PHYSICAL REVIEW E **75**, 061204 (2007)

Algebraic perturbation theory for dense liquids with discrete potentials

Artur B. Adib[*]
Laboratory of Chemical Physics, NIDDK, National Institutes of Health, Bethesda, Maryland 20892-0520, USA

(Received 27 January 2007; revised manuscript received 9 April 2007; published 20 June 2007)

A simple theory for the leading-order correction $g_1(r)$ to the structure of a hard-sphere liquid with discrete (e.g., square-well) potential perturbations is proposed. The theory makes use of a general approximation that effectively eliminates four-particle correlations from $g_1(r)$ with good accuracy at high densities. For the particular case of discrete perturbations, the remaining three-particle correlations can be modeled with a simple volume-exclusion argument, resulting in an algebraic and surprisingly accurate expression for $g_1(r)$. The structure of a discrete "core-softened" model for liquids with anomalous thermodynamic properties is reproduced as an application.

DOI: 10.1103/PhysRevE.75.061204 PACS number(s): 61.20.Gy, 61.20.Ne, 05.20.Jj

I. INTRODUCTION

Although in principle the properties of complex physical systems can be computed to arbitrary accuracy through computer simulations, perturbation theory remains instrumental across quantum, classical, and statistical mechanics. Its utility is apparent whenever one is interested in getting quantitative insights into the behavior of a system under different conditions, a task that would otherwise require several—often costly—simulations spanning the desired parameters. The underlying assumption is that there exists a well-characterized reference system, the properties of which are relatively similar to that of the system of interest, so that discrepancies between the two can be quantified through a small parameter expansion. The use of a perturbative approach is then justified if the leading-order terms in this expansion can be computed with greater ease than those required by exact methods.

When applied to the structure of simple atomic liquids, in which the interaction potential is comprised of a small, smooth and short-ranged attractive component outside a sharply repulsive core, liquid-state perturbation theory [1] takes on a especially simple form: According to the Weeks-Chandler-Andersen theory (see, e.g., Ref. [2]), the structure of such systems is largely dominated by the repulsive part of the potential, and particularly at high densities it can be approximated by the structure $g_0(r)$ of the purely repulsive fluid alone with excellent accuracy [3]; in this rather peculiar case, perturbative corrections to the reference structure are hardly necessary [4,5].

For more complex liquid models with radial interactions other than such specific attractions, however, one cannot expect to always find simple reference systems with this property. Interest in such models stems in particular from recent efforts to model [6–8] and explain [9–13] the properties of anomalous liquids through the existence of multiple length scales in the interaction potential, which introduce additional repulsive and attractive interactions outside the atomic core. In these and similar cases, perturbation theory needs to account for terms beyond the reference (repulsive-core) structure $g_0(r)$.

Unfortunately, the leading-order correction $g_1(r)$ to the radial distribution function of a liquid due to an arbitrary perturbing potential is in general a function of two-, three-, and four-particle correlations of the reference fluid (see Refs. [2,14]). Consequently, over the years several approximation schemes have been proposed to simplify this correction [14–21]. Such efforts have focused either on the superposition approximation, which eliminates high-order correlation functions but is known to fail at moderately high densities [14], or on the use of integral equations with different approximate closures, which have been applied with varying degrees of success to single square-well liquids [14–21].

The present paper introduces novel, conceptually simple approximations that lead to algebraic corrections to a given hard-sphere reference structure $g_0(r)$ [see Eq. (5)] when the perturbing potential is a generic discrete function of r (i.e., comprised of "steps"), yielding quantitative results of competitive accuracies at high densities. The theory is illustrated for liquids with one [14] and two [9,10] steps in the interaction potential.

