

# Calculation of the Entropies and Chemical Potentials of Hard-Sphere Solutes Solvated in Hard-Sphere Solids Using the Radial Free-Space Distribution Function

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The entropies and chemical potentials of hard-sphere solutes solvated in hard-sphere solids were calculated by Monte Carlo method using the radial free-space distribution function. This method is based on calculating the entropy by comparing the free volume of a molecule with that of an ideal gas, and is applicable even when the size of solute is very large and the solvent is a solid. When the diameter of hard-sphere solute is small the solute molecule behaves as like as a fluid in solid structures, but when the diameter of solute becomes large, a fluid-to-solid phase transition takes place. The fluid-to-solid phase transition occurs at the region of the smaller size of solute with the more increase of solvent density. The least square fit values of analytical form of the radial free-space distribution functions of solute molecules are presented for future uses.

## Introduction

The chemical potential is one of the most important thermodynamic properties since it is a criterion to determine the direction of spontaneous processes. The entropy is involved in the chemical potential, however the theoretical estimation for entropy is not simply made by ensemble average.<sup>1</sup> The insertion method,<sup>2-4</sup> *i.e.*, calculating the probability of inserting a particle into an equilibrated ensemble, has been the most practical one that has been used in Monte Carlo (MC) simulations. The chemical potentials of hard-sphere solutes solvated in hard-sphere fluid solvents have been calculated<sup>5,6</sup> by the insertion method. However the insertion method has a limit when the density of a system is high and the size of solute is very large. This limit is reached when the chemical potentials are greater than about  $14 kT$  because in this case the insertion probability is less than  $10^{-6}$ , *i.e.*, the lowest probability detected when the usual number of simulation trial steps are of the order of millions. In the previous work,<sup>7</sup> the different method employing the radial free-space distribution function (RFSDF) has been used. The method using RFSDF overcomes the difficulties<sup>8</sup> that might arise when the density is high and the size of solute is very large. This method has been provided good results for estimating the free energies of fluid and solid systems with hard-sphere and Lennard-Jones potentials and for calculating the solvation free energies of different sizes of hard-sphere solutes in hard-sphere fluids.<sup>7-9</sup> In this work, the method is applied to the system of hard-sphere solutes with different sizes solvated in hard-sphere solids.

## Method

In order to calculate the entropies and chemical potentials employing the RFSDF of hard-sphere solutes solvated in hard-sphere solids, the same method as in ref. [7] has been used except that the solvent structures are, in this paper, solids instead of fluids. However the method is briefly

explained again.

The RFSDF,  $\zeta(r)$ , is obtained in MC procedure by the following ratio:

$$\zeta(r) = \frac{\text{Acceptances of displacement of } r}{\text{Trials of displacement of } r} \quad (1)$$

$\zeta(r)$  starts from unity at  $r = 0$  and decreases exponentially at large  $r$ . The RFSDF is the distribution function of particle-cavity (including the cavity formed by removing the particle) relations. In the case of hard-sphere fluid and solid, the particle and cavity are interchangeable. The excess entropy over an ideal gas is calculated by comparing the free volumes as follows,

$$S^{ex} = R \ln \left( \frac{V^f}{V_{id}^f} \right) \quad (2)$$

in which  $R$  is the gas constant,  $V^f$  is the molecular free volume, and  $V_{id}^f$  is that of an ideal gas. The free volume  $V^f$  is calculated by integrating the RFSDF.

