Comparing four hard-sphere approximations for the low-temperature WCA melting line

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By combining interface-pinning simulations with numerical integration of the Clausius-Clapeyron equation we determine accurately the melting-line coexistence pressure and fluid/crystal densities of the Weeks-Chandler-Andersen (WCA) system covering four decades of temperature. The data are used for comparing the melting-line predictions of the Boltzmann, Andersen-Weeks-Chandler, Barker-Henderson, and Stillinger hard-sphere approximations. The Andersen-Weeks-Chandler and the Barker-Henderson theories give the most accurate predictions, and they both work excellently in the zero-temperature limit for which analytical expressions are derived here.

I. INTRODUCTION

While systems of purely repulsive particles are rarely found in nature, they provide convenient models for both fluids and solids [1]. Examples are the inverse-power law (IPL) systems based on a homogeneous pair potential that varies with distance r as $(r/\sigma)^{-n}$ in which σ is a length [2–5] and the exponential repulsive (EXP) pair potential that varies with distance as $\exp(-r/\sigma)$ [6–8]. The oldest and most important purely repulsive system is that of hard spheres (HS) [9–12], which despite its simplicity provides a good zeroth-order model of realistic systems with both repulsive and attractive interactions [13–18]. A purely repulsive system has a single fluid phase and no gas-liquid phase transition. In contrast, the symmetrybreaking liquid-solid transition is present in all purely repulsive systems and, because of the absence of a gas phase, here the liquid-solid phase boundary extends to zero temperature.

This paper studies the noted Weeks, Chandler, and Andersen (WCA) purely repulsive system [17–44], which is arrived at by cutting and shifting the Lennard-Jones (LJ) interaction at its minimum [17]. In contrast to the IPL and EXP systems, the WCA pair potential has a finite range beyond which pair forces are zero, like those of the HS system. At the cutoff, the WCA pair potential and pair forces are smooth, and at low temperatures one expects HS approximations to apply because only insignificant "overlaps" are possible. Thus studies of the low-temperature melting line of the WCA system provides an excellent testing ground for comparing different HS approximations. This motivates the present study. In Sec. II we introduce the WCA system and the four HS approximations considered, as well as give a few simulation details. Section III details how we determined the WCA melting line by interface pinning and Clausius-Clapeyron integration. The predictions of the different HS approximations in regard to pressure and fluid/solid densities at melting are compared in Sec. IV. Finally,

Sec. V provides a brief outlook.

II. THE WCA SYSTEM AND HARD-SPHERE APPROXIMATIONS

A. The WCA system

We consider mono-disperse systems. Let $\mathbf{R} = (\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ be the collective coordinate vector of N particles with mass m confined to the volume V (with periodic boundaries) and define the number density by $\rho \equiv N/V$. The potential part $\mathcal{U}(\mathbf{R})$ of the Hamiltonian, $\mathcal{H}(\mathbf{R}) = \mathcal{U}(\mathbf{R}) + \mathcal{K}(\dot{\mathbf{R}})$, is assumed to be a sum of pair-potential contributions,

$$\mathcal{U}(\mathbf{R}) = \sum_{n>m}^{N} v(|\mathbf{r}_m - \mathbf{r}_n|).$$
 (1)

We recall that the LJ pair potential is defined [45, 46] by

$$v(r) \equiv 4\varepsilon \left[(r/\sigma)^{-12} - (r/\sigma)^{-6} \right]$$
(2)

in which ε has units of energy and σ units of length. The WCA pair potential (Fig. 1) is defined by cutting and shifting the LJ potential at its minimum, which leads to [17]

$$v(r) = 4\varepsilon \left[(r/\sigma)^{-12} - (r/\sigma)^{-6} \right] + 1/4 \right] \text{ for } r \le r_c \quad (3)$$

and zero otherwise where

$$r_c = \sqrt[6]{2}\sigma \simeq 1.1225\sigma \tag{4}$$

The WCA pair potential is purely repulsive since the pair force $-dv/dr \ge 0$ for all r's, and it is smooth since both v(r) and its first derivative are continuous (the second derivative is discontinuous at r_c , though). All quantities obtained by simulations are below reported in units derived from m, σ, ε and the Boltzmann constant k_B .

Simulations of the WCA system are conducted using the RUMD software package version 3.5 [47]. An initial configuration is first constructed by replicating $8 \times 8 \times$

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FIG. 1. (a) The WCA pair potential Eq. (3). (b) The same pair potential on a logarithmic energy scale, showing a steep slope at low pair energies.

