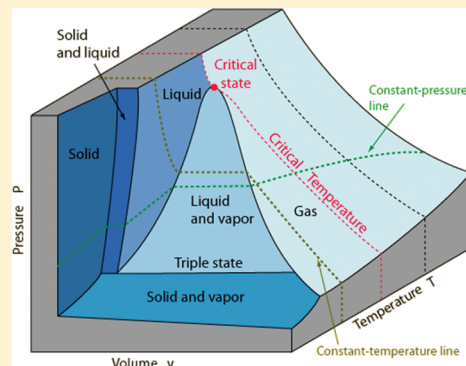


Thermodynamic Description of Liquid-State Limits

Leslie V. Woodcock*

Manchester Interdisciplinary Biocentre, University of Manchester, Manchester M1 7DN, United Kingdom

ABSTRACT: A state of random close packing (RCP) of spheres is found to have a thermodynamic status and a fundamental role in the description of liquid-state equilibria. The RCP limiting amorphous ground state, with reproducible density and well-characterized structure, is obtained by well-defined irreversible and reversible processes. The limiting packing fraction $y_{\text{RCP}} = 0.6366 \pm 0.0005$ (Buffon's constant within the uncertainty), and a residual entropy per sphere $\Delta S_{(\text{RCP-FCC})} \simeq k_{\text{B}}$ (Boltzmann's constant). Since the Mayer virial expansion does not represent dense fluid equations-of-state for densities exceeding the available-volume percolation transition (ρ_{pa}), we infer that a RCP state belongs to the same thermodynamic phase as prepercolation equilibrium dense hard-sphere fluid and likewise for hard-core fluids with attractive forces. Monte Carlo (MC) calculation of the liquid-state coexistence properties of square-well (SW) attractive spheres, together with existing MC results for liquid–vapor coexistence in the SW fluid, support this conclusion. Further findings for liquid–vapor coexistence limits are reported. The extremely weak second-order available-volume percolation transition of the hard-sphere fluid is strengthened by square-well perturbation as temperature is reduced. At the critical temperature, this transition becomes first order, whereupon a liquid at the percolation density coexists in thermodynamic equilibrium with its vapor at a lower density. The critical coexisting vapor density relates to the extended-volume bonded cluster percolation transition $\rho_{\text{pe}}(\lambda)$ defined for given well width (λ). Taking experimental liquid argon data as an example, it can be seen that the thermodynamic description of the coexistence limits, found here for square-well fluids, applies to real liquids.



INTRODUCTION

It has been 50 years since J.D. Bernal¹ first suggested that the state of random close packing (RCP) of spheres was a more appropriate starting point for the theory of liquids than the traditional nonideal gas, suggested by the original attractive mean-field perturbation theory of van der Waals² or the perfect crystal.³ Modern theories of liquids⁴ have almost exclusively been based upon graph representation of the Mayer cluster integrals⁵ in the belief that, provided the whole of the virial series could be evaluated, or accurately approximated, we would have a formal description of dense fluids up to and beyond liquid state densities. This premise, on which the general theory of liquids has been largely based for more than 70 years,^{4,5} now seems to be essentially a theory of nonideal gases.

The first attempt to reconcile the virial series with the high density region of the hard-sphere thermodynamic equilibrium fluid, metastable states, and RCP was Le Fevre.⁶ He simply plotted $1/Z$ where Z is $pV/Nk_{\text{B}}T$ for hard spheres obtained from MD data against packing fraction $y = (\pi/6)N\sigma^3/V$ (σ is the hard-sphere collision diameter) and found y_{RCP} to be 0.64. With recent advances in high-performance computing, we now have the thermodynamic $p(V,T)$ equation-of-state of the hard-sphere fluid to an accuracy of six figures.⁷ A linear plot of $1/Z$, in the spirit of Le Fevre, but using only equilibrium MD data in the “liquid” density range, for systems of one million spheres, gives an intercept packing fraction at $Z \rightarrow \infty$ as $y_{\text{RCP}} = 0.6375$ (Figure 1).