$$V^f = 4\pi \int_0^{r^f} r^2 \zeta(r) dr \quad (3)$$

where  $r^f$  is a cut-off distance to specify the *molecular* volume and this has been formally defined as half of the average nearest-neighbor distance. When the cut-off distance has been defined, the free volume for an ideal gas is simply  $V_{id}^f = (4/3)\pi(r^f)^3$ , because RFSDF for ideal gas is unity at all values of  $r$ . The cut-off distance for hard sphere fluid solvent,  $r_0^f$ , has been defined<sup>9,10</sup> as follows:

$$r_0^f = \frac{1}{2\rho^{1/3}\sigma} \quad (4)$$

where  $\rho$  is the number density and  $\sigma$  is the diameter of the hard sphere. In order to calculate the free volume of solute that has a different size from the solvent molecule, it is not easy to define the cut-off distance for the solute molecule

surrounded by solvent molecules, but the following mean value has been used<sup>7</sup> as an analogy of the case of pressure in Eq. (7) below,

$$r^f = \frac{(1+d)r_0^f}{2} \quad (5)$$

where  $d$  is the ratio of the diameter of solute to that of solvent and when the sizes of solvent and solute molecules are the same ( $d=1$ ), the cut-off distances become equal to each other. For the excess chemical potential over an ideal gas,  $\mu^{ex}$ , then the entropy term is added to the pressure term,

$$\frac{\mu^{ex}}{kT} = \frac{p^{ex}V}{RT} - \frac{S^{ex}}{R} \quad (6)$$

in which  $k$  is the Boltzmann constant and  $T$  is temperature. The excess internal energy is zero for hard-sphere interactions. The excess pressure of solute is calculated from the radial distribution function (RDF) as follows,<sup>11</sup>

$$\frac{p^{ex}V}{RT} = \frac{2}{3}\pi\rho\left(\sigma\frac{1+d}{2}\right)^3 g_{10}\left(\frac{1+d}{2}\right). \quad (7)$$

In Eq. (7),  $g_{10}$  is the RDF of solvent molecules around a solute molecule, and  $g_{10}((1+d)/2)$  is the value when the surfaces of solute and solvent molecules contact.

For the pressure of solvent,  $p_0^{ex}$ , the following equation has been used.

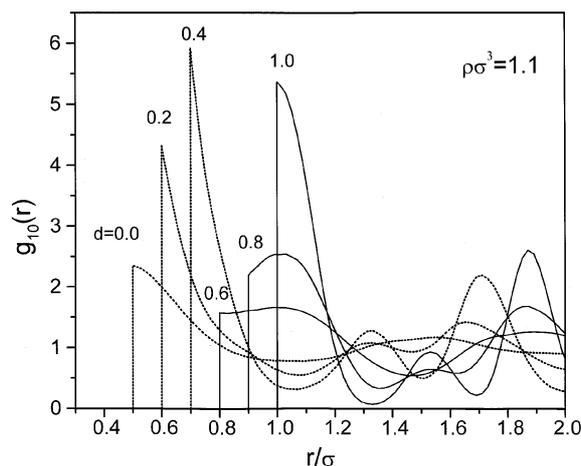
$$\frac{p_0^{ex}V}{RT} = \left(\frac{N-1}{N}\right)\frac{2}{3}\pi\rho\sigma^3 g_{00}(1) + \frac{1}{N}\frac{p^{ex}V}{RT} \quad (8)$$

where  $N$  is the number of molecules used in the simulation and  $g_{00}(1)$  is the value of RDF of solvent-solvent at contact and the last term is a small correction of the contribution of solvent-solute interaction in Eq. (7). For the entropy of solvent molecule, the RFSDF for solvent has been used and the cut-off distance in Eq. (4) has been used. For the entropy of solute molecule, the RFSDF for solute has been calculated separately and the cut-off distance in Eq. (5) has been used.

We have used 108 molecules (107 solvent molecules and one solute molecule) in MC calculations and have taken an average of  $4 \times 10^6$  samplings (trials of move) for solvent molecules and  $2 \times 10^6$  samplings for solute molecule after discarding  $6 \times 10^5$  configurations starting from the initial face-centered-cubic structure. The densities of hard-sphere solids are chosen as  $\rho\sigma^3 = 1.0, 1.1, \text{ and } 1.2$ .

