

The vanishing limit of the square-well fluid: The adhesive hard-sphere model as a reference system

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We report a simulation study of the gas-liquid critical point for the square-well potential, for values of well width δ as small as 0.005 times the particle diameter σ . For small δ , the reduced second virial coefficient at the critical point B_2^{*c} is found to depend linearly on δ . The observed weak linear dependence is not sufficient to produce any significant observable effect if the critical temperature T_c is estimated via a constant B_2^{*c} assumption, due to the highly nonlinear transformation between B_2^{*c} and T_c . This explains the previously observed validity of the law of corresponding states. The critical density ρ_c is also found to be constant when measured in units of the cube of the average distance between two bonded particles $(1+0.5\delta)\sigma$. The possibility of describing the $\delta \rightarrow 0$ dependence with precise functional forms provides improved accurate estimates of the critical parameters of the adhesive hard-sphere model. © 2008 American Institute of Physics.

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I. INTRODUCTION

Investigation of protein and colloidal systems has focused the attention of the scientific community on the phase-diagram behavior of short-ranged attractive potentials and of the role of the range of interaction in controlling the thermodynamic and dynamic properties of the system.¹⁻⁵ Colloidal particles, due to their nano- or microscopic size, are often characterized by effective interactions⁶ whose range is significantly smaller than the particle diameter. Under these conditions, it has been argued that the actual shape of the potential is irrelevant and that the thermodynamics,⁷ as well as the dynamics,⁸ of different systems approximately satisfy an extended law of corresponding states.⁹ This law allows for a comparison between different systems, once the effective diameter of the particle is known (i.e., when the repulsive part of the interaction can be mapped into an equivalent hard-sphere diameter¹⁰). It has been proposed that the second virial coefficient, normalized by the corresponding hard-sphere second virial coefficient, B_2^* , may act as a proper scaling variable. Therefore, systems with equal second virial coefficient and effective diameter should have similar thermodynamical properties.

The adhesive hard-sphere (AHS) potential,¹¹ the limiting behavior of an infinitesimal interaction range coupled to infinite interaction strength such that B_2 is finite, has also received significant attention. For this potential $B_2^* = 1 - 1/4\tau$, where τ , which acts as an effective scaled temperature, is the so-called stickiness parameter. Despite the known thermodynamic anomalies,¹² an analytic evaluation of the (metastable)

critical point within the Percus–Yevick closure with both the energy and the compressibility routes is available^{11,13} for this potential. In the energy route the critical point is located at $B_2^{*c} = -1.1097$ ($\tau_c = 0.1185$) and reduced number density $\rho = 0.609$.

The availability of analytic predictions for this model has favored its application in the interpretation of experimental data for several disparate colloid (and protein) systems,^{2-5,14-16} an application whose validity has been reinforced by the extended law of corresponding states. For this reason, it is important to try to accurately estimate the properties of the AHS model as a reference, to support existing predictions, or to suggest improvements to available theoretical approaches. Numerical simulations of the AHS model have been attempted in the past.¹⁷⁻¹⁹ A recent effort in the direction of evaluating the phase diagram of the model has been provided by Miller and Frenkel,²⁰ based on an ingenious identification of the appropriate Monte Carlo (MC) moves for this potential.^{17,18} Their study provides an estimate of the location of the critical point at $B_2^{*c} = -1.21(1)$ [$\tau_c = 0.1133(5)$] and $\rho_c = 0.508(10)$.

In this article, we propose a different approach to the numerical evaluation of the critical properties of the AHS model, based on extrapolation of standard grand canonical MC simulation results for a sequence of square-well (SW) potentials with progressively smaller attraction ranges δ (down to $\delta = 0.005$, in units of the hard-sphere diameter σ).

The SW potential is defined as

$$U(r) = \begin{cases} \infty & \text{if } r \leq \sigma \\ -\epsilon & \text{if } \sigma < r \leq \sigma + \delta\sigma \\ 0 & \text{if } r > \sigma + \delta\sigma. \end{cases} \quad (1)$$

The SW fluid has been profusely studied²¹⁻²⁷ for $\delta > 0.1$. It has been shown^{24,25} that for $\delta \leq 0.25$ gas-liquid separation

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becomes metastable with respect to the fluid-solid equilibrium. Despite its metastable character, investigation of smaller δ values retains its importance, since the crystallization time is often much longer than the experimental one and gas-liquid phase separation is readily accessed (an effect facilitated by the large difference between the fluid density and the crystal density and, in experiments, by the intrinsic sample polydispersity).