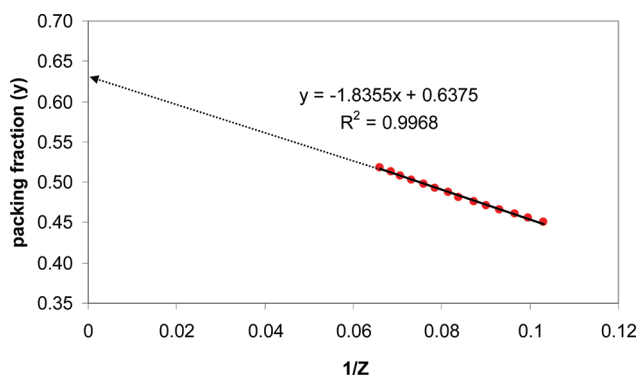


Figure 1. Reproduction of Le Fevre's extrapolation⁶ of pressure data for hard-sphere fluids using the most recent high-precision equilibrium thermodynamic pressure ($Z = pV/Nk_{\text{B}}T$), except with metastable points omitted. The intercept gives $y_{\text{RCP}} = 0.6375$.

This value, plus or minus 0.001 or thereabouts, has been reproducible by many granular sphere experiments and mathematical analyses⁸ and also by computer “experiments” going back 30 years.^{9–11} Just why it is so reproducible, however, is a question that is still being asked.¹² Here, we find that it is because the density of RCP is a limiting

Received: December 2, 2011

Revised: March 3, 2012

Published: March 19, 2012

thermodynamic amorphous ground state of the hard-sphere fluid, albeit metastable with respect to maximum crystal close packing. The evidence is set out in the sections that follow.

There are several papers in the literature where glassy states have been compacted or grown by a variety of computational algorithms; indeed, there are a great number of imaginable processes that will generate amorphous assemblies of “jammed” spheres which are nonequilibrium. As suggested in the question by Torquato et al.,¹³ it is because the process by which these states are produced is very often not well-defined. Here, we report results from both an irreversible process that is well-defined by a single rate constant, so the amorphous state is therefore also well-defined. Then, a reversible path is described that permits the amorphous hard-sphere RCP ground state to be produced by constraining the spheres in a cubic cell that prohibits crystallization but in a narrow region of the rate constant enables relaxation to access states very close to the amorphous RCP ground state.

We will also review the abiding suggestion that the amorphous ground state of hard spheres is the packing fraction of Buffon’s constant, an observation that might be helpful in the eventual development of a statistical theory. Then we will investigate and report on the relationships between the hard-sphere RCP state and the amorphous ground states of square-well fluids and the relationship of percolation transitions to critical gas–liquid condensation phenomena in square-well liquids.

■ CLOSED VIRIAL EQUATIONS

Le Fevre was the first to suggest that the hard-sphere virial equation should have its leading pole at RCP and be continuous in all its derivatives from ideal gas to RCP, but there have been many similar equations-of-state proposed since. We now know, however, that there is no continuity of phase from low to high density or gas-like to liquid-like. The Mayer virial expansion, which describes the low density phase, does not converge onto any high-density thermodynamic pressure equation-of-state for hard-core fluids, even below the freezing transition.

Recent investigations of the virial equations-of-state for hard spheres,^{14,15} hard disks,^{16,17} hard parallel cubes and squares,¹⁷ and four-dimensional hyper-spheres¹⁸ all show that the Mayer virial expansion does not represent the thermodynamic equation-of-state for densities exceeding the accessible-volume percolation transition. Using reduced hard-sphere units of temperature $T^* = k_B T / p\sigma^3$, where k_B is Boltzmann’s constant, and if p is a constant pressure, the three phases are shown in Figure 2 as a function of the packing fraction (γ). The gas phase extends from ideal gas, $T = \infty$, down to a temperature close to $T^* = 0.5$, where the available free volume changes from being extensive to intensive, called a percolation transition.¹⁵ At this point, there is a weak second-order thermodynamic phase change to the dense-fluid, liquid-like, phase whereupon the available volume that percolated the whole system in the gas-like phase becomes a distribution of disconnected holes. For temperatures below the freezing transition, $T^* < 0.0833$, the face centered cubic (FCC) crystal becomes the equilibrium phase with the reduced number density ($\rho = N\sigma^3/V$) maximum $\rho_0 = \sqrt{2}$.