## Results and Discussion

In the previous work,<sup>7</sup> it has been stimulative that the excess chemical potentials over ideal gases were evaluated well using the method explained in the above section for the hard-sphere fluid solution system, and the good results were obtained at high densities and for large solutes. Therefore the results of calculations in this work are also believed reasonable even though there have been no other comparable predictions or calculations so far. The RDFs of solvent molecules around the solute molecule at  $\rho\sigma^3 = 1.1$  for different sizes of solute are shown in Figure 1. As the size of sol-



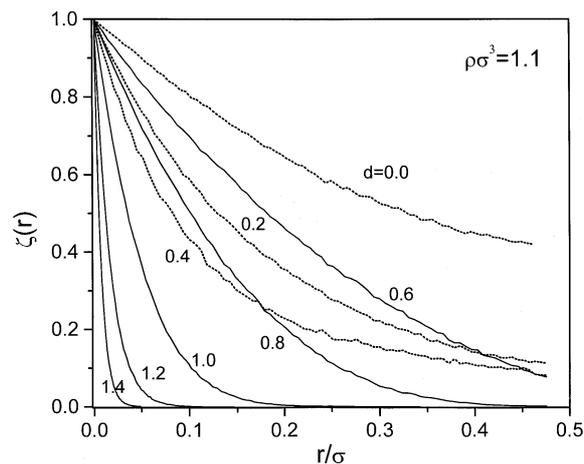
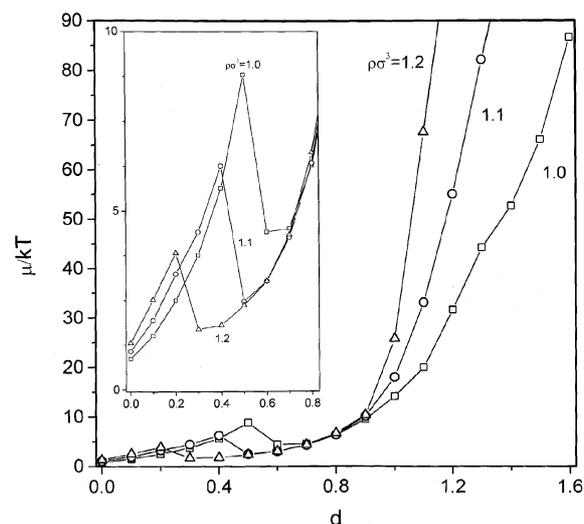
**Figure 1.** The radial distribution functions of hard-sphere solvent molecules around a hard-sphere solute molecule at  $\rho\sigma^3 = 1.1$  for different sizes of solute denoted on the curves. The dotted lines are fluid phases and the solid lines are solid phases.  $\sigma$  is the diameter of solvent molecule.

ute increases, the first peaks of RDF increase but the RDFs of small sizes take on different shapes from those of large sizes, *i.e.*, a phase transition occurs. In case of the small sizes of solute, the solute molecule behaves as like as a fluid even though the main solvent structure is a solid, and for large sizes of solute (even smaller than the size of solvent molecule) the solute becomes a solid. For the fluid phase of solute, the tangents of RDFs at contacting surfaces of solute and solvent molecules are steep, however the slopes for solid phase are low. The negative tangent at contacting surfaces for  $d=0.8$  is interesting, *i.e.*, the highest peak is at  $r = \sigma$ . This means that the lattice of nearest neighbor of solute is not disrupted but maintains the original solid structure so that a big hole as large as the size of solvent molecule is formed. Therefore the solute molecule is located around the middle of the hole and thus the contacting probability is even smaller than the peak at  $r = \sigma$ . (This can be also seen for  $d=0.6$ .) The RDFs for larger solutes than  $d=1.0$  are not shown in the figure since the first peaks are very high. The first peaks can be calculated from the pressure data in Table 1 with Eq. (7).