20 face centered cubic (FCC) unit cells, resulting in a system of N = 5120 particles. This initial configuration is then scaled uniformly to the desired density ρ . If a liquid configuration is needed, the crystal is melted in a high-temperature simulation. The Newtonian equations of motion are discretized using the leap-frog algorithm [48] with the temperature-dependent time step

$$dt = 0.001 \frac{\sigma}{\sqrt{k_B T/m}} \,. \tag{5}$$

Simulations in the NVT ensemble [47–51] are realized using a Langevin thermostat with relaxation time $t_T = m/\alpha$ where α is a friction coefficient given by

$$t_T = 0.2 \frac{\sigma}{\sqrt{k_B T/m}} \,. \tag{6}$$

For Np_zT Langevin simulations [47, 50, 51] we used the same thermostat relaxation time and the barostat relaxation time

$$t_p = 100 \, \frac{\sigma}{\sqrt{k_B T/m}} \,. \tag{7}$$

We have found that introducing this $1/\sqrt{T}$ scaling to the relaxation times [52] provides a simple way to ensure stability and efficiency of computations spanning several orders of magnitude in temperature (see Ref. 43 for a different approach). Note that in this way the average number of steps needed to travel the distance σ for a thermal particle is the same for all temperatures.

B. Hard-Sphere approximations to the WCA system

Perturbation theories have proven successful for describing many fluids near freezing [1, 15-25, 53-67]. The

basic assumption is that the pair interaction can be written as

$$v(r) = v_0(r) + v_1(r)$$
 (8)

in which $v_0(r)$ is the pair potential of a (well-known) reference system and $v_1(r)$ is a small perturbation potential. Often, the HS system is used as the reference. Several suggestions have been made for choosing the appropriate HS diameter, *d*. Below we list four well-known HS criteria; in Sec. IV these are evaluated with respect to their ability to locate the solid-liquid coexistence line.

In the zero-temperature limit $(T \rightarrow 0)$ the WCA pair potential approaches that of a HS [9–12] system with diameter $d = r_c$, i.e., the system described by

$$v_d(r) = \infty \text{ for } r < d \tag{9}$$

and zero otherwise. While this may not be intuitively obvious since the WCA pair potential goes smoothly to zero at the cutoff, it becomes clear when the WCA potential is shown in a log-plot (Fig. 1(b)). The simplest way of assigning an effective HS diameter to a WCA particle is to use the truncation distance

$$d = r_c \,. \tag{10}$$

This criterion is exact for $T \rightarrow 0$. At finite temperatures, however, the effective HS diameter will be smaller, and here one needs to make some physical assumption in order to improve Eq. (10) to arrive at better approximations. We list below four such approximations.

1. Boltzmann's hard-sphere criterion

In his 1890 Lectures on Gas Theory [68] Boltzmann suggested that the effective HS diameter d should be identified with the distance of closest approach when the velocities of two head-on colliding particles are given by their average kinetic energy at far distances. This criterion can be written as

$$v(d) = k_B T \,, \tag{11}$$

which for the WCA system results in

$$d = \frac{r_c}{\sqrt[6]{1 + \sqrt{k_B T/\varepsilon}}}.$$
 (12)

Boltzmann's idea, which provides the simplest HS approximation, has been used to estimate the effective HS diameter of the WCA system by a number of authors [19–22, 24, 25].

2. The Andersen-Weeks-Chandler hard-sphere criterion

A more sophisticated HS criterion was suggested in 1971 by Andersen, Weeks, and Chandler (AWC) [57]. Their motivation was to match as well as possible the Helmholtz free energy of the pair potential in question to the associated HS system. The AWC criterion may be summarized as follows. If

$$e(r) = \exp(-v(r)/k_B T) \tag{13}$$

is the pair-potential Boltzmann probability factor, the AWC effective HS diameter d is identified from

$$\int_0^\infty r^2 y_d(r) \Delta e(r) dr = 0 \tag{14}$$

in which $\Delta e(r) = e(r) - e_d(r)$ is the blip function and $y_d(r)$ the cavity function of the HS fluid. In the Percus-Yevic approximation the cavity function is given analytically [1, 60–63, 69, 70], which is convenient for applications of Eq. (14). The appearance of the blip function in Eq. (14) effectively limits the AWC integral to values near d. Thus it is sufficient to consider the zeroth and first shell of $y_d(r)$ to evaluate the AWC integral of Eq. (14) with a high accuracy. We used the following implementation of the cavity function in the determination of the HS diameter d via Eq. (14) [61]. If $s \equiv r/d$,

$$y_d(s) = \begin{cases} c_0 - c_1 s + c_3 s^3 & \text{for } s < 1\\ H_1(s)/s & \text{for } 1 < s < 2 \end{cases}$$
(15)

where

$$H_1(s) = a_1 \exp A(s-1)r + a_2 \exp B(s-1) \cos C(s-1) + a_3 \exp B(s-1) \sin C(s-1).$$
(16)

