

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/5896885>

# The free energy of the metastable supersaturated vapor via restricted ensemble simulations

ARTICLE in THE JOURNAL OF CHEMICAL PHYSICS · NOVEMBER 2007

Impact Factor: 2.95 · DOI: 10.1063/1.2794752 · Source: PubMed

---

CITATIONS

7

---

READS

27

## 3 AUTHORS:



**Chu Nie**

Wuhan University

**10** PUBLICATIONS **74** CITATIONS

SEE PROFILE



**Jun Geng**

State Nuclear Power Technology Corporation

**9** PUBLICATIONS **16** CITATIONS

SEE PROFILE



**W. H. Marlow**

Texas A&M University

**77** PUBLICATIONS **809** CITATIONS

SEE PROFILE

# The free energy of the metastable supersaturated vapor via restricted ensemble simulations. II. Effects of constraints and comparison with molecular dynamics simulations

Chu Nie,<sup>1,a)</sup> Jun Geng,<sup>2</sup> and W. H. Marlow<sup>2</sup>

<sup>1</sup>*School of Physics and Information Engineering, Jiangnan University, Wuhan 430056, People's Republic of China*

<sup>2</sup>*Department of Nuclear Engineering, Texas A&M University, College Station, Texas 77843, USA*

(Received 6 February 2008; accepted 9 May 2008; published online 19 June 2008)

Extensive restricted canonical ensemble Monte Carlo simulations [D. S. Corti and P. Debenedetti, *Chem. Eng. Sci.* **49**, 2717 (1994)] were performed. Pressure, excess chemical potential, and excess free energy with respect to ideal gas data were obtained at different densities of the supersaturated Lennard-Jones (LJ) vapor at reduced temperatures from 0.7 to 1.0. Among different constraints imposed on the system studied, the one with the local minimum of the excess free energy was taken to be the approximated equilibrium state of the metastable LJ vapor. Also, a comparison of our results with molecular dynamic simulations [A. Linhart *et al.*, *J. Chem. Phys.* **122**, 144506 (2005)] was made. © 2008 American Institute of Physics. [DOI: [10.1063/1.2937893](https://doi.org/10.1063/1.2937893)]

## I. INTRODUCTION

The thermal properties of the supersaturated vapor are interesting and important to know because of their scientific and engineering applications. Numerous research efforts contribute to this field with their special interests.<sup>1–19</sup> For example, some focus on the free energy barrier of the nucleus, critical size of the liquidlike drop, or homogeneous condensation of the supersaturated vapor,<sup>1–13</sup> some works discuss the failure of the integral equation with (Percus–Yevick) or hypernetted chain approximation when applied to metastable systems,<sup>14,15</sup> while little work has been reported dealing with the thermal properties of the supersaturated vapor itself.<sup>16–22</sup>

Baidakov and Protesenko<sup>16</sup> pointed out that when dealing with a metastable system with Monte Carlo (MC) or molecular dynamics (MD) simulation methods, a long range cutoff of least 5 or 6 times  $\sigma$ , where  $\sigma$  is the hard sphere radius, is essential. Corti and Debenedetti<sup>18</sup> emphasized that the difference of equilibrium between the normal state and the metastable state lies in the number of configurations appearing in the two kinds of systems. For a normal state, the probability of the appearance of a configuration is governed by the Boltzmann factor and the higher the system energy is, the lower is its probability to appear. However, in the metastable system, there exists an energy barrier; once the system overcomes the barrier, a bifurcation of the system elements occurs, i.e., it goes to phase separation. Therefore, the central task for a simulation in the metastable region is to prevent the system from going to phase separation. They divided the system into small three-dimensional cells and limit the number of particles in each cell to remain a certain number; thus, the phase separation is effectively prohibited. They also pointed out that the way to prevent phase separation is not

unique. Their method is something similar to global density constraint; however, some other technique might also work, for example, to limit the maximum density of the surroundings of a particle and so on.