Most real liquids can be supercooled; the thermodynamic state functions volume and entropy, for example, extrapolate smoothly into a metastable region and eventually undergo a glass transition, on any finite time scale, i.e., a freezing transition

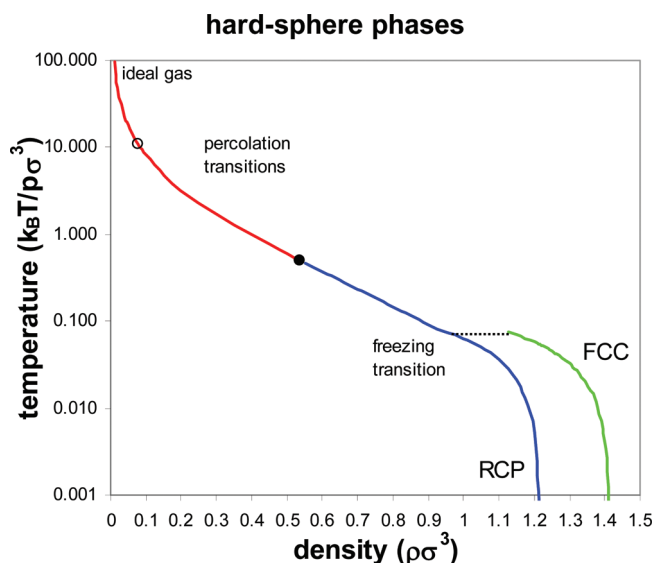


Figure 2. Thermodynamic phases of the hard-sphere model: red line, gas-like phase up to the percolation threshold; blue line, liquid-like high-density phase from percolation transition to RCP. For densities above the freezing transition, the dense-fluid phase becomes metastable with respect to FCC (green line).

to a nonequilibrium glassy state. The hard-sphere fluid has long been known to behave like real liquids in this respect,⁹ showing a similar glass transition on configurational arrest when the cooling rate is too fast for re-equilibration. Nonetheless, if the high-density equilibrium fluid phase is continuous in all its derivatives, there should exist an extrapolation to absolute zero of the state functions at constant pressure. There will therefore be an amorphous ground state. Here we find that the amorphous ground state of the limiting metastable fluid branch of hard spheres and square-well liquids is essentially the RCP state of spheres, first suggested as a starting point for liquid-state theory by Bernal.¹

■ IRREVERSIBLE COMPACTION ROUTE TO RCP

Structural properties such as distribution functions^{10,11} or order parameters^{12,13} may be used to characterize the state of RCP, but nonequilibrium solid states of matter can be defined only by fixing macroscopic state and process variables. For single homogeneous phases, temperature and pressure usually define the state. The thermodynamic properties such as enthalpy or entropy are single-valued state functions. Most composite solid materials, and all glasses, exhibit thermodynamic properties which are not single-valued state functions. Nonequilibrium solid states are only as well-defined as the process that produces them and possibly also the initial equilibrium state from which that process began. Therefore, when an equilibrium hard-sphere fluid configuration undergoes a compaction process which is zeroth-order in free volume (or pressure), i.e., $d\sigma/dt$ is held constant, the compaction misses the “RCP window”. For such processes, if the rate of compaction is high enough to avoid nucleation, it is too high for re-equilibration onto the RCP state.

Here we utilize an isothermal compaction process defined by a rate law which is first-order in free volume.

$$dV/dt = -k_1(V(t) - V_\infty) \quad (1)$$

V is the volume of a cube containing N spheres with periodic boundary conditions. V_∞ is the limiting close-packed state at $kT/p\sigma^3 = 0$, and is a priori unknown, but can be predicted in any time Δt from the mean pressure using the self-consistent free volume (SCFV) equation-of-state

$$V_\infty = \langle V(\Delta t) \rangle [1 - 1/\langle Z(\Delta t) \rangle]^3 \quad (2)$$

where $Z = pV/Nk_B T$ and the angular brackets denote an average over Δt .

If V is fixed, the sphere expansion rate $d\sigma/dt$, at any time t , is

$$d\sigma/dt = k_1 \sigma (1 - V_\infty/V(t))/3 \quad (3)$$

and is incorporated continuously into the equations-of-motion. Since the compaction process is well-defined, then the resultant state is also well-defined, albeit subject to statistical fluctuation and ensemble averaging for small finite systems.