The parameters depend on the packing fraction η (see Eqs. (6) and (15)-(17) in Ref. 61). For the coexistence packing fraction $\eta = 0.4909$, corresponding to the density $\rho_l = 0.9375\sigma^{-3}$, we have $c_0 = 58.4514$, $c_1 = 67.9928$, $c_3 = 14.3461$, A = 1.58498, B = -3.68494, C = 3.85160 $a_1 = 0.56770$, $a_2 = 4.23705$ and $a_3 = -1.41141$. We evaluated the AWC integral numerically using the Python module SciPy's [71] implementation of QUADPACK [72].

3. The Barker- Henderson hard-sphere criterion

The Barker and Henderson (BH) theory [56], which predates the AWC theory, can be viewed as a simplification of the AWC theory [1]. Specifically, it is assumed that *r*-squared times the cavity-function is a constant, $r^2y_d = \text{const.}$, implying that Eq. (14) can be written

$$0 = \int_0^\infty [1 - e(r)] - [1 - e_d(r)] dr.$$
 (17)

Since the integral of $1 - e_d(r)$ is d, one arrives at the following HS criterion

$$d = \int_0^\infty [1 - e(r)] dr \,.$$
 (18)

The $r^2 y_d$ =const. assumption is reasonable since the blip function limits the integral to values near d where y_d does not change much when the temperature is sufficiently low. As T is lowered, the blip function narrows; thus the AWC diameter reduces to the BH criterion when $T \rightarrow 0$. Note that the BH criteria depends on temperature but not on density (the AWC criteria depends on both temperature and density). The BH integral of Eq. (18) is easily evaluated numerically using, e.g., the Python module SciPy's [71] implementation of QUADPACK [72].

4. Stillinger's hard-sphere criterion

At low temperatures, the integrand of the BH criterion Eq. (18) changes rapidly from nearly unity for r < dto nearly zero for r > d. This motivates the HS criterion proposed by Stillinger in 1976 [40, 73, 74]. He pragmatically identified the HS diameter from where the pair-potential Boltzmann factor equals one half, i.e.,

$$e(d) = \frac{1}{2}.$$
 (19)

Stillinger introduced this in connection with his study of the Gaussian-core model [73]. The same idea can also be applied to the WCA potential, however, leading [40] to

$$d = \frac{r_c}{\sqrt[6]{1 + \sqrt{k_B T \ln(2)/\varepsilon}}}.$$
 (20)

The functional form of this HS criterion is identical to that of Boltzmann if T is replaced by $T \ln(2)$: The factor 2 is here from Eq. (19), and with $e(d) = 1/\exp(1)$ one arrives at Boltzmann's criterion [24].

III. NUMERICAL DETERMINATION OF THE PHASE TRANSITION LINE

The interface pinning method [75–84] is used to compute the solid-liquid chemical potential difference $\Delta \mu$ for isothermal state-points at temperatures $0.002\varepsilon/k_B$, $0.02\varepsilon/k_B$, $0.2\varepsilon/k_B$, and $2\varepsilon/k_B$. For a given temperature, we first set up a FCC crystal elongated in the z-direction with the given density and compute the equilibrium pressure in an NVT simulation. We then construct a configuration of half-crystal and half-fluid by a high-temperature simulation, where particle positions are only updated for half of the particles (resulting in melting for these particles). This produces a configuration similar to the one shown in the inset of Fig. 2. We then perform an Np_zT simulation by adding a harmonic bias-field to the potential part of the Hamiltonian,

$$\mathcal{U}_{\rm IP}(\mathbf{R}) = \mathcal{U}(\mathbf{R}) + \frac{\kappa}{2} \left(Q(\mathbf{R}) - a \right)^2, \qquad (21)$$

which forces the system toward configurations with a fluid-crystal interface. Here, κ and a are parameters of

TABLE I. Selected state points on the coexistence line determined with the interface pinning (IP) method and by numerical integration of the Clausius-Clapeyron (CC) relation (the Supplementary Material gives all computed data). The numbers in parenthesis give the statistical uncertainty (95% confidence interval).