II. THEORY

A. Solvation approximation

To begin the derivation, let $\lambda U(\mathbf{r}^N)$ be the N-body perturbation potential of a homogeneous, single-component fluid. The two-particle density can then be expanded in powers of λ, and a convenient expression for the leading-order correction $\lambda\rho_1^{(2)}(\mathbf{r}_1,\mathbf{r}_2)$ to the reference density $\rho_0^{(2)}(\mathbf{r}_1,\mathbf{r}_2)$ can be found by directly λ differentiating the definition of the two-particle density in the canonical ensemble, yielding [22]

$$\rho_1^{(2)}(\mathbf{r}_1,\mathbf{r}_2) = -\beta\rho_0^{(2)}(\mathbf{r}_1,\mathbf{r}_2)[\langle U\rangle_0^{(1,2)} - \langle U\rangle_0]. \tag{1a}$$

Here $\beta=1/kT$ is the usual temperature parameter, $\langle\cdot\rangle_0$ is the ensemble average with respect to the reference system, and $\langle\cdots\rangle_0^{(1,2)}$ is the same average with the constraint that particles 1 and 2 are held fixed at $\mathbf{r}_1$ and $\mathbf{r}_2$, respectively. Let us now decompose U in terms of one-particle energies $U(\mathbf{r}^N) = \frac{1}{2}\Sigma_{i=1}^N u_i(\mathbf{r}^N)$, where $u_i(\mathbf{r}^N)=\Sigma_{j\neq i}u(\mathbf{r}_i,\mathbf{r}_j)$ is the perturbation energy of particle i with the remaining ones, and $u(\mathbf{r}_i,\mathbf{r}_j) = u(|\mathbf{r}_i-\mathbf{r}_j|)$ is the (spherically symmetric) pairwise perturba-

---

[*] Electronic address: adiba@mail.nih.gov

tion energy between particles i and j; Eq. (1a) can thus be written as

$$\rho_1^{(2)}(\mathbf{r}_1,\mathbf{r}_2) = -\beta\rho_0^{(2)}(\mathbf{r}_1,\mathbf{r}_2)\left[\langle u_1\rangle_0^{(1,2)} - \langle u_1\rangle_0 + \frac{N-2}{2}(\langle u_3\rangle_0^{(1,2)} - \langle u_3\rangle_0)\right], \tag{1b}$$

where use was made of the indistinguishability of the particles wherever allowed. Consider now the last term in parentheses. Since the inhomogeneities caused by particles 1 and 2 occupy volumes of molecular size only, one expects the difference $\langle u_3\rangle_0^{(1,2)} - \langle u_3\rangle_0$ to scale down extensively with the total volume of the fluid, which makes the contribution due to the second line above in principle intensive. Moreover, as argued below, at high enough densities this term can be neglected in comparison to the (also intensive) difference $\langle u_1\rangle_0^{(1,2)} - \langle u_1\rangle_0$, leading to the first approximation of the present paper

$$\rho_1^{(2)}(\mathbf{r}_1,\mathbf{r}_2) \approx -\beta\rho_0^{(2)}(\mathbf{r}_1,\mathbf{r}_2)[\langle u_1\rangle_0^{(1,2)} - \langle u_1\rangle_0]. \tag{2a}$$

Although not immediately apparent, this expression is considerably simpler than the full correction; indeed, rewriting it in terms of distribution functions, one sees that it has effectively eliminated four-particle correlations from Eq. (1a):

$$g_1(r) \approx -\beta g_0(r)\left[u(r) + \rho\int d\mathbf{r}' u(r')\Delta g_0(\mathbf{r}'|\mathbf{r})\right], \tag{2b}$$

where $\rho = N/V$ is the particle density, and $\Delta g_0(\mathbf{r}'|\mathbf{r}) \equiv g_0(\mathbf{r}'|\mathbf{r}) - g_0(\mathbf{r}')$ is the change in the local structure at $\mathbf{r}'$ from a given fluid particle due to the presence of another particle fixed at $\mathbf{r}$ from it (note that this contains only three-body information).