In Figure 2, the RFSDFs of solute molecule in the cavity surrounded by solvent molecules at the same density as in Figure 1 are shown. From Figure 2, one can see that the RFSDF of solute becomes off from that of an ideal gas (*i.e.*, unity for all values of  $r$ ) as the size of solute becomes large, and can also examine the phase transition between  $d=0.4$  and  $0.6$ . The RDFs and RFSDFs for other densities show similar trend to those of  $\rho\sigma^3 = 1.1$  and therefore they are not shown. The fluid phase and solid phase are verified by the curvature shape of RFSDF: It has been found<sup>10</sup> that when  $-\ln \zeta(r)$  is fitted to the function  $-\ln \zeta(r) = Ar + Br^3$ , the coefficient  $B$  is negative and the function is convex for fluid phase, and the coefficient  $B$  is positive (the function is concave) for solid phase. The least square fit values of the coefficients  $A$  and  $B$  are listed in Table 1 to describe the RFSDFs for future uses. The excess pressures and entropies calculated using

**Table 1.** The excess pressures, entropies, and the chemical potentials of solvent and solute of hard-sphere system and the coefficients<sup>a</sup> *A* and *B* at different solute-solvent ratios

<i>d</i>	Solvent			Solute			<i>A</i>	<i>B</i>
	$\frac{p_0^{ex}V}{RT}$	$-\frac{S^{ex}}{R}$	$\frac{\mu^{ex}}{kT}$	$\frac{p^{ex}V}{RT}$	$-\frac{S^{ex}}{R}$	$\frac{\mu^{ex}}{kT}$		
$\rho\sigma^3 = 1.0$								
0.0	9.33	4.66	13.99	0.54	0.33	0.87	1.730	-0.483
0.1	9.32	4.66	13.98	0.96	0.55	1.51	2.720	-1.348
0.2	9.32	4.67	13.99	1.62	0.87	2.50	4.117	-2.225
0.3	9.39	4.67	14.06	2.49	1.28	3.77	5.674	-2.910
0.4	9.28	4.67	13.95	3.78	1.85	5.63	8.068	-6.596
0.5	9.47	4.69	14.16	6.23	2.60	8.83	11.901	-17.527
0.6	9.36	4.67	14.03	3.03	1.39	4.42	4.973	0.516
0.7	9.24	4.66	13.90	2.74	1.76	4.50	5.014	9.121
0.8	9.26	4.67	13.93	3.93	2.47	6.40	6.651	16.203
0.9	9.32	4.69	14.01	6.99	3.45	10.44	9.779	23.980
1.0	9.26	4.68	13.95	9.26	4.75	14.01	14.714	69.965
1.1	9.21	4.70	13.91	14.63	5.95	20.58	22.642	105.630
1.2	9.48	4.74	14.22	24.68	7.14	31.81	33.905	135.76
1.3	9.69	4.80	14.49	37.39	8.24	45.63	48.027	168.25
1.4	10.31	4.89	15.20	44.92	8.82	53.74	55.525	379.72
1.5	11.12	5.00	16.12	61.36	9.78	71.14	73.594	599.41
1.6	12.35	5.13	17.48	86.73	10.77	97.50	100.06	854.99
$\rho\sigma^3 = 1.1$								
0.0	12.34	5.58	17.92	0.68	0.39	1.08	2.181	-1.020
0.1	12.43	5.59	18.02	1.26	0.68	1.94	3.554	-2.284
0.2	12.40	5.58	17.98	2.16	1.08	3.24	5.329	-3.061
0.3	12.36	5.59	17.95	2.96	1.45	4.41	6.317	-5.876
0.4	12.36	5.60	17.96	4.68	1.57	6.25	8.466	-18.175
0.5	12.39	5.59	17.98	1.47	0.99	2.46	2.904	3.334
0.6	12.36	5.59	17.95	1.85	1.18	3.03	3.408	9.025
0.7	12.26	5.59	17.85	2.52	1.73	4.25	4.412	17.587
0.8	12.30	5.59	17.89	3.69	2.65	6.35	6.272	36.153
0.9	12.20	5.59	17.79	6.13	3.96	10.08	10.121	83.821
1.0	12.26	5.60	17.86	11.87	5.63	16.50	19.004	190.66
1.1	12.48	5.64	18.12	25.88	7.32	33.20	36.518	411.79
1.2	12.96	5.72	18.68	45.63	8.78	54.41	63.328	673.22
1.3	14.23	5.84	20.07	72.63	10.35	82.98	95.265	2531.7
1.4	16.06	6.01	22.07	116.84	11.54	128.38	141.90	4555.9
1.5	19.72	6.24	25.96	235.8	13.7	249.5	286.51	49870.
$\rho\sigma^3 = 1.2$								
0.0	18.80	6.84	25.64	0.83	0.47	1.30	2.630	-1.012
0.1	18.98	6.84	25.82	1.67	0.84	2.51	4.470	-2.650
0.2	18.91	6.85	25.76	2.59	1.20	3.79	5.992	-0.343
0.3	19.01	6.86	25.87	1.13	0.57	1.70	2.474	0.447
0.4	18.88	6.84	25.72	1.30	0.67	1.97	2.614	2.358
0.5	19.01	6.85	25.86	1.50	0.86	2.36	2.862	6.106
0.6	18.96	6.84	25.80	1.85	1.20	3.05	3.362	13.061
0.7	19.01	6.85	25.86	2.49	1.85	4.34	4.216	30.385
0.8	18.81	6.84	25.65	3.77	2.94	6.71	6.099	75.586
0.9	18.92	6.85	25.77	6.91	4.53	11.44	11.193	229.97
1.0	18.76	6.85	25.61	18.01	6.85	24.86	27.977	1115.5
1.1	19.48	6.93	26.41	57.71	9.53	67.24	81.023	4612.9
1.2	21.86	7.15	29.01	121.9	11.6	133.5	159.56	19425.4
1.3	27.00	7.41	34.41	254.4	14.5	268.9	382.68	355350.