Other researchers<sup>1,6–8</sup> imposed a different constraint on the system when studying the free energy barrier of homogeneous condensation. They defined clusters by identifying the mean-center distance between atoms and considered two atoms to be in the same cluster only if their mean-center distance is less than  $1.5\sigma$ . By limiting the maximum in an atomic cluster, the system could be maintained in its one phase state. This method is efficient when studying the free energy barrier but not suitable to study the thermal properties of supersaturated vapor. Linhart *et al.*<sup>19</sup> developed a MD simulation method to study the thermal properties of the supersaturated vapor up to spinodal density at different temperatures. They average the thermal properties before the system goes to phase separation. They used the instantaneous pressure, the numbers of atoms in the largest cluster, and the number of atoms not belonging to any cluster as the indication of phase separation. What they found is that the atomic cluster exists even near the spinodal density, as would be expected in the coexistence region. Hence, simply limiting the distance between two atoms is not sufficient to prevent phase separation because by doing so, too many configurations will be eliminated. However, two aspects of their method have shortcomings. First, their method requires varying the system size to maintain a longer induction period especially when density approaches spinodal. It is also very interesting to point out that no conclusion has been reached on the system size of metastable liquid simulation. For example, in Ref. 20, the authors found that the metastable phase can exist longer the smaller the box is. This is probably because small simulation systems suppress phase separation, in which large density fluctuations leading to phase separation are difficult to create. Thus, small simulation sys-

<sup>a)</sup>Electronic mail: niechu@hotmail.com.

tems allow reaching spinodal more closely. However, in our work, in order to eliminate the effects of periodic boundary conditions, we choose the system size relatively large. Second, their method provides no quantitative criteria for identifying the phase separation. Because the instantaneous pressure, maximum number in an atomic cluster, and the number of atoms not belonging to any cluster all vary continuously in the coexistence region and they do not evolve like step functions, one has to judge phase separation based on their experience and different persons may have different judgment. Therefore, uncertainty will be introduced in this stage.

Recently, we reported the pressure, excess chemical potential, and excess free energy, with respect to ideal gas data at different densities of the supersaturated LJ vapor at the reduced temperature of 0.7 with restricted canonical ensemble MC simulation method.<sup>21</sup> At each density studied, we imposed different constraints on the system and found that those densities below the spinodal density would exhibit a free energy local minimum, as discussed in Ref. 18, which is close to the equilibrium state of the metastable system. In that work, we only performed simulations at reduced temperature  $T^*=0.7$ , where  $T^*=kT/\varepsilon$ , and in this work we extend the simulation from  $T^*=0.7$  to 1.0. With the data obtained, we may estimate the thermal properties, as well as the spinodal densities at different temperatures.

## II. METHODS AND SIMULATIONS

Here, we recapitulate the methodology we used in our previous work.<sup>21</sup> In this work, the vapor is modeled by simulations with Lennard-Jones (LJ) model interactions for atoms,

$$u(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right]. \quad (2.1)$$

First, divide the system into subcells based on the number of atoms and density of the system studied. The length of the cubic subcell is taken with the following relations:

$$l = \frac{L}{N^{(1/3)}}, \quad (2.2)$$

where  $L$  is the length of an edge of the simulation box and  $N$  is the total number of particles during simulation. Therefore, the ideal homogenous case should correspond to one atom per cell. However, density fluctuations exist and limiting the maximum number of atoms in each subcell to  $d_{\max}$  may help to maintain the one phase state for the system being studied. For a given density, a series of runs starts from  $d_{\max}$ , when no number limitation is imposed onto the subcell, to  $d_2$ , when only two atoms are allowed to remain in one subcell; otherwise, the trial movement of a selected atom will be rejected. For each run, the excess chemical potential and pressure are averaged and recorded. With the obtained excess chemical potential and pressure, the excess free energy can be computed with the following formula:

$$f^{\text{ex}} = \mu^{\text{ex}} - P^{\text{ex}}/\rho, \quad (2.3)$$

where  $f^{\text{ex}}$  is the excess free energy per particle,  $\mu^{\text{ex}}$  is the

excess chemical potential, and  $P^{\text{ex}}$  is the excess pressure of the system with respect to the ideal case. In this work, initially, all the atoms were placed on a simple cubic lattice. For all simulation, the system size was set at least to  $40\sigma$ . The number of steps to reach equilibrium is  $10 \times 10^6$  moves, and another  $200 \times 10^6$  moves were used to sample the phase space. The cutoff distance is set to be  $8.0\sigma$ , and beyond the cut off distance, standard long range corrections were employed. The simulations are carried out at  $T^*=0.7, 0.75, 0.8, 0.9$ , and  $1.0$ , where  $T^*=kT/\varepsilon$ . For  $T^*=0.7, 0.75$ , and  $0.8$ , the number of particles involved in the simulation is 3375, and for  $T^*=0.9$  and  $1.0$ , the numbers of particles involved in the simulation are 5832 and 6859, respectively. The excess chemical potential is measured by performing the brute force sampling of  $\exp(-\beta u)$ , where it is the energy increase brought by the insertion of a test atom. To see the original idea of the atom insertion method, the reader may go to Ref. 23 and our program is written based on the classical textbooks on molecular simulation.<sup>24,25</sup>