To understand the scope of the above approximation, it proves useful to take the viewpoint that particles 1 and 2 are "solutes" imbedded in a "solvent" comprised of the remaining particles $3,\ldots,N$, and that the total perturbation energy can be decomposed into two separate terms, namely, $\lambda_A U_A \equiv \lambda_A(u_1+u_2)/2$ and $\lambda_B U_B \equiv \lambda_B \Sigma_{i=3}^N u_i/2$. In this picture, λ_A perturbs the solute-solute and solute-solvent interactions, while λ_B does the same for solvent-solvent and (the remaining half) solute-solvent interactions. Consider now the interesting case where the solute particles 1 and 2 are relatively close to each other, and let us monitor the structural rearrangements that occur in the solvent as these perturbations are introduced. As λ_A increases from zero, any given solvent particle near the solutes will in principle experience a net average displacement, as the newly added forces due to particles 1 and 2 will in general not cancel; by contrast, as λ_B is introduced, the new forces acting on a given solvent particle should approximately cancel at sufficiently high densities by pairwise vectorial addition [23], and hence in this regime the solvent rearrangements due to λ_B should be comparatively smaller than those due to λ_A. (Unlike the uniform case [23], here the force cancellation argument is only approximately true—out of the ≈12 neighbors around a given solvent particle, here one or two of them could be fixed rather than mobile, depending on the relative position of the solvent particle with respect to the solutes, which could lead to a small net force.) Therefore, to the extent that the relative arrangement of the solvent particles near the solutes determine the solute-solute pair correlation function $\rho^{(2)}(\mathbf{r}_1,\mathbf{r}_2)$, this argument suggests that the perturbation due to λ_B can be neglected in comparison to λ_A, at least at high densities. But Eq. (2) is precisely the correction due to λ_A alone (compare with the hydrophobic perturbation theory of Pratt and Chandler [24]), and thus this "solvation approximation" is expected to work well at high densities. More succinctly, in the language of Weeks and collaborators (see, e.g., Ref. [25]), the foregoing approximation amounts to identifying and retaining only the predominant unbalanced forces that arise in this nonuniform picture.

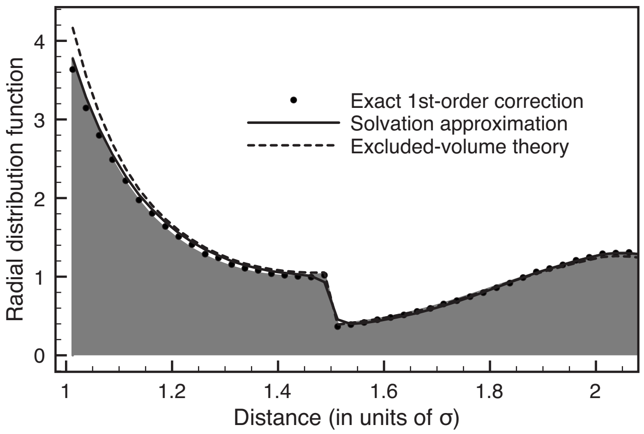

FIG. 1. Radial distribution function for a hard-sphere fluid with a single square well of depth $\varepsilon/kT=1$ extending from $r/\sigma=1$ to $r/\sigma=1.5$, corrected according to the various expressions for $g_1(r)$ in the paper. The particle density is $\rho\sigma^3=0.85$. The shaded curve is the "exact" $g(r)$ obtained by direct Monte Carlo simulation (discontinuities are not perfectly vertical due to the finite spacing between points). The exact first-order correction is computed with Eq. (1a), the solvation approximation with Eq. (2a), and the excluded-volume theory with Eqs. (3) and (4).

As illustrated in Figs. 1 and 2 for the discrete models of present interest, the solvation approximation provides good quantitative results for both one- and two-step potentials at high densities ($\rho\sigma^3=0.85$). In agreement with the above discussion, however, the quality of the approximation decreases at lower densities (see Fig. 6 and Sec. II C below). It is worth mentioning that in these numerical experiments, the sampling quality of Eq. (2a) was much better than that of the exact correction (1a), the latter requiring simulations at least two orders of magnitude longer than the former in order to achieve the same apparent noise level (this is not surprising, as N-particle states contribute with only one sample to the exact correction, namely, $U(\mathbf{r}^N)$, while roughly N samples are contributed to the solvation approximation thanks to the indistinguishability of the particles). It would be interesting to investigate whether the unbiased estimators for $g(r)$ of Ref. [26] can improve the quality of such perturbative corrections as well.