$T\left[\varepsilon/k ight]$	$p \left[\varepsilon / \sigma^3 \right]$	$ ho_l \left[1/\sigma^3 ight]$	$\rho_s \left[1/\sigma^3\right]$	Method
20	633.309	1.78328	1.85850	CC
2	31.8086(66)	1.08441(5)	1.15192(6)	IP
2	31.7532	1.08413	1.15163	CC
0.2	2.05169(33)	0.80004(3)	0.87356(4)	IP
0.2	2.05118	0.79992	0.87358	CC
0.02	0.174944(47)	0.70638(5)	0.77889(6)	IP
0.002	0.016687(3)	0.67717(3)	0.74791(3)	IP
0.002	0.016680	0.67705	0.74792	CC



FIG. 2. Determination of the coexistence pressure at the temperature $T_0 = 2\varepsilon/k_B$ (red diamond) by means of the interface-pinning method [75–84]. See the text for details. The inset shows an interface-pinned configuration where the colors indicate the rotational bond order parameter \bar{q}_4 defined in Ref. 85. With this coloring crystalline particles are reddish, while fluid particles are greenish.

the bias-field, and $Q(\mathbf{R})$ is an order-parameter that measure crystallinity though long-range order (see Eq. (15) in Ref. 75). The chemical potential difference between the two phases, $\Delta \mu$, is computed from the average force, $\kappa(\langle Q(\mathbf{R}) \rangle - a)$, which the bias field results in on the system (see Eq. (9) in Ref. 75). This is then repeated for several FCC densities (and thus pressures) near coexistence. As an example, Fig. 2 shows the pressures versus the computed chemical potentials at $2\varepsilon/k_B$, considering eleven pressures slightly above $31.7\varepsilon/\sigma^3$. The coexistence state point at $\Delta \mu = 0$ is determined by linear regression, compare the solid line on Fig. 2. From this we find the coexistence pressure $p = 31.8086(66)\varepsilon/\sigma^3$ where the number in parenthesis gives the statistical error on the last two digits using a 95% confidence interval. Table I reports the thermodynamic coexistence data obtained by the interface-pinning (IP) method and numerical integration of the Clausius-Clapeyron (CC) relation as detailed below.

While the interface-pinning method is accurate and provides specific error estimates, it can be computationally expensive because long simulations are needed to properly represent interface fluctuations, which are usually significantly slower than fluctuations of the bulk solid and fluid [75]. As an alternative, we determine most points on the coexistence line by numerical integration of the Clausius-Clapeyron relation (below s and v are the entropy and volume per particle)

$$\frac{dp}{dT} = \frac{\Delta s}{\Delta v} \,. \tag{22}$$

This is an example of the Gibbs-Duhem integration methods discussed by Kofke [86, 87], which do not involve slow fluctuations of an interface. The volume difference $\Delta v = v_l - v_s$ and the entropy difference $\Delta s = s_l - s_s = (\Delta u + p\Delta v - \Delta \mu)/T$ can both be evaluated from standard NpT simulations of the two bulk phases at coexistence (where of course $\Delta \mu = 0$).

We use a trapezoidal predictor-corrector method to compute coexistence pressures at the temperatures $T_i = 0.02 \times 10^{(i/24)}$ where *i* is an integer, compare the solid black line on Fig. 3. Substituting t = T and y = p we can write the first-order differential equation to be solved in the standard form

$$y' = f(t, y) \tag{23}$$

where f is the slope evaluated as $\Delta s / \Delta v$ (Eq.(22)). Suppose one knows the point (t_i, y_i) on the coexistence line, either from the interface-pinning method or from a previous step of the Clausius-Clapeyron integration, and wish to compute the next point (t_{i+1}, y_{i+1}) . Let the step length in t be $h = t_{i+1} - t_i$. The prediction of the simple Euler algorithm is

$$y_{i+1}^{(0)} = y_i + hf(t_i, y_i).$$
(24)



FIG. 3. Coexistence pressure as a function of the temperature. (a) The solid black line shows the reduced coexistence pressure p/k_BT as a function of the temperature (this study). The black dashed line gives the $T \rightarrow 0$ HS limit, p_{\bullet}/k_BT , and the colored dots represent literature coexistence pressures [42–44]. The red diamonds were computed with the interface-pinning method (this study). The blue dashed line shows that at low temperatures the pressure scales as $T^{3/2}$, as expected from HS theories (see the text). (b) The absolute value of the coexistence pressure in excess of its $T \rightarrow 0$ limit.