Despite the importance of the SW model in relation to the AHS potential, no studies of the δ dependence of the critical point location have been previously reported for very small δ . This is in large part due to the fact that for smaller and smaller δ , the critical temperature significantly decreases. Indeed, according to the constant B_2^{*c} prediction of Noro and Frenkel,⁷ it should vary as

$$\frac{k_B T_c}{\epsilon} = \left[\ln \left(1 + \frac{1 - B_2^{*c}}{(1 + \delta)^3 - 1} \right) \right]^{-1}, \quad (2)$$

making bond-breaking (changes of the particle energy of order ϵ) events rarer and rarer in the simulation. Moreover, the size of the translational step in the MC code is of the order of δ . On the other hand, the location of the critical point becomes more and more metastable which, in principle, poses a limit to the smallest δ which can be studied.

Despite these numerical difficulties, we have been able to estimate the location of the critical point down to $\delta = 0.005$. We present here the δ dependence of the critical temperature and density and the values of the second virial coefficient and energy at the critical point. In all cases, a short linear extrapolation to $\delta = 0$ provides novel accurate estimates of the corresponding quantities for the AHS model.

II. MONTE CARLO SIMULATIONS

We have simulated the SW system in the grand canonical (GC) ensemble in order to locate the gas-liquid critical point for different δ values. The critical point is identified by mapping the GC density distribution onto the universal Ising model distribution, following the method described by Bruce and Wilding.²⁸ Histogram reweighting²⁹ was used to achieve an accurate estimate of the critical point, and the field mixing parameter was always found to be negligible. We define a MC step as 100 trial moves, with an average of 95% translation and 5% trial insertions or removals of one particle in the system. A translational move is defined as a displacement in a random direction by a random amount between $\pm \delta/2$. We simulate different realizations of the same system (at the same chemical potential and temperature) to improve statistics. Simulations lasted more than 10^7 MC steps. We have studied cubic boxes of side 5σ and/or 8σ to estimate the importance of finite-size effects. Additionally, for $\delta = 0.05$ we have studied several other box sizes to estimate the deviation of the value of the critical parameter for the bulk limit case. Proper finite size studies for $\delta < 0.05$ are at this moment computationally prohibitive.

We have occasionally observed a transition to a denser stable phase, signaling that indeed the values of the chemical potential studied admit metastable fluid solutions. In all cases

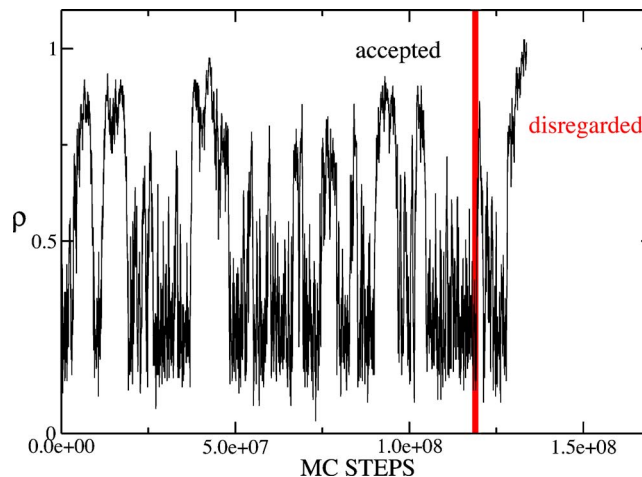


FIG. 1. (Color online) Density evolution for a single run of a SW fluid with $\delta = 0.01$, $T^* = 0.233$, and $\mu/kT = -2.41$ (close to the critical point). At long time, a transition to a dense phase is observed and consequently the simulation on the right side of the vertical line is disregarded.

where a transition to a denser phase was observed, the simulation was interrupted and the 10% of configurations saved just before the transition were disregarded. This procedure is shown graphically in Fig. 1.