Although not directly relevant to the algebraic development below, it is also interesting to investigate the performance of the solvation approximation in the case of continu-

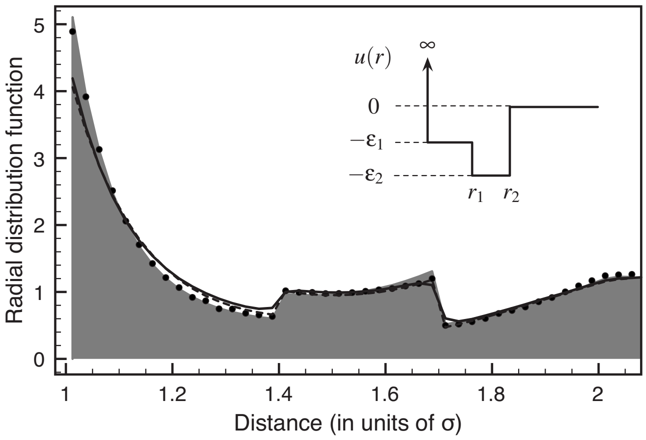

FIG. 2. Radial distribution function for the double square-well potential of Ref. [9] at $\rho\sigma^3=0.85$. Legends as in Fig. 1. The step depths are $\varepsilon_1/kT=0.5$ and $\varepsilon_2/kT=1$, corresponding to the steps ending at $r_1/\sigma=1.4$ and $r_2/\sigma=1.7$, respectively (inset). The excluded-volume theory is given by Eq. (5) with $M=2$.

ous potentials. In Fig. 3 the solvation approximation is applied to the Barker-Henderson reference system for Lennard-Jones potentials [2], and compared to the exact first order correction. It is clear from the figure that the approximation performs well for this reference choice, correctly moving and shaping the peak of the distribution towards that of the full Lennard-Jones system. For the Weeks-Chandler-Anderson choice (Fig. 4), the results are less satisfactory: although the approximation corrects the width of the first coordination shell as well as the minimum between the first and second shells, it introduces a spurious population increase at the first coordination peak. The origin of this discrepancy is presently not clear, and since the subsequent development is not concerned with such potentials, this question will be left for future investigations.

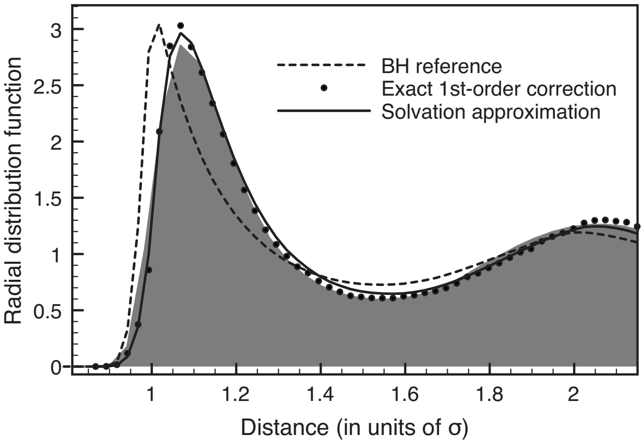

FIG. 3. Radial distribution functions at $\rho\sigma^3=0.85$ and $kT/\epsilon=0.88$ for a Lennard-Jones system. The reference system is the Barker-Henderson (BH) choice [2]. The shaded curve corresponds to an "exact" Lennard-Jones simulation at the same conditions. The remaining legends are as in Fig. 1.