A better estimate is provided using Heun's method:

$$y_{i+1}^{(1)} = y_i + \frac{h}{2} [f(t_i, y_i) + f(t_i + h, y_{i+1}^0)]$$
(25)

The next estimate in an iterative predictor-corrector approach is

$$y_{i+1}^{(2)} = y_i + \frac{h}{2} [f(t_i, y_i) + f(t_i + h, y_{i+1}^1)]$$
(26)

or, in general,

$$y_{i+1}^{k+1} = y_i + \frac{h}{2} [f(t_i, y_i) + f(t_i + h, y_{i+1}^k)].$$
(27)



FIG. 4. Fluid density at freezing and solid density at melting as functions of the temperature. (a) The solid black line shows the density of the fluid at coexistence (this study). The dashed line marks the $T \rightarrow 0$ limit and the colored dots are literature data [42–44]. The red diamonds are densities computed with the interface-pinning method. (b) The solid black line shows the density of the solid at coexistence (this study), the dashed line is the $T \rightarrow 0$ limit, and the colored dots represent literature data [42–44].

In the limit of large k's this converges to the trapezoidal rule of integration where forward and backward integrations yield the same result.

Which criterion to use in order to determine when the predictor-corrector iterations have converged? To answer this we note that since slopes are evaluated from finite NpT simulations, we expect a significant statistical error on the f's used above. If $\bar{f}(t, y)$ is the theoretical slope, $f(t, y) = \bar{f}(t, y) + e_f$ where e_f is drawn from a normal distribution with standard deviation σ_f . This error is estimated by dividing NpT simulations into statistically independent blocks [88]. The error on y_{i+1}^{k+1} is $e_y = he_f$ and $\sigma_y = |h|\sigma_f$. It is sensible to terminate the predictor-

corrector iteration when

$$|y_{i+1}^{k+1} - y_{i+1}^{k}| < \sigma_y \tag{28}$$

since this indicates that changes of y_{i+1} 's are mainly due to the statistical uncertainty on the slopes.

In summary, numerical integration of the Clausius-Clapeyron relation comes with errors from ignoring higher-order terms and from the statistical uncertainty of the slopes. To quantify the overall error of the integration we can compare to the accurate estimates from interface pinning at selected state points. As an example, for $T_{48} = 2\varepsilon/k_B$ from the Clausius-Clapeyron integration we estimate the coexistence pressure to be $31.7532\varepsilon/\sigma^3$, which should be compared to $31.8086(66)\varepsilon/\sigma^3$ for the interface-pinning method, see Table I. The error of the computed phase-transition line is not visible in most figures of this paper, with notable exceptions at low temperatures (error bars are shown in the below figures whenever errors are significant).

Figures 3 and 4 show coexistence pressures and densities, respectively, from this study and from the literature [42–44]. We note that the low-temperature estimates of Ref. 43 are not accurate, while the high-temperature estimates of Refs. 42–44 are consistent with our results. As a consistency check, we note that the computed coexistence line reaches the HS limit [89] when $T \rightarrow 0$ (the dashed lines on Figs. 3 and 4 show the HS limits).

IV. COMPARING THE PREDICTIONS OF THE DIFFERENT HARD-SPHERE THEORIES

Having accurately located the WCA phase transition, we can now use this to test the four HS theories by comparing their predictions to the low-temperature WCA melting-line data.

A. Coexistence pressure and densities

Starting with the coexistence pressure, we first need coexistence information on the HS system. Fernandez et al. [90] estimate that the HS coexistence pressure is given by $p_d = 11.5727(10)k_BT/d^3$. This value is consistent with

$$p_d = 11.5712(10) \ k_B T/d^3 \tag{29}$$

computed more recently by Pieprzik et al. [89]; we use the latter value in this paper. In the zero-temperature limit, the HS diameter of the WCA interaction is $d = r_c$, which gives the coexistence pressure

$$p_{\bullet} = 8.1821(7) \ k_B T / \sigma^3 \,. \tag{30}$$

The bullet subscript "•" refers throughout the paper to the HS limit of the WCA model that is approached when $T \rightarrow 0$, i.e., setting $d = r_c$.