## III. RESULT AND DISCUSSION

Table I gives simulation results for the excess free energy per particle, pressure, and constraints imposed on the supersaturated vapor system. Actually, the excess free energy listed in Table I is defined by

$$f' = \mu^{\text{ex}} - (P^{\text{id}} + P^{\text{ex}})/\rho. \quad (3.1)$$

It does not eliminate the ideal partial contribution to the free energy per particle; however, the inclusion of the ideal part of pressure does not affect the comparison of the excess free energy for the same density. Together with Table I in Ref. 21, the current work gives a relatively complete table of all our simulation result from  $T^*=0.7$  to  $1.0$ . We note that for most of the simulations with the same density, as the constraint number  $d_{\max}$  changes, the free energy changes and there is a local minimum of the free energy. As we pointed in Ref. 21, for a certain constraint imposed on the system, sometimes the system may very closely approach the equilibrium configuration; hence the excess free energy per particle exhibits a local minimum. With the loosening of the constraint, the system gradually starts phase separation, until, finally, full phase separation occurs when the system has a larger excess free energy compared with that of gas phase. This is the reason why the excess free energy of the system finally decreases. The state with the local minimum of free energy should be very close to the equilibrium state and the thermal properties obtained under that constraint can be viewed as the approximate thermal properties of that state. Thus, most states in Table I can be easily determined and only some exceptions exist, for example,  $T^*=0.75$  and  $\rho\sigma^3=0.035$ . At a first glance, the series of data has no local minimum, but this does not mean the failure of our method. Because we only imposed coarse constraints on the system studied based on the number of particles and system size, we perhaps missed the local minimum due to this coarse selection. Observing the data for 0.035, they are smooth and we may apply the polynomial interpolation to find the local minimum if we do not want to introduce the extra labor to locate the local mini-

TABLE I. Simulation results for the excess free energy [actually, in the table,  $f' = \mu^{\text{ex}} - (P^{\text{id}} + P^{\text{ex}})/\rho$  is listed] and constraints imposed on the system of supersaturated vapor. The cutoff distance was  $r_c = 8.0\sigma$ .

$\rho\sigma^3$	$\rho\sigma^3/\varepsilon$	$f'/\varepsilon$	$d_{\text{max}}$
$T^* = 0.75$			
0.030	0.016 51	-1.0651	4
	0.016 45	-1.0762	5
	0.016 32	-1.0824	6
	0.016 20	-1.0852	7
	0.016 16	-1.0870	8
	0.015 97	-1.0889	9
	0.013 71	-1.0853	10
0.035	0.018 20	-1.1171	4
	0.017 91	-1.1320	5
	0.017 58	-1.1405	6
	0.017 30	-1.1450	7
	0.015 85	-1.1457	8
	0.013 13	-1.1320	9
	0.010 14	-1.1917	10
0.04	0.018 87	-1.1888	5
	0.018 89	-1.2009	6
	0.016 34	-1.1982	7
0.045	0.020 22	-1.2218	4
	0.019 21	-1.2441	5
	0.017 35	-1.2516	6
	0.011 70	-1.2277	7
0.05	0.020 53	-1.2765	4
	0.018 76	-1.3009	5
	0.013 94	-1.3010	6
	0.004 80	-1.2727	7
$T^* = 0.80$			
0.03	0.018 46	-1.0691	4
	0.018 33	-1.0783	5
	0.018 24	-1.0825	6
	0.018 21	-1.0843	7
	0.018 20	-1.0852	8
	0.018 16	-1.0857	9
	0.018 17	-1.0860	10
0.035	0.020 44	-1.1143	4
	0.020 24	-1.1248	5
	0.020 09	-1.1302	6
	0.020 02	-1.1328	7
	0.019 94	-1.1340	8
	0.019 84	-1.1351	9
	0.018 81	-1.1286	10
0.04	0.022 09	-1.1590	4
	0.021 76	-1.1775	5
	0.021 54	-1.1801	6
	0.021 29	-1.1824	7
	0.020 68	-1.1828	8
	0.017 27	-1.1630	9
	0.011 51	-1.1347	10
0.45	0.023 37	-1.2044	4
	0.022 90	-1.1291	5
	0.022 43	-1.2276	6
	0.021 33	-1.2301	7

TABLE I. (Continued.)