III. RESULTS

Figures 2(a) and 2(b) show the δ dependence of the critical temperature and the corresponding critical second virial coefficient B_2^{*c} (see also Table I). For SW, the virial can be calculated as

$$B_2^*(T) = 1 - ((\delta + 1)^3 - 1)(e^{1/T} - 1). \quad (3)$$

For small δ , a clear linear dependence of B_2^{*c} is observed. The data are well represented by a functional form $B_2^{*c}(\delta) = -1.174 - 1.774\delta$. The extrapolated value of B_2^{*c} for $\delta = 0$ ($B_2^{*c} = -1.174$) is slightly higher than the value $-1.21(1)$ estimated by Miller and Frenkel for the AHS potential. The δ dependence of B_2^{*c} formally violates the idea that B_2^{*c} is the correct scaling variable for collapsing the phase diagram of different short-ranged attractive potentials onto a single master curve. Nevertheless, the constant B_2^{*c} approximation is sufficiently good to explain the T_c dependence, due to the nonlinearity of the transformation [Eq. (2)]. To prove this point we show in Fig. 2(a) T_c predicted according to $B_2^{*c} = -1.174$. In this representation, the assumption of constant B_2^{*c} is sufficient to describe the δ dependence of T_c up to $\delta = 0.05$, with an error less than 1% (growing with δ).

Next we compare the energy per particle of the system at the critical point in Fig. 2(c), to provide a measure of the number of contacts per particle. This quantity also shows a linear dependence on δ .

The study of the δ dependence of the critical density ρ_c has received considerably less attention than the δ dependence of T_c . Recently, Ref. 30 suggested a plausible relation for the δ dependence of ρ_c in the limit of small well width:

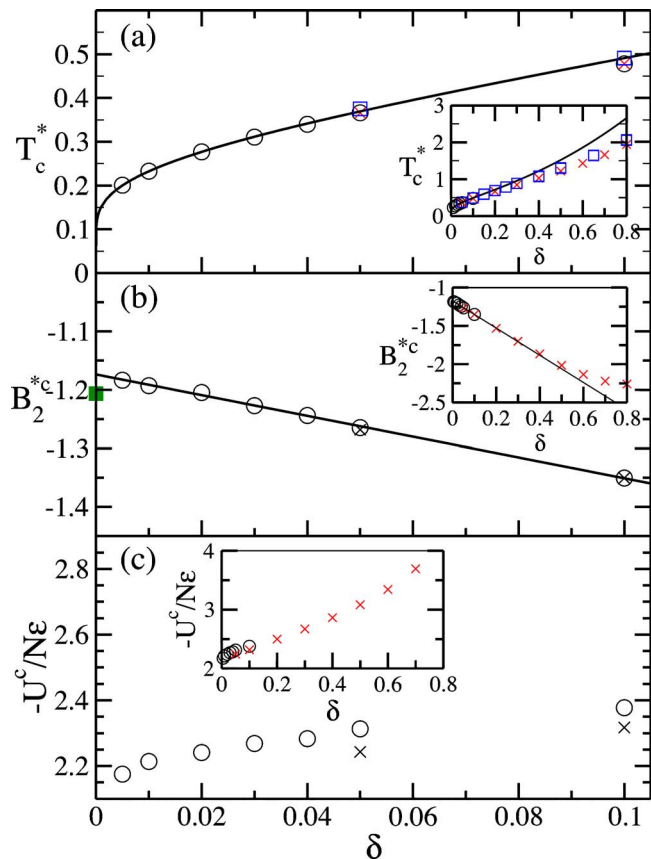


FIG. 2. (Color online) Dependence of the critical temperature (a), of the second virial coefficient (b), and of the potential energy (c) on the range of the potential δ . The circles and crosses label simulation data of this work with box sides 5σ and 8σ , respectively. The line in (a) is the theoretical prediction for the critical temperature provided by Eq. (2). The line in (b) corresponds to the best linear fit of the simulation data for $\delta \leq 0.10$ (-1.174 to 1.774δ). The open squares correspond to the simulation data from Ref. 4. The filled squares are the AHS B_2^{*c} results from Ref. 20. The inset presents the whole range of δ values studied.