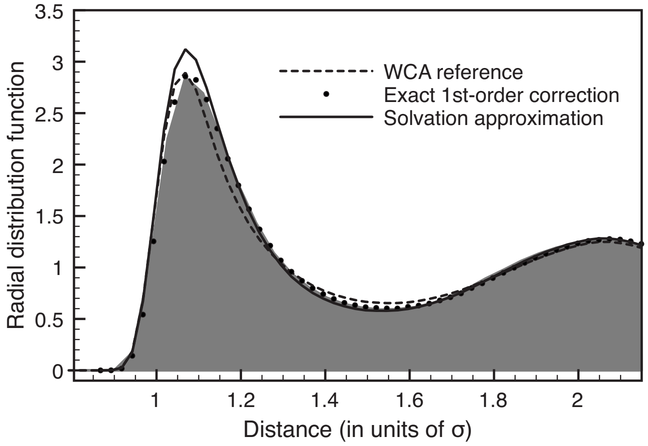

FIG. 4. Radial distribution functions at $\rho\sigma^3=0.85$ and $kT/\epsilon=0.88$ for a Lennard-Jones system. The reference system is the Weeks-Chandler-Anderson (WCA) choice [2]. The remaining legends are as in Fig. 1.

B. Excluded-volume theory

We now return to the case of discrete potentials, for which the solvation approximation is considerably simplified. Consider for example the square-well perturbation to a hard-sphere fluid where $u(r)=-\varepsilon$ for $r<r^*$, and $u(r)=0$ otherwise, with $r^*>\sigma$. Inserting this expression in Eq. (2) yields

$$g_1(r)=-\beta g_0(r)[u(r)-\varepsilon\Delta n_0^*(r)], \tag{3}$$

where $\Delta n_0^*(r)$ is the net change in the average number of particles inside a shell of radius r^* surrounding a given particle, due to the presence of another particle fixed at a distance r from it. The problem of computing the leading-order correction to $g_0(r)$ for such systems thus reduces to that of quantifying population changes in the coordination shell defined by the radius r^* due to an "intruder" particle at r in the reference fluid. In the following, a simple volume-exclusion theory for $\Delta n_0^*(r)$ will be presented.

For the sake of clarity, let us focus on the single square-well case with $r^*=1.5\sigma$, and let us monitor the average number of particles within the r^* shell of particle 1 as particle 2 is brought to a distance r from it (see Fig. 5). To a first approximation, appreciable changes in the average number of particles inside the r^*-shell of particle 1 should occur whenever particle 2 occupies a volume that would otherwise be occupied by the particles inside that shell. At sufficiently high densities, wherein the particles are tightly packed around each other, this should happen progressively as the body of particle 2 infiltrates the r^* shell; a simple model that captures this idea is thus

$$\Delta n_0^*(r)=-\frac{v^*(r)}{v_\sigma}, \tag{4}$$

where $v^*(r)$ is the two-sphere intersection volume shown in Fig. 5, and $v_\sigma=\pi\sigma^3/6$ is the volume of a sphere of diameter σ. Note that this expression is normalized so that $\Delta n_0^*(\sigma)=-1$, i.e., exactly one particle is excluded from the r^* shell when particle 2 is fully inside the $r<r^*$ region. Since a poly-

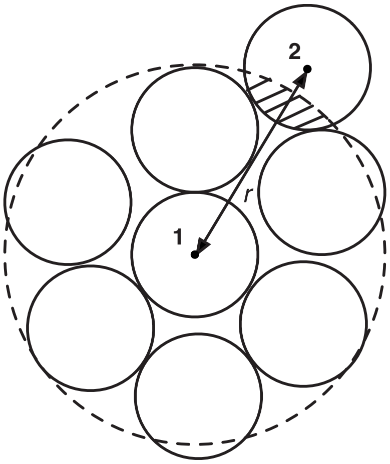

FIG. 5. Two-dimensional representation of the excluded-volume model [Eq. (4)] for the single square-well potential with $r^*=1.5\sigma$. Solid circles represent the hard spheres of the reference system with diameter σ, while the larger dashed circle represents the outer radius r^* of the perturbation well. The shaded area represents the volume $v^*(r)$ of particle 2 inside the perturbation well.

nomial expression for the intersection volume $v^*(r)$ of the spheres can be obtained by simple quadrature, Eqs. (3) and (4) yield the desired algebraic theory for the leading-order correction to $g_0(r)$ in the particular single square-well case. Notwithstanding its simplicity, the resulting theory is in striking quantitative agreement with "exact" Monte Carlo results (Fig. 1).