$\rho\sigma^3$	$\rho\sigma^3/\varepsilon$	$f'/\varepsilon$	$d_{\text{max}}$
0.05	0.015 86	-1.1952	8
	0.024 30	-1.2491	4
	0.023 47	-1.2650	5
	0.022 46	-1.2761	6
	0.017 01	-1.2513	7
0.055	0.024 86	-1.2932	4
	0.023 46	-1.3111	5
	0.019 75	-1.3101	6
	0.009 05	-1.2592	7
0.06	0.024 94	-1.3387	4
	0.022 44	-1.3615	5
	0.012 24	-1.3090	6
	0.000 82	-1.2555	7
$T^* = 0.90$			
0.03	0.021 97	-1.1010	4
	0.021 88	-1.1069	5
	0.021 85	-1.1097	6
	0.021 82	-1.1103	7
	0.021 81	-1.1105	8
	0.021 81	-1.1107	9
	0.021 81	-1.1104	10
0.04	0.027 03	-1.1676	4
	0.026 88	-1.1757	5
	0.026 80	-1.1793	6
	0.026 74	-1.1796	7
	0.026 74	-1.1814	8
	0.026 75	-1.1819	9
	0.026 75	-1.1813	10
0.05	0.030 94	-1.2340	4
	0.030 64	-1.2436	5
	0.030 50	-1.2484	6
	0.030 38	-1.2513	7
	0.030 36	-1.2525	8
	0.030 29	-1.2519	9
	0.027 34	-1.2338	10
0.06	0.033 67	-1.3007	4
	0.033 08	-1.3116	5
	0.032 70	-1.3188	6
	0.031 20	-1.3181	7
	0.023 43	-1.2791	8
	0.016 56	-1.2528	9
	0.012 98	-1.2858	10
0.07	0.035 01	-1.3642	4
	0.034 07	-1.3810	5
	0.029 14	-1.3717	6
	0.017 31	-1.3272	7
0.08	0.034 88	-1.4299	4
	0.029 80	-1.4316	5
	0.012 44	-1.3600	6
	0.005 03	-1.4032	7
0.085	0.034 38	-1.4638	4
	0.023 56	-1.4351	5
	0.008 02	-1.4148	6

TABLE I. (Continued.)

$\rho\sigma^3$	$\rho\sigma^3/\varepsilon$	$f'/\varepsilon$	$d_{\max}$
	0.000 60	-1.4619	7
	$T^*=1.00$		
0.04	0.031 74	-1.2025	4
	0.031 66	-1.2081	5
	0.031 62	-1.2110	6
	0.031 61	-1.2114	7
0.05	0.037 12	-1.2533	4
	0.036 99	-1.2595	5
	0.036 92	-1.2619	6
	0.036 91	-1.2632	7
0.06	0.041 46	-1.3030	4
	0.412 7	-1.3107	5
	0.411 9	-1.3142	6
	0.411 3	-1.3152	7
0.07	0.447 6	-1.3534	4
	0.044 50	-1.3609	5
	0.044 36	-1.3669	6
	0.044 22	-1.3676	7
0.08	0.046 98	-1.4022	4
	0.046 55	-1.4130	5
	0.046 16	-1.4167	6
	0.044 73	-1.4145	7
0.09	0.048 14	-1.4517	4
	0.047 41	-1.4658	5
	0.042 33	-1.4568	6
	0.033 72	-1.4536	7
0.1	0.047 97	-1.5002	4
	0.041 28	-1.4943	5
	0.029 36	-1.4802	6
	0.028 86	-1.5368	7

mum. We perform the polynomial interpolation for the 0.035 case and the result is displayed in Fig. 1, which clearly tells us that the location of the free energy minimum is between  $d_{\max}=7$  and  $d_{\max}=8$ . Thus, we may conclude that the pressure for 0.035 under  $T^*=0.75$  is between 0.017 30 and 0.017 58. The other exception is for  $T^*=1.0$  and  $\rho\sigma^3=0.1$  and  $T^*=1.0$  and  $\rho\sigma^3=0.04$ , where no local minimum of free energy is found. Apparently, for that case, we have not reached the local minimum of free energy because of the fact that we did not search for the  $d_{\max}\leq 3$  and  $d_{\max}\geq 7$  cases.