TABLE I. Critical point parameters for the SW fluid for width δ , resulting from simulations of boxes of side $L=5$ (top part of the table) and 8σ (bottom part of the table), respectively.

| δ | T_c^* | ρ_c | μ_c |
|----------|---------|----------|---------|
| 0.005 | 0.2007 | 0.542 | -0.4817 |
| 0.01 | 0.2328 | 0.540 | -0.5614 |
| 0.02 | 0.2769 | 0.538 | -0.6693 |
| 0.03 | 0.3106 | 0.530 | -0.7575 |
| 0.04 | 0.3398 | 0.522 | -0.8333 |
| 0.05 | 0.3660 | 0.516 | -0.9042 |
| 0.10 | 0.4780 | 0.478 | -1.2120 |
| 0.05 | 0.3658 | 0.513 | -0.9062 |
| 0.10 | 0.4780 | 0.478 | -1.2138 |
| 0.20 | 0.667 | 0.421 | -1.7812 |
| 0.30 | 0.847 | 0.376 | -2.3505 |
| 0.40 | 1.029 | 0.339 | -2.9525 |
| 0.50 | 1.220 | 0.310 | -3.6002 |
| 0.60 | 1.430 | 0.287 | -4.3051 |
| 0.70 | 1.665 | 0.272 | -5.0890 |
| 0.80 | 1.940 | 0.263 | -5.9636 |

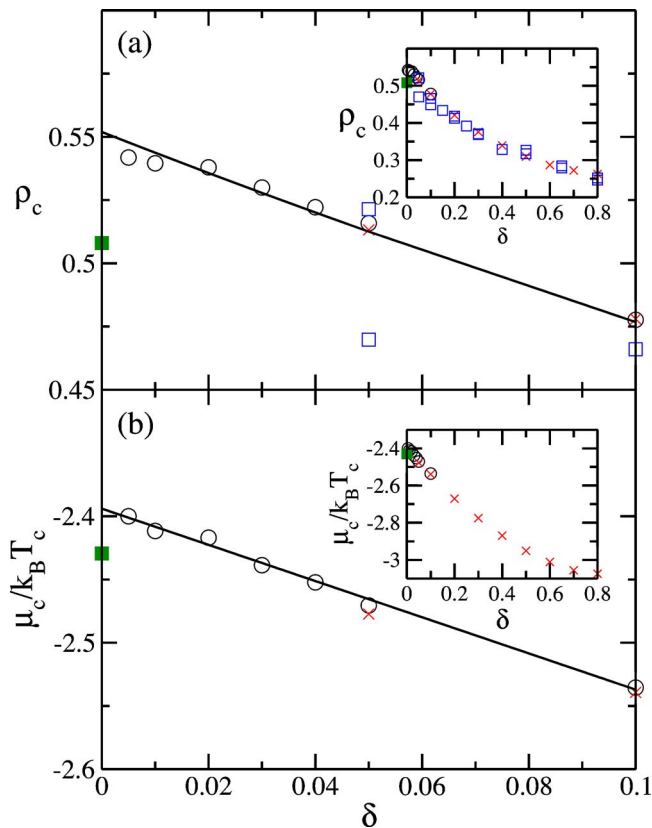


FIG. 3. (Color online) Evolution of the critical density (a) and chemical potential (b) with the range of the potential δ . The circles and crosses correspond to box sides $L=5\sigma$ and $L=8\sigma$, respectively. The empty squares in (a) are data from Ref. 4. The lines correspond to the best fit of (a) ρ_c for $\delta \leq 0.10$ ($0.5519/(1+\delta/2)^3$) and (b) $\mu_c/k_B T_c$ for $\delta \leq 0.10$ (-2.394 to 1.431δ). The filled squares represent AHS results from Ref. 20. The inset presents the whole range of δ values studied in this work.

$$\rho_c(\delta) = \frac{\rho_c(0)}{(1 + \delta/2)^3}. \quad (4)$$

The relation is based on the hypothesis that ρ_c should be constant if measured using the average distance between two bonded particles $(1 + \delta/2)\sigma$ as the unit of length. The relation was also supported by a potential energy landscape interpretation of the generalized law of corresponding states³¹ which shows that configurations with the same Boltzmann weight are generated under an isotropic scaling (to change the interparticle distances preserving the same bonding pattern) and a simultaneous change of both δ and T such that the bond free energy remains constant.