The results obtained for the close-packed state from isotropic compressions spanning eight orders-of-magnitude of the compression rate constant k_1 are shown in Figure 3. At very

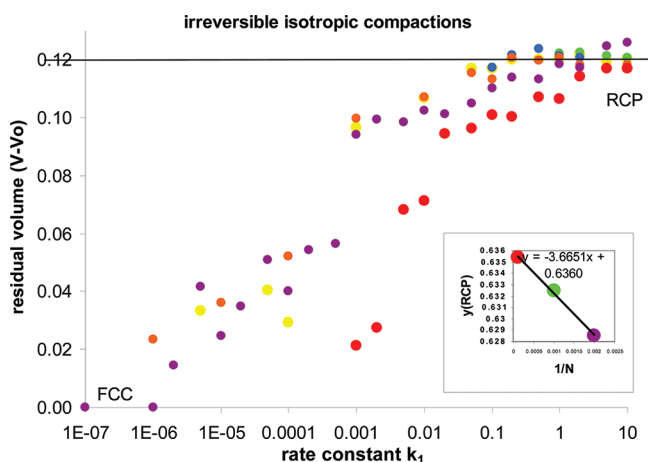


Figure 3. Residual volumes ($\Delta V/N\sigma^3$) of close-packed states of hard spheres plotted as a function of the compaction rate constant in dimensions of $(m\sigma^2/k_B T)^{1/2}$. In the limit of slow compaction, crystallization occurs ($V_{\text{residual}} = 0$ for FCC crystal). Violet circles are results for $N = 500$ starting at $\rho_1 \sigma^3 = 0.90$. Points corresponding to $N = 1000$ for different starting densities $\rho_1 \sigma^3 = 0.95$ (orange); 0.75 (green); 0.55 (yellow); and 0.35 (blue); $N = 8000$ (red).

low k_1 , the system can crystallize to a perfect face-centered cubic crystal for $N = 500$, whereupon for the close-packed crystal volume $V_0 = 2^{-1/2}N\sigma^3$. In Figure 3, the fractional excess volume obtained at the end of single compression simulation “experiments” is plotted against compression rate. As the rate constant k_1 increases, increasingly defective crystalline states are obtained. There is a narrow intermediate range of steeply increasing residual volume, which could be heterogeneous states for larger systems, i.e., glasses with small crystal nuclei, and eventually an RCP plateau.

For very high values of k_1 , 20 and above, a range of so-called jammed amorphous states can be produced going down to quite low densities with open structures. These nonequilibrium jammed structures have no thermodynamic status.

The residual volume of the RCP state fluctuates for small systems. As N increases, there is a slight number dependence, and the RCP state for various sized systems converges to a residual volume close to 0.12, i.e., 12% above FCC density, corresponding to $y_{\text{RCP}} = 0.633$. For a plot of y_{RCP} against $1/N$,

however, for the rate $k_1 = 10$, for three different sized systems, i.e., 500, 1000, and 8000 (inset Figure 3), the slightly higher value of 0.636 ± 0.002 is obtained. Thus, we now have another independent value for RCP in close agreement with Le Fevre’s extrapolation. In the next section, we report a reversible pathway to RCP that gives essentially the same result for the RCP packing fraction.

REVERSIBLE ROUTE TO RCP

RCP states of the hard-sphere glass obtained by the above irreversible process can be accessed reversibly. One thermodynamic pathway to RCP makes use of a single-occupancy (SO) system. The idea of a reversible pathway from fluid to crystal, using an FCC single-occupancy (FCCSO) cell system, was originally introduced by Hoover and Ree,¹⁹ to determine the hard-sphere freezing transition. The center of each sphere is confined within the walls of its cell, as defined by the FCC primary Voronoi polyhedra. Starting with the ideal gas, the p – V equation-of-state provides a reversible path from fluid to crystal which enabled Hoover and Ree to obtain thermodynamic properties such as the relative free energy, and hence the crystallization transition pressure, to be calculated.