Figures 2 and 3 show the comparisons of pressure from our simulation and those from Ref. 19 at  $T^*=0.75$  and  $T^*=1.0$ , respectively. It is obvious that at higher temperature, both results correspond very well but at low temperature the discrepancy is large. At this stage the reason why the huge discrepancy arises at low temperature is not clear; it may be ascribed to the uncertainties in identifying the beginning and ending of the induction period in Ref. 19 or the constraints imposed on the system in our simulation.

We would also like to estimate the spinodal density for a given temperature with the simulated data. Here, we omit

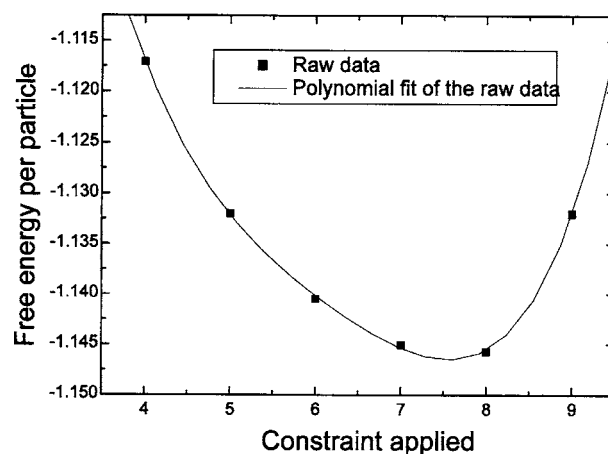


FIG. 1. Polynomial interpolation on the free energies for different constraints imposed on to  $T^*=0.75$  and  $\rho\sigma^3=0.035$ .

this stage because our data do not span a sufficient range to calculate this density. Our purpose here is to test the robustness of our method for a large range of densities and temperatures.

#### IV. SUMMARY

In this work we extend our simulation of free energies of the supersaturated LJ vapor from  $T^*=0.7$  to 1.0 and compared our data with those reported in Ref. 19. As concluding remarks, several things have to be pointed out. First, compared with the method used in Ref. 19, our method provides an effective way to identify the configurations which belong to the phase separation or close to the equilibrium of the metastable state, and it requires no judgment to determine the beginning of phase separation; second, our method is not difficult to apply. On average, four or five runs are enough to determine the thermal properties at given densities because the polynomial interpolation could be very useful when it is hard to determine the local minimum of the free energy due to the smoothness of the free energy data. Third, the system size remains unchanged during simulations for a certain temperature. In our method, what is required is to lower the  $d_{\max}$  value; thus, there is no need to increase the system size in

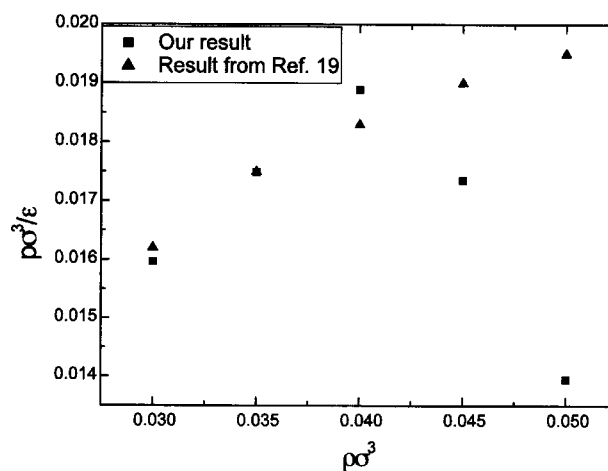
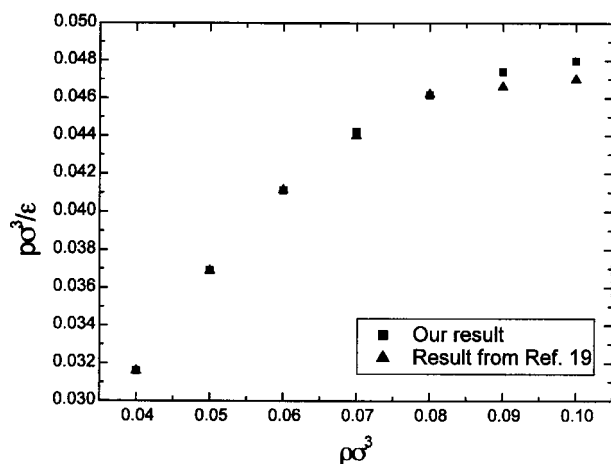


FIG. 2. Pressure-density data at  $T^*=0.75$ .