Figure 3(a) shows the calculated evolution of the critical density with the range of the interaction (see also Table I). It also reports previous estimates for the same system⁴ as well as the critical density for the AHS model from Ref. 20. As the range of the SW potential is reduced, the critical density becomes higher, since a bonding now requires a closer interparticle distance. Data for $\delta < 0.1$ are properly represented by Eq. (4), with a resulting fitting parameter $\rho_c(0)=0.552$. This value is significantly higher than the AHS critical density $\rho_c=0.508$ reported in Ref. 20.

For completeness we show in Fig. 3(b) the δ dependence of $\mu_c/k_B T_c$, where μ_c is the value of the chemical potential at the critical point. $\mu_c/k_B T_c$ also shows a linear dependence,

TABLE II. Critical parameters for the SW system of $\delta=0.05$ obtained with four different boxes of side $L=5, 6, 8, 10$.

| L | T_c | ρ_c | μ_c |
|-----|--------|----------|---------|
| 5 | 0.3660 | 0.516 | -0.9042 |
| 6 | 0.3660 | 0.516 | -0.9051 |
| 8 | 0.3658 | 0.513 | -0.9062 |
| 10 | 0.3657 | 0.511 | -0.9069 |

with an intercept at -2.394 , corresponding to a critical activity $\exp(\mu_c/k_B T_c)=0.091$, to be compared with the corresponding value of 0.087 of Miller and Frenkel.

It is known that the finite size of the system modifies the position of the critical point.³² A precise estimate of the critical point requires a complete finite-size scaling study to extrapolate the results to an infinite system. We have not attempted to perform such a careful study since it would be computationally prohibitive for the small ranges studied here and we have limited ourselves to four different box sizes ($L=5, 6, 8$, and 10) for $\delta=0.05$ only. The results are reported in Table II. As already suggested by the minor differences in the $L=5$ and $L=8$ data shown in the previous figures, no significant changes in the critical parameters are observed. From the scatter in the data (similar to that found by Miller and Frenkel²⁰), it is possible to estimate errors in the critical parameters. The resulting values of and errors in the critical parameters at $\delta=0.05$ are $T_c=0.3658 \pm 0.0005$, $\rho_c=0.513 \pm 0.008$, and $\mu_c=0.9064 \pm 0.0008$.

IV. DISCUSSION

Our study provides a set of values for the limiting AHS case, based on an accurate extrapolation of the critical parameters of the SW potential to $\delta \rightarrow 0$. These values are outside the error bars of Miller and Frenkel's investigation. In particular, both the critical density and the critical virial appear to be higher than the previous estimates.

The special techniques employed in the simulation of the AHS system^{18,20,33} only consider moves that make or break up to three contacts. A particle can readily gain more than three contacts, since higher coordination states are established by a succession of such moves. Apparently, however, the constraint on the possible moves disfavors the formation of small nuclei of solid phases, since crystallization was extremely rarely observed with this algorithm, and then only in fluids with a very high mean reduced density (greater than 0.9). In the SW simulation, the transient solidlike nuclei are more readily formed (and indeed we do occasionally observe crystallization during the simulation) suggesting that the SW simulations sample a larger region of configuration space than that accessible with the AHS algorithm. This could indeed explain why the critical density extrapolated from the SW simulations is significantly higher than that calculated previously.

To support this interpretation we have compared the distribution of the number of contacts per particle (proportional to the energy of the particle) for the AHS and a SW with