FIG. 5. Melting-line pressure compared to HS predictions. (a) The solid black line shows the reduced coexistence pressure, p/k_BT . The dashed lines show predictions of the HS theories (see text for details). The red diamonds show coexistence pressures computed with the interface-pinning method. (b) $\alpha_p(T) = 2(p/p_{\bullet} - 1)/\sqrt{k_BT/\varepsilon}$ (Eq. (43)) along the computed phase transition line (black solid) and the theoretical predictions also shown in the upper panel (dashed lines). The blue dashed line ($\alpha_0 = 0.89(1)$) is the $T \rightarrow 0$ limit determined from coexistence densities, see Fig. 6(b). AWC and BH give accurate predictions in the low-temperature limit. The red diamonds are the results of the interface-pinning method where blue error bars indicate the statistical error. We note a systematic inaccuracy of the Clausius-Clapeyron integration (solid black) at the lowest temperatures.

The solid black line in Fig. 5(a) shows the coexistence pressure divided by the thermal energy, p/k_BT , and the black dashed line shows the $d = r_c$ prediction. The predicted pressure is too low since the effective HS diameter is smaller than r_c at finite temperature where particles are allowed to overlap. In Fig. 5(a) we also consider other criteria for d's (by insertions into Eq. (29)). At



FIG. 6. Density-temperature phase diagram. (a) The solid black lines are the coexistence densities, compare Fig. 4. The vertical black dashed lines mark the $T \rightarrow 0$ HS limits, i.e., the quantities $\rho_{\bullet}^{(l)}$ and $\rho_{\bullet}^{(s)}$. The turquoise, green, yellow, and red dashed curves are predictions of the HS theories (see the text for details). The two blue dashed lines are the lowtemperature fits $\rho_l = \rho_{\bullet}^{(l)} [1 + 0.445 \sqrt{k_B T/\varepsilon}]$ and $\rho_s = \rho_{\bullet}^{(s)} [1 + 0.445 \sqrt{k_B T/\varepsilon}]$ $0.445\sqrt{k_BT/\varepsilon}$]. (b) The black +'s show $\alpha_{\rho}(T) = 2(\rho/\rho_{\bullet} - \rho_{\bullet})$ 1)/ $\sqrt{k_B T/\varepsilon}$ where the densities ρ and ρ_{\bullet} refer to the fluid. The green \times 's is $\alpha_{\rho}(T)$ using the solid densities. The red diamonds are densities computed with the interface-pinning method. The blue error bars indicate the 95% confidence interval. We find that the zero-temperature limit gives $\alpha_0 =$ $\lim_{T\to 0} \alpha(T) = 0.89(1)$. The turquoise, green, yellow, and red dashed curves are predictions of the HS theories. The AWC and BH give the correct low-temperature limit within the statistical accuracy.

 $T = 0.02\varepsilon/k_B$ the $d = r_c$ criterion underestimates the coexistence pressure by 7%, while both the AWC and BH criterion give only a 1% error. Thus, the HS theories give a significant improvement of the predicted coexistence pressure. It is hard to decide from Fig. 5 which

theory is best since this depends on the temperature. We return below to the low-temperature limit that provides a definite answer. First, we turn to the HS theories' predictions of the melting- and freezing densities.

Turning next to the freezing density, we first note that the HS fluid freezing density has been computed recently by Moir, Lue and Bannerman to the value [91]

$$\rho_d^{(l)} = 0.93890(7)/d^3 \tag{31}$$

and the melting density of the solid to

$$\rho_d^{(s)} = 1.03715(9)/d^3 \tag{32}$$

In the zero-temperature limit of the WCA system $(d = r_c)$ we get

$$\rho_{\bullet}^{(l)} = 0.66390(5)/\sigma^3 \tag{33}$$

and

$$\rho_{\bullet}^{(s)} = 0.73337(6) / \sigma^3 \tag{34}$$

When inserting the d's of the above HS criterions we get the temperature-dependent density predictions shown in Fig. 6(a) as colored dashed lines.

B. Analytical treatment of the low-temperature limit

Inspired by the functional form of Stillingers's and Boltzmann's HS criteria (Eq. (20) and Eq. (12)) we write the low-temperature limit of the effective HS diameter as

$$d_{\alpha} = r_c \left(1 - \frac{\alpha_0}{6} \sqrt{k_B T/\varepsilon} \right) \text{ for } T \to 0, \qquad (35)$$

which implies

$$d_{\alpha}^{-3} = r_c^{-3} \left(1 + \frac{\alpha_0}{2} \sqrt{k_B T/\varepsilon} \right) \text{ for } T \to 0.$$
 (36)

For the Boltzmann criterion one has $\alpha_0 = 1$ while Stillinger's criterion gives $\alpha_0 = \sqrt{\ln(2)} \simeq 0.83$.