<sup>a</sup> The coefficients of the function  $-\ln \zeta(r) = Ar + Br^3$ .**Figure 2.** The radial free-space distribution functions of a hard-sphere solute molecule surrounded by hard-sphere solvent molecules at  $\rho\sigma^3 = 1.1$  for different sizes of solute denoted on the curves. The dotted lines ( $d = 0.0, 0.2,$  and  $0.4$ ) are fluid phases and the solid lines ( $d = 0.6, 0.8, 1.0, 1.2,$  and  $1.4$ ) are solid phases.  $\sigma$  is the diameter of solvent molecule.**Figure 3.** The excess chemical potentials of hard-sphere solutes of different sizes solvated in hard-sphere solids at the densities denoted on the curves. Inlet is the same for small sizes of solute but the scale of vertical axis for the chemical potential is expanded.

these two functions (RDF with Eq. (7) and RFSDF with Eqs. (2) and (3), respectively) and the excess chemical potentials are given in Table 1. The error ranges are not given but not large (see ref. [7]) and these can be estimated as the difference of the values of solvent and solute for  $d = 1$ . Those values must be identical and so the differences indicate the fluctuation range of this calculation. The excess chemical potentials of solute in Table 1 are plotted in Figure 3. The phase transition is clearly seen in Figure 3. The phase transition occurs at the smaller size of solute as the more increase of the solvent density. In other words, the higher density solid melts by inserting the smaller solute. The chemical potentials over about  $14 kT$  cannot be obtained by the insertion method and the chemical potentials of solid phase cannot be calculated by integrating the pressure (equation of

state) since there exists a phase transition. However these difficulties are overcome in this method.

One of the main advantages of this method is that the entropy and chemical potential are calculated for the system of high density solvent and large solute. We can also calculate the pressure and the entropy separately in one simulation. And another importance is that the entropy of a *single* molecule (solute) can be calculated by tracing the molecule separately from other (solvent) molecules. When a small number of molecules are used in the simulation, the effect of the solute size on pressure could be larger (see the solvent pressures in Table 1) than the case with infinite number of molecules in the simulation. Therefore, we are studying the effect of the number of molecules in simulations.

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