}{z+2} + e^{-z}\right],$$

$$\tau_z = \frac{1}{2z}\left[\frac{z^2 + 2z - 4}{4 + 2z - z^2} + e^{-z}\right],$$

$$U_1 = \left(2 - \sqrt{p}\right)U_0 - \frac{z}{2}\sqrt{(A - p + U_0)U_0},$$

$$y = \frac{4 + 2z - z^2}{2(2+z)}\left(\frac{U_0}{U_1}\right),$$

$$K = \frac{z^2}{6\eta(z+2)^2}\left[\frac{\sigma_z - \tau_z y}{(\sigma_z - \tau_z)y}\right]^2 U_0,$$

$$v = K\left(\frac{1-y}{\sigma_z - \tau_z y}\right),$$

$$b = \frac{1}{4}\left[2vz - \frac{v^2}{K}e^{-z} - 24\eta y_0^2\right].$$

All the parameters above are finally given as functions of η. Thus the structure factor is obtained by the Fourier transformation of Eq. (15) and is expressed, in analytic form as follows:

$$S(k^*) = \frac{1}{1 - \rho C(k^*)},$$

$$\begin{aligned} \rho C(k^*) \quad &= -\frac{24\eta}{k^{*6}}\Bigg\{ + ak^{*3}[\sin k^* - k^* \cos k^*] \\ &+ bk^{*2}[2k^* \sin k^* - (k^{*2} - 2)\cos k^* - 2] \\ &+ \frac{a\eta}{2}[(4k^{*3} - 24k^*)\sin k^* - (k^{*4} - 12k^{*2} + 24)\cos k^* + 24] \\ &+ \frac{vk^{*5}}{z}\left[\frac{1 - \cos k^*}{k*} + \frac{(z \sin k^* + k^* \cos k^*)e^z - k^*}{z^2 + k^{*2}}\right] \\ &+ \frac{v^2 k^{*5}}{2kz^2 e^z}\left[\frac{(z \sinh z)\sin k^* - (k^* \cosh z)\cos k^* + k^*}{z^2 + k^{*2}} - \frac{1 - \cos k^*}{k^*}\right] \\ &- \frac{Kk^{*5}}{z^2 + k^{*2}}[z \sin k^* + k^* \cos k^*]\Bigg\} \end{aligned} \tag{16}$$

We calculate the structure factor from $k^* = 0$ to 10000 by 0.01 so as to estimate the pair distribution function with good accuracy. The values of $g(x)$ were calculated from $x = 1$ to 10 in intervals of 0.001 to obtain the fine peak feature and integrate it precisely to obtain $s^{(2)}$. The detailed calculation process is described in [16]. The results for the correlation entropies are summarized in Table II.

3.3. One-component plasma model

The OCP model is a well-studied system. It corresponds to the inverse-power potential at $n = 1$ and may be regarded as the system with the largest softness among familiar model systems. The thermodynamic state is characterized by a plasma parameter,

$\Gamma_{\mathrm{OCP}} = z^2 e^2 \beta / a$, where $a = (4\pi\rho/3)^{-1/3}$ and $\beta = (k_B T)^{-1}$. Computed structure factor data of the OCP model calculated using a modified HNC equation are provided by Rogers *et al.* [20]. Slattery *et al.* [21] carried out the MC simulations of the OCP model with various Γ_{OCP} and postulates that the freezing point of the OCP model itself exists at $\Gamma_{\mathrm{OCP}} = 178$. Therefore, we can calculate the correlation entropies using

TABLE II Correlation entropies of hard-sphere fluids at their freezing points

$s^{(2)}$	$s^{(3)}$	$s^{(2)} + s^{(3)}$
−4.73	−1.68	−6.41

TABLE III Correlation entropies of one-component plasma model at their freezing points

$s^{(2)}$	$s^{(3)}$	$s^{(2)}+s^{(3)}$
−3.24	−1.85	−5.09

their results. We employed structure factor data for both $\Gamma_{\mathrm{OCP}}=170$ and 180 to calculate $s^{(2)}$ and $s^{(3)}$ at $\Gamma_{\mathrm{OCP}}=178$.

The results for the correlation entropies are shown in Table III. We have to carry out a numerical integration twice to calculate $s^{(2)}$. The numerical data corresponding to r less than the starting position of the first peak of the $g(r)$, which is obtained from the structure factor data, may be regarded as the error for $s^{(2)}$ and was found to be 0.29.

4. EXCESS ENTROPY

The correlation entropies of three model liquids were calculated, on the basis of BE theory, from the structural data of MD and MC simulations. The sum of the series of correlation entropies in Eq. (1) including terms that are of sufficiently high order should equal the excess entropy which is estimated in a thermodynamic way from the free energy of the model system. Comparing the excess entropies with the sum of the calculable correlation entropies, the size of the higher order correlation entropy can be estimated.

Excess entropies of some model fluids have been studied in thermodynamic approaches for a long time. Expressions of excess entropies have been given in analytic form [9,22,23]. In the case of the HS model, we can use the excess entropy expression, ΔS_{CS}, derived from the Carnahan–Starling equation of state: $\Delta S_{\mathrm{CS}}/k_{\mathrm{B}}=\eta(3\eta-4)/(1-\eta)^2$. We applied this function to estimate the value at the freezing point and it was found to be −4.77. For the nth-inverse-power potential system at the freezing point, Rosenfeld provides −4.00, −3.68, −3.64, −3.85 for the excess entropies, $\Delta Sn/k_{\mathrm{B}}$ at $n=4,6,9,12,$ respectively [10]. These values depend on the excess entropy expression by Rosenfeld and the values of Γ_{INV} at the freezing conditions. Therefore, finally, the computer experimental results due to [13,14] are responsible for these values.