Since d is the same for the AWC and BH criteria in the $T \rightarrow 0$ limit (see Sec. II B 3), the α_0 's are also identical. To evaluate α_0 we first note that the BH integral defining the HS diameter (Eq. (18)) can be written

$$d = r_c - \int_0^{r_c} \exp(-v(r)/k_B T) dr.$$
 (37)

Since the WCA pair potential is purely repulsive, it reaches its minimum at zero when $r = r_c$. Thus at low temperatures the above integral is centered near r_c , i.e., near x = 0 where $x = r_c - r$. Keeping the first nonvanishing term in a Taylor expansion we get

$$v(x) = \frac{1}{2}k_2 x^2 \text{ for } T \to 0$$
(38)

TABLE II. α_0 values.

		()
From simulations		0.89(1)
Boltzmann		1
AWC and BH	$\frac{1}{2}\sqrt{\pi} =$	$0.886227\ldots$
Stillinger	$\sqrt{\ln(2)} =$	$0.832555\ldots$

with (see Ref. 35)

$$k_2 \equiv \left. \frac{d^2 v}{dr^2} \right|_{r_c} = 36\sqrt[3]{4\varepsilon}/\sigma^2 \,. \tag{39}$$

Finding d from Eq. (37) involves solving a Gaussian integral in x. Expanding the upper limit of the integral to infinity, which is exact as $T \to 0$, we find

$$d = r_c - \sqrt{\frac{\pi k_B T}{2k_2}} \,. \tag{40}$$

By equating $d = d_{\alpha}$ (Eqs. (40) and (35)) we get

$$\alpha_0 = \frac{6}{r_c} \sqrt{\frac{\pi\varepsilon}{2k_2}} \tag{41}$$

or $\alpha_0 = \sqrt{\pi}/2 \approx 0.886227$. The theoretical α_0 values are summarized in Table II.

To estimate α_0 from the simulations we insert d_{α}^{-3} of Eq. (36) into Eq. (29) for the coexistence pressure, leading to

$$p = p_{\bullet} \left[1 + \frac{\alpha_0}{2} \sqrt{k_B T/\varepsilon} \right] \text{ for } T \to 0.$$
 (42)

Thus, a way to determine α_0 is to define the function (Fig. 5(b))

$$\alpha_p(T) = \frac{2}{\sqrt{k_B T/\varepsilon}} \left[\frac{p(T)}{p_{\bullet}} - 1 \right]$$
(43)

for which we note that $\alpha_0 = \alpha(T)$ for $T \to 0$. Similarly, we get for the densities $\rho = \rho_l$ or $\rho = \rho_s$

$$\rho = \rho_{\bullet} \left(1 + \frac{\alpha_0}{2} \sqrt{k_B T/\varepsilon}\right) \text{ for } T \to 0$$
(44)

and define

$$\alpha_{\rho}(T) = \frac{2}{\sqrt{k_B T/\varepsilon}} \left[\frac{\rho(T)}{\rho_{\bullet}} - 1 \right].$$
 (45)

Figure 6(a) shows the temperature dependence of the fluid and solid densities at coexistence (solid lines). These densities yield the $\alpha_{\rho}(T)$'s shown with black +'s and green x's, respectively, on Fig. 6(b). From the low-temperature points we estimate $\alpha_0 = 0.89(1)$. The colored dashed lines show the predictions of the HS theories (the $T \to 0$ limits agree with the values of Table II). We conclude that the AWC and BH theories gives excellent agreement as $T \to 0$. Figure 5(b) shows $\alpha_p(T)$ computed using the coexistence pressure. In agreement with the

results for the $\alpha_{\rho}(T)$'s we find that $\alpha_0 = 0.89(1)$ (blue dashed line).

The success of the AWC and BH theories suggests writing the coexistence pressure and densities as follows (inserting $\alpha_0 = \sqrt{\pi}/2$ into Eqs. (42) and (44))

$$p = p_{\bullet} \left(1 + \sqrt{\frac{\pi k_B T}{16\varepsilon}} \right) \tag{46}$$

and

$$\rho = \rho_{\bullet} \left(1 + \sqrt{\frac{\pi k_B T}{16\varepsilon}} \right), \tag{47}$$

respectively, see the blue dashed lines of Figs. 3-6. Interestingly, this low-temperature approximation gives better predictions than the *neat* HS theories – even at high temperatures (with the exception of Boltzmann's criterion near $T \simeq 0.5\varepsilon/k_B$). We do not have an explanation for this.