The simple-cubic SO system (SCSO) can also provide a reversible path to high density states. Its close-packed crystal configuration ($\rho = 1$) is unstable with respect to slip in all directions, and nucleation to alternative crystal structures is prohibited. The system shows no phase transition, as it compacts smoothly and reversibly from the SO-ideal gas at low density, through its own SCSO-lattice fraction of $y = \pi/6$, at the “simple cubic” crystal close packed density at $\rho = 1$, to a RCP structure at $y = 0.637$, for $N = 8000$ spheres (Figure 3). The SCSO p – V equation-of-state appears to be everywhere continuous. It becomes equal to the hard-sphere fluid in the limit of both low density, where it obeys the ideal gas law, and high density, obeying the SCFV equation as it approaches SO-RCP reversibly.

The SCSO pathway appears to be reversible on the time-scale of our computer calculations. We have found, however, lattice structures with vacancies that suggest the path taken for SCSO may be metastable with respect to locally ordered phases that have very large numbers of spheres and a few crystal vacancies in the periodic unit cell and that can fit into the SCSO sublattice. However these “crystal” states are not generally accessible on the time scale of the re-equilibration and pressure sampling of the data points shown in Figure 4. Starting from a low density SO gas phase, a repeated sequence of compression, re-equilibration, and sample pressure leads to time-independent pressures for millions of collisions per sphere all the way from ideal gas to SO-RCP.

The extrapolation to $N = \infty$ in Figure 5 would suggest a slightly lower RCP fraction than has been obtained irreversibly above, but we note that the SO-RCP state may be very slightly less dense than the unconstrained RCP state for the following reason. The ratio of particle–wall collisions to particle–particle collisions at equilibrium for the SCSO model fluid is infinity for the ideal dilute gas and gradually reduces with density, but it does not go to zero at SO-RCP. It approaches a constant value as RCP is approached, of around 0.03 or 3%, as the pressure diverges; i.e., the total number of collisions per unit time goes to infinity, but the ratio of sphere–sphere to sphere–wall collisions remains constant. This suggests that the SO walls are to a very slight extent stabilizing the SO-RCP state. To obtain the unconstrained RCP state, the single-occupancy constraint

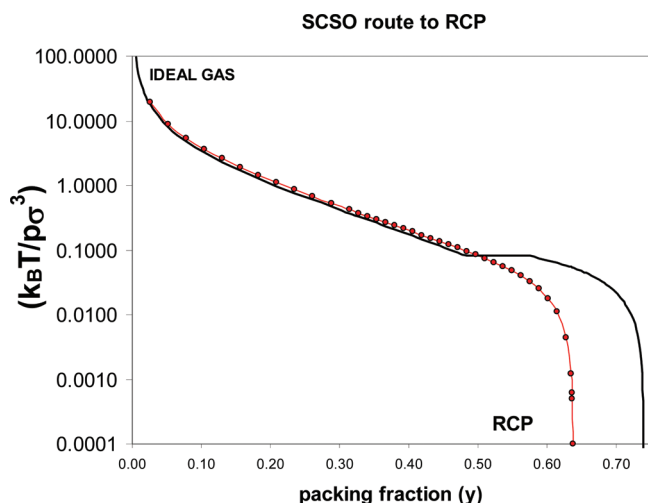


Figure 4. Equation-of-state for T at constant p data from MD simulations for the amorphous simple-cubic single-occupancy (SCSO) model, showing a reversible path to RCP (open circle data points $N = 8000$); solid black line is the equilibrium hard-sphere fluid, two-phase coexistence line, and FCC crystal.

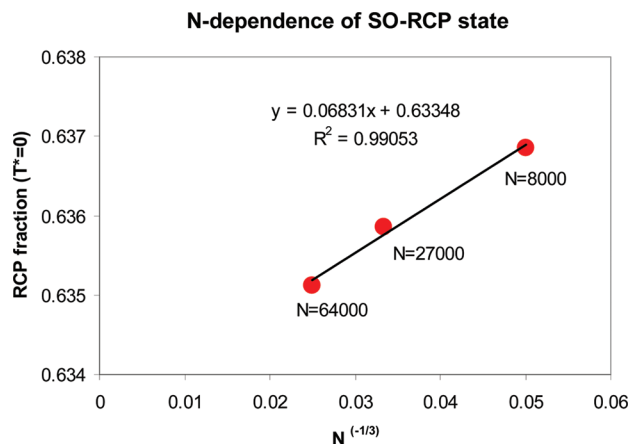


Figure 5. Number dependence of the SO-RCP state from MD computations; the packing fraction is obtained by extrapolating the limiting pressure to infinite pressure using the SCFV free volume (eq 2).

can be removed in the immediate vicinity of close packing to permit relaxation to the RCP ground state. The result for a system of 64 000 spheres is shown in Figure 6.