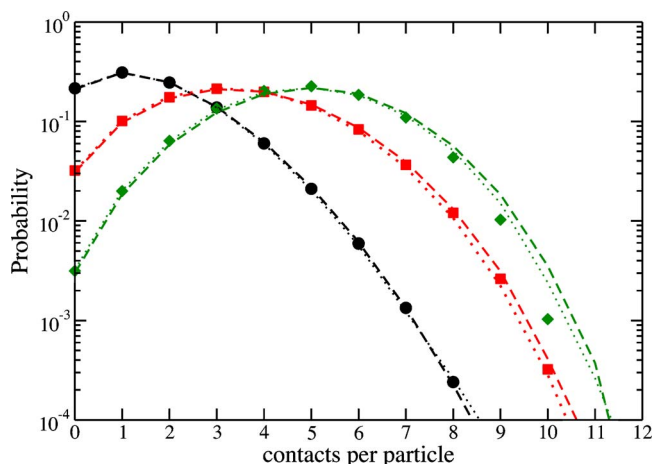


FIG. 4. (Color online) Probability distribution of the number of contacts per particle for the AHS system and the SW with $\delta=0.01$, for different densities. The comparison has been made at a slightly supercritical stickiness parameter $\tau=0.120$, in the case of the AHS, and the corresponding temperature provided by Eq. (2) for the SW of $\delta=0.01$. The simulations were performed in the NVT canonical ensemble with volume $V=512\sigma^3$. The symbols correspond to AHS simulation data, for $\rho=0.195$ (circles), 0.488 (squares), and 0.781 (diamonds). The dashed lines correspond to SW simulation data and the dotted lines to SW simulations at the rescaled densities of [see Eq. (4)] 0.192 , 0.481 , and 0.770 , respectively.

$\delta=0.01$ at the same virial coefficient (slightly above the critical one) and same density for three different state points. The results of MC simulations in the NVT canonical ensemble for different densities are reported in Fig. 4. The distributions of the number of contacts per particle are coincident for low densities, but discrepancies appear as the density is increased, confirming that the algorithm used in Ref. 20 explores configurations with a somewhat smaller coordination number than does the standard MC SW simulation. Figure 4 nevertheless confirms that the AHS algorithm permits the formation of high coordination states. To avoid any potential artifact due to the *a priori* unknown mapping in the density between the AHS and the SW potential, we have also repeated the calculation at a lower density, scaled according to Eq. (4). However, as shown in Fig. 4, even when the density is scaled to account for the different bond distances in the AHS and SW models, at high density the disagreement between the two set of simulations remains.

V. CONCLUSIONS

We have reported a simulation study aimed at evaluating the dependence of the critical parameters of the short-ranged SW potential for interaction ranges approaching zero down to $\delta=0.005$. The resulting values for B_2^{*c} and $\beta_c \mu_c$ in the range $0.005 < \delta < 0.1$ are very well described by a linear dependence on δ , providing an estimate for the $\delta \rightarrow 0$ limit. From the resulting value of B_2^{*c} at $\delta=0$, it is possible to evaluate also the corresponding critical value of the AHS model via the relation $B_2^* = 1 - 1/4\tau$. In the same range, the critical density is well represented by the previously proposed functional form of Eq. (4). More precisely, our extrapolation for the AHS limit is

$$B_2^{*c}(\delta=0) = -1.174 \pm 0.002, \quad (5)$$

$$\tau_c = 0.1150 \pm 0.0001, \quad (6)$$

$$\rho_c(\delta=0) = 0.552 \pm 0.001, \quad (7)$$

$$\beta_c \mu_c(\delta=0) = -2.394 \pm 0.001, \quad (8)$$

where the error bars are based on the spread of results from the different box sizes in this study.

Three important observations are in order.

- (i) Even for short-range interactions, B_2^{*c} shows a slight linear dependence on δ , apparently contradicting the law of corresponding states. While this is technically correct, one must also remember that the small changes of B_2^{*c} with δ , in the range $0 < \delta < 0.05$, are not sufficient to produce any significant observable effect in the critical temperature estimated using a constant B_2^{*c} assumption via Eq. (2). This is due to the highly nonlinear relationship between the two quantities, explaining the success of the law of corresponding states in the interpretation of simulation and experimental data of short-ranged attractive potentials. From a more academic point of view, the law of corresponding states may still hold but with a scaling variable more complicated than the reduced virial coefficient itself and with a proper scaling of the density.
- (ii) The “best” critical parameters of the $\delta=0$ case are found to be different from those reported by Miller and Frenkel.²⁰ We believe that this discrepancy is related to an incomplete mapping of the configuration space in Ref. 20 which manifests itself in a less complete sampling of the dense region. The extreme rarity of any hint of crystallization in the simulations of Miller and Frenkel is consistent with this proposed explanation.
- (iii) The higher critical temperature and density established by the SW extrapolation suggest that the Percus–Yevick energy route offers a more accurate estimate of the AHS critical point than the Percus–Yevick compressibility route.

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