The above model can be directly extended to encompass multiple steps of arbitrary widths; thus, for a potential with M steps,

$$g_1(r) = -\beta g_0(r)\left[u(r) + \sum_{i=1}^{M}\varepsilon_i \frac{v^{(i)}(r)}{v_\sigma}\right], \tag{5}$$

where $-\varepsilon_i$ is the energy of the ith step, and $v^{(i)}(r)$ is the volume of the intruder particle inside the ith step region [defined analogously to $v^*(r)$ in Fig. 5]. A representative application of this model for $M=2$ is shown in Fig. 2. With the exception of the more pronounced deviation near the contact distance $r/\sigma \approx 1$ (chiefly due to the solvation approximation, and not to the model itself), the volume-exclusion theory is again in good quantitative agreement with direct simulation results.

C. Thermodynamics

Since corrections at a given order to the structure furnish corrections at next order to thermodynamics, it is of interest to investigate the consequences of the above first-order structural theory to second-order corrections in the free energy A_2 [14]. For the models studied, the theory predicts A_2 with relative errors of the order of 10% at densities $\rho\sigma^3 \gtrsim 0.8$, the source of discrepancy at lower densities being traced back to the underlying solvation approximation (Fig. 6), as already anticipated. It should be emphasized, however, that the volume-exclusion model above is in principle justified only at high densities, and hence the gradual breakdown of the solvation approximation at lower densities is consistent with the scope of the algebraic theory.

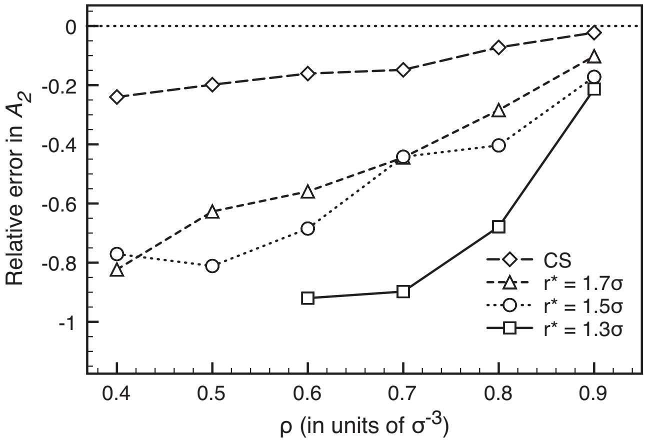

FIG. 6. Relative error $(A_2^{\mathrm{solv}}-A_2^{\mathrm{exact}})/|A_2^{\mathrm{exact}}|$ in the second-order correction to the free energy, viz., $A_2/N=(\rho/4)\int d\mathbf{r}u(r)g_1(r)$ [14], versus density, where the superscripts specify the use of Eq. (1a) (A_2^{exact}) or Eq. (2a) (A_2^{solv}) for the computation of $g_1(r)$. From top to bottom: Discrete core-softened (CS) model of Fig. 2, and single-well potentials with ranges $r^*/\sigma=1.7$, 1.5, and 1.3.