FIG. 3. Pressure-density data at  $T^*=1.0$ .

order to obtain longer induction time. Finally, our method is easy to extend to more complex molecular systems such as the water case.

We also need to point out that the discrepancies arising in the low temperature cases are not fully resolved. Further investigations are needed to explore the exact reasons for this disagreement with prior work.

## ACKNOWLEDGMENTS

This work was partially supported by the Texas A&M University Center for Atmosphere Chemistry and the Environment.

- <sup>1</sup> P. R. Wolde and D. Frenkel, *J. Chem. Phys.* **109**, 9901 (1998).
- <sup>2</sup> D. W. Oxtoby and R. Evans, *J. Chem. Phys.* **89**, 7521 (1988).
- <sup>3</sup> X. C. Zeng and D. W. Oxtoby, *J. Chem. Phys.* **94**, 4472 (1991).
- <sup>4</sup> R. M. Nyquist, V. Talanquer, and D. W. Oxtoby, *J. Chem. Phys.* **103**, 1175 (1995).
- <sup>5</sup> V. Talanquer and D. W. Oxtoby, *J. Chem. Phys.* **112**, 851 (1999).
- <sup>6</sup> B. Senger, P. Schaaf, D. S. Corti, R. Bowles, J. C. Vogel, and H. Reiss, *J. Chem. Phys.* **110**, 6421 (1999).
- <sup>7</sup> K. J. Oh and X. C. Zeng, *J. Chem. Phys.* **110**, 4471 (1999).
- <sup>8</sup> K. J. Oh and X. C. Zeng, *J. Chem. Phys.* **112**, 294 (2000).
- <sup>9</sup> Z. Kozisek, K. Sato, P. Demo, and A. M. Sveshnikov, *J. Chem. Phys.* **120**, 6660 (2004).
- <sup>10</sup> D. I. Zhukhovitskii, *J. Chem. Phys.* **103**, 9401 (1995).
- <sup>11</sup> T. Kraska, *J. Chem. Phys.* **124**, 054507 (2006).
- <sup>12</sup> D. W. Oxtoby, *J. Phys.: Condens. Matter* **4**, 7627 (1992).
- <sup>13</sup> E. Ruckenstein and Y. S. Djikaev, *Adv. Colloid Interface Sci.* **118**, 51 (2005).
- <sup>14</sup> G. Sarkisov and E. Lomba, *J. Chem. Phys.* **122**, 214504 (2005).
- <sup>15</sup> A. T. Peplow, R. E. Beardmore, and F. Bresme, *Phys. Rev. E* **74**, 046705 (2006).
- <sup>16</sup> V. G. Baidakov and S. P. Protesenko, *High Temp.* **41**, 195 (2003).
- <sup>17</sup> G. Sh. Boltachev and V. G. Baidakov, *High Temp.* **41**, 270 (2003).
- <sup>18</sup> D. S. Corti and P. Debenedetti, *Chem. Eng. Sci.* **49**, 2717 (1994).
- <sup>19</sup> A. Linhart, C. C. Chen, J. Vrabec, and H. Hasse, *J. Chem. Phys.* **122**, 144506 (2005).
- <sup>20</sup> L. G. MacDowell, V. K. Shen, and J. R. Errington, *J. Chem. Phys.* **125**, 034705 (2006).
- <sup>21</sup> N. Chu, G. Jun, and W. H. Marlow, *J. Chem. Phys.* **127**, 154505 (2007).
- <sup>22</sup> A. R. Imre, G. Mayer, G. Hazi, R. Rozas, and T. Kraska, *J. Chem. Phys.* **128**, 114708 (2008).
- <sup>23</sup> B. Widom, *J. Chem. Phys.* **39**, 2808 (1963).
- <sup>24</sup> M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Oxford University Press, Oxford, 1989).
- <sup>25</sup> D. Frenkel and B. Smit, *Understanding Molecular Simulation* (Academic, New York, 1996).