Equations (46) and (47) summarize an important result of this paper, providing an analytical HS approximation for the low-temperature freezing of the WCA fluid. This can be generalized to any other purely repulsive pair-potential that is truncated smoothly at $r = r_c$ by the following steps:

- 1. Compute k_2 using Eq. (39) and
- 2. derive α_0 within the BH theory by inserting k_2 into Eq. (41).
- 3. Low-temperature predictions for coexistence pressure and densities are then provided by inserting α_0 into Eqs. (42) and (44), respectively.

V. OUTLOOK

We have shown that HS theories give excellent predictions of the WCA melting line at low temperatures, in particular for the AWC and BH approximations. At higher temperatures the HS theories are less accurate. This is not surprising because the WCA model only resembles a HS system at low temperatures. How to predict the WCA melting-line pressures and coexistence densities at high temperatures? One possibility is to generalize the low-temperature HS approximation by considering the lines of constant excess entropy $S_{\rm ex}$ (this is the entropy in excess of the ideal gas entropy at the same density and temperature, a negative quantity that in some textbooks [92] is referred to as the residual entropy). For the HS system these lines are determined entirely by the density, i.e., they are vertical in the density-temperature phase diagram. In Ref. 35 it has been shown that the WCA system's structure and dynamics are near-invariant along the lines of constant excess entropy, which are referred to as isomorphs [93, 94]. An isomorph can be computed



FIG. 7. The solid black line shows the reduced coexistence pressure p/k_BT as a function of the temperature. The red and green dashed curves are isomorphs of the fluid, i.a., lines along which the excess entropy, S_{ex} , is constant. The isomorphs touch the phase-transition line at $T_{\star} = 0.02\varepsilon/k_B$ and $T_{\star} = 2\varepsilon/k_B$, respectively. The turquoise dashed line is the prediction of the AWC theory.

by numerical integration in the $\ln T - \ln \rho$ plane (e.g., using the fourth-order Runge-Kutta method (RK4) [35]) for which the required slope is $f = 1/\gamma$ where [93, 95, 96]

$$\gamma \equiv \left(\frac{\partial \ln T}{\partial \ln \rho}\right)_{S_{\text{ex}}}.$$
(48)

The "density-scaling exponent" γ may be computed from virial- and potential-energy fluctuations in the NVTensemble via the general statistical-mechanical identity

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 $\gamma = \langle \Delta W \Delta U \rangle / \langle (\Delta U)^2 \rangle$ [93]. Figure 7 shows the reduced pressure p/k_BT of two fluid isomorphs that overlap with the coexistence line at $T_{\star} = 0.02\varepsilon/k_B$ and $T_{\star} = 2\varepsilon/k_B$, respectively (dashed green and red lines). For comparison, the turquoise dashed line shows the prediction of the reduced coexistence pressure of the AWC theory. For the entire temperature span the isomorphs gives predictions with an overall accuracy comparable to that of the best HS approximation (AWC).

Figures 8 and 9 show the structure and dynamics along the melting line and the fluid isomorph in reduced units [93]. Interestingly, the physics is more invariant along the coexistence lines than along the isomorph. This is in contrast to previous findings for the LJ system, where the opposite applies [97]. We note, however, that isomorphs only follow the coexistence lines to a first approximation. For the LJ system, accurate predictions for the thermodynamics of freezing and melting can be arrived at within the isomorph-theoretical perturbation framework proposed in Ref. 97 – we hope to apply the same method to the WCA system in the near future.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

DATA AVAILABILITY

The data that support the findings of this study are openly available in Zenodo at http://doi.org/10. 5281/zenodo.6505218, reference number 6505218.

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FIG. 8. (a) The radial distribution g(r) for the fluid at coexistence. (b) The radial distribution as a function of the reduced distance $\tilde{r} = r \sqrt[3]{\rho}$ for the fluid at coexistence. (c) The radial distribution as a function of the reduced distance $\tilde{r} = r \sqrt[3]{\rho}$ for a fluid isomorph that touch the coexistence line at $T_{\star} = 2\varepsilon/k_B$.



FIG. 9. The solid lines show the mean-square displacement $\langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle$ for selected state-points along the coexistence line (see Table I). The dashed lines are long-time fits to $\langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle = 6Dt$ where D is the diffusion coefficient. The dots in the inset show the reduced diffusion coefficient $\tilde{D} = D\rho^{1/3}T^{1/2}$. The red x's and green +'s is the reduced diffusion coefficient for state points along the isomorphs with $T_{\star} = 2\varepsilon/k : B$ and $T_{\star} = 0.02\varepsilon/k_B$, respectively.

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