In the case of the OCP model, the thermodynamic functions in anlaytic form are obtained by DeWitt [22] and Slatery *et al.* [23]. We employed Young's explicit expression [25] based on Slattery's form,

$$\Delta S_{\mathrm{OCP}}/k_{\mathrm{B}}=B_0\Gamma^{1/4}+B_1\Gamma^{-1/4}+C_0\log\Gamma+D_0;$$

$$B_0=-2.83632,\quad B_1=0.89770,\quad C_0=0.80049,\quad D_0=1.78559,$$

for the excess entropy of the OCP model. We also used the other values for the excess entropies of the OCP model shown by Galam and Hansen [24] and Rosenfeld [10] to estimate the error in ΔS_{OCP}. The result, $\Delta S_{\mathrm{OCP}}/k_{\mathrm{B}}=-4.18\pm0.11$ at the freezing point was obtained.

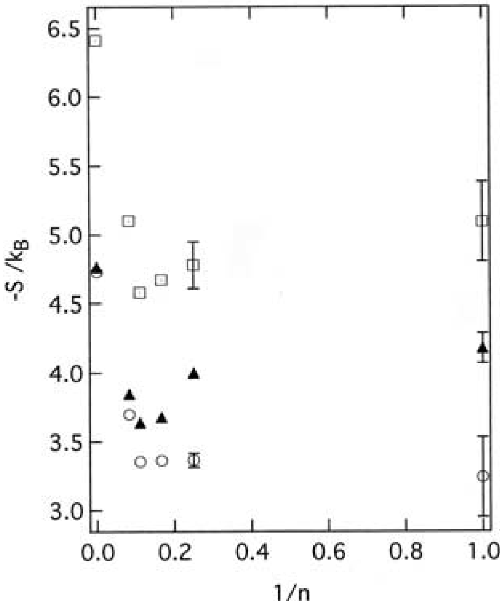

FIGURE 3 Correlation entropies per particle at their freezing points of the OCP model, soft-core and hard-sphere fluids. The open circle represents $s^{(2)}$, open square stands for $s^{(3)} + s^{(2)}$ and full triangle excess entropy. The vertical line indicates the estimated error.

These results are illustrated in Fig. 3 together with the results for the correlation entropies to show more clearly the effect of the softness of the repulsive potentials on the entropy. In Fig. 3, the vertical axis represents entropies ($s^{(2)}$, $s^{(2)} + s^{(3)}$ and excess entropy ΔS) per particle. The horizontal axis represents the strength of the softness of the inverse-power potential. The values for the HS model are plotted at $1/n = 0.0$; the values for the OCP model are at $1/n = 1.0$. It can be seen that the entropy of a non-attractive potential system does not simply change with the softness, although $s^{(2)}$ became almost flat in the region where $1/n > 0.1$, $s^{(2)} + s^{(3)}$ and ΔS have minimum near $n = 9$ ($s^{(3)}$ also has a minimum at $n = 9$, which is not shown in Fig. 3). This implies that there may exist a special geometrical configuration which leads to the minimization of the configurational entropy. The physics behind this is not known at the moment. We can not conclude this speculation for the minimization. Because this minimization originally comes from the old computer simulation results [13,14]. We have to make an effort to study using recent computer simulation results such as works of Agrawal and Kofke [26].

One can say that the excess entropy is always less than the value of $s^{(2)}$ except for the value at $1/n = 0.0$. The two-body correlation entropy of the HS model at the freezing point appears to equal the excess entropy of the HS model. This is because multi-body collision seldom occurs in the HS model. Comparing $s^{(2)} + s^{(3)}$ with the excess entropy, $s^{(2)} + s^{(3)}$ is always much bigger than the excess entropy, that is, the sum of the higher order correlation terms more than the three-body of the configurational entropy, i.e., $s^{(4)} + s^{(5)} + \cdots$ should always have a positive value. However, it is reasonable to say that if we define the sum of the correlation entropies more than two-body as the multi-body correlation entropy, it has a negative value and the absolute value becomes gradually bigger as the softness parameter $1/n$ increases. The multi-body correlation entropy is actually non-existent at the freezing point in the HS model. The effect of the softness on the excess entropy, two-body correlation entropy and multi-body correlation entropy gives positive contributions and is, at most, 1.1 (0.6 unless the minimum at $n=9$ exists), 1.5 and 0.9 k_B, respectively.

Recently Yokoyama [27] has shown, for actual liquid metals data, that the total entropy (thermodynamic entropy) of liquid metals near their melting point can be well explained by the sum of the excess entropy of the HS liquid and an entropy contribution arising from softness of the interatomic forces. The values of the contribution from the softness are about 0.6 k_B for most liquid metals. The basic idea goes back to the work of Young [28]. Yokoyama's work for entropies of actual liquid metals supports the present result.

5. CONCLUSIONS

We have calculated the two and three-body correlation entropies of the inverse-power potentials at $n=4$, 6, 9 and 12 and also for OCP and HS model fluids at their freezing points. The numerical values for the entropies of three model fluids lead to the following conclusions:

(a) The value of the excess entropy at the freezing points of the inverse-power potentials always lies between the values of $s^{(2)}$ and $s^{(2)} + s^{(3)}$.
(b) At the freezing point of HS system, the value of $s^{(2)}$ is almost the same as that of the excess entropy.
(c) If one calls $s^{(3)} + s^{(4)} + \cdots$ the multi-body correlation entropy, it always has a negative value, and the absolute value gradually becomes large as the softness of the repulsive potential increases. The multi-body correlation entropy does not actually exist at the freezing point in HS model,

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