III. CONCLUSIONS

In summary, the present study has offered algebraic corrections of unprecedented simplicity to the structure of dense liquids with generic discrete potentials (compare with previous analytic results, e.g., Refs. [17–21], derived for single-well liquids). This was achieved through the introduction of two novel ideas: the solvation approximation [Eq. (2)]—in principle applicable to any sufficiently dense liquid with either discrete or continuous potentials—and a simple volume-exclusion model for three-particle correlations in liquids with discrete potentials (Fig. 5). Given its ability to easily handle wells with multiple depths, it is hoped that the methodological development put forward in this paper will help elucidate the role of length scales in liquid models with thermodynamic anomalies [9,10], as well as in perturbative treatments of the hydrophobic effect [24,27].

ACKNOWLEDGMENTS

The author acknowledges useful discussions and/or correspondences with Attila Szabo, John Weeks, Gerhard Hummer, Yng-Wei Chen, and Douglas Henderson. This research was supported by the Intramural Research Program of the NIH, NIDDK.

[1] R. Zwanzig, J. Chem. Phys. **22**, 1420 (1954).

[2] J.-P. Hansen and I. R. McDonald, *Theory of Simple Liquids* 2nd ed. (Academic, San Diego, CA, 1986).

[3] D. Chandler and J. D. Weeks, Phys. Rev. Lett. **25**, 149 (1970).

[4] J. D. Weeks, D. Chandler, and H. C. Andersen, J. Chem. Phys. **54**, 5237 (1971).

[5] D. Chandler, J. D. Weeks, and H. C. Andersen, Science **220**, 789 (1983).

[6] T. Head-Gordon, Chem. Phys. Lett. **227**, 215 (1994).

[7] T. Head-Gordon, J. Am. Chem. Soc. **117**, 501 (1995).

[8] S. Garde and H. S. Ashbaugh, J. Chem. Phys. **115**, 977 (2001).

[9] M. R. Sadr-Lahijany, A. Scala, S. V. Buldyrev, and H. E. Stanley, Phys. Rev. Lett. **81**, 4895 (1998).

[10] G. Franzese, G. Malescio, A. Skibinsky, S. V. Buldyrev, and H. E. Stanley, Nature (London) **409**, 692 (2001).

[11] Z. Yan, S. V. Buldyrev, N. Giovambattista, and H. E. Stanley, Phys. Rev. Lett. **95**, 130604 (2005).

[12] A. B. de Oliveira, P. A. Netz, T. Colla, and M. C. Barbosa, J. Chem. Phys. **124**, 084505 (2006).

[13] A. B. de Oliveira, P. A. Netz, T. Colla, and M. C. Barbosa, J. Chem. Phys. **125**, 124503 (2006).

[14] J. A. Barker and D. Henderson, Rev. Mod. Phys. **48**, 587 (1976).

[15] W. R. Smith, D. Henderson, and Y. Tago, J. Chem. Phys. **67**, 5308 (1976).

[16] D. Henderson, W. G. Madden, and D. D. Fitts, J. Chem. Phys. **64**, 5026 (1976).

[17] M. Chen, D. Henderson, and J. A. Barker, Can. J. Phys. **47**, 2009 (1968).

[18] D. Henderson and M. Chen, J. Math. Phys. **16**, 2042 (1975).

[19] Y. Tang and B. C.-Y. Lu, J. Chem. Phys. **100**, 3079 (1994).

[20] Y. Tang and B. C.-Y. Lu, J. Chem. Phys. **100**, 6665 (1994).

[21] J. Largo, J. R. Solana, S. B. Yuste, and A. Santos, J. Chem. Phys. **122**, 084510 (2005).

[22] B. A. Lowry, H. T. Davis, and S. A. Rice, Phys. Fluids **7**, 402 (1964).

[23] B. Widom, Science **157**, 375 (1967).

[24] L. R. Pratt and D. Chandler, J. Chem. Phys. **73**, 3434 (1980).

[25] K. V. J. D. Weeks and K. Katsov, Physica A **244**, 461 (1997).

[26] A. B. Adib and C. Jarzynski, J. Chem. Phys. **122**, 014114 (2005).

[27] G. Hummer and S. Garde, Phys. Rev. Lett. **80**, 4193 (1998).