When the SO constraint is removed at a very high pressure, the system relaxes from SO-RCP to unconstrained RCP. The packing fraction y_{RCP} shown in Figure 6 is predicted from pressure development, using the SCFV free-volume formula (eq 2). The asymptotic limiting value obtained for the system of 64 000 spheres is 0.6365 ± 0.001 , in very close agreement with previous values obtained from both the Le Fevre extrapolation (Figure 1) and the irreversible compactions (Figure 3).

Communal entropy can be defined as the entropy difference between a SO cell model and the free fluid at the same temperature and volume ($\Delta S_{\text{T,V}}$). In the low density ideal gas limit, all SO systems approach the ideal-gas equation, and the communal entropy $\Delta S_{\text{T,V}}$ is exactly Nk_{B} . This result provides a check on the reversibility of the SCSO pathway to RCP. If the two states, equilibrium SCSO and metastable HS-glass, at RCP

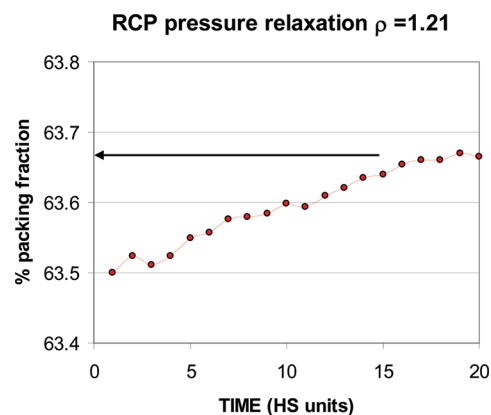


Figure 6. Limiting packing fraction obtained from a system of 64 000 SCSO at the density 1.21 permitting relaxation after removal of the single-occupancy constraint.

are indeed identical, the communal entropy must disappear along the reversible pathway between $y = 0$ and RCP in Figure 4. The integral of the difference between SCSO and the free hard-sphere fluid and its metastable branch from ideal gas to RCP (eq 4) equates to the communal entropy, i.e.

$$\Delta S_{\text{com}}/Nk_{\text{B}} = [(p/T)_{\text{HS}} - (p/T)_{\text{SO}}]dV = 1 \quad (4)$$

The residual entropy of the RCP state can be estimated from the difference between the SCSO and FCCSO $p(V)_T$ equations-of-state. From the first and second law of thermodynamics, any change in Gibbs energy is given by the differential equation $dG = Vdp$ at constant T . Also, for hard spheres the enthalpy change $dH = pdV$. Since, $dG = dH - TdS$, the entropy difference between FCCSO and SCSO at same T, p is

$$\Delta S_{T,p} = (p/T)\Delta V_{T,p} - \int \Delta V_{T,p} dp/T \quad (5)$$

Not only are the two equations-of-state identical in the low density limit but also they are very close, almost the same, for all pressures below $\sim 8.5(\sigma^3/kT)$, i.e., that of the ordering transition in the FCCSO equation-of-state. Moreover, for pressures greater than around $15(\sigma^3/kT)$, the residual volume of the SCSO becomes constant with a further increase in pressure. Beyond this pressure, the two terms in eq 7 effectively cancel. This means that both systems have identical thermal expansivities and heat capacities in the high p , or low T , region, i.e., for $p\sigma^3/kT > \sim 15$. As the temperature nears 0 K, the RCP entropy, relative to FCC at the same pressure, is estimated by matching the areas numerically as shown in Figure 7. A value $\Delta S_0 = 1.0 \pm 0.1Nk_{\text{B}}$ is in accord with previous estimates obtained by integrating fluid heat capacity from an equation-of-state beyond a glass transition.⁹

BUFFON'S CONSTANT

From the foregoing results, we can answer the question posed in a recent paper¹³ “is RCP well-defined”? Yes, phenomenologically, the thermodynamic RCP ground state is unique, but at present there is no statistical theory or proof. For all other amorphous close-packed states, the answer is the same as for any other nonequilibrium solid. The state is only as well-defined as the process that produces it and the initial state whence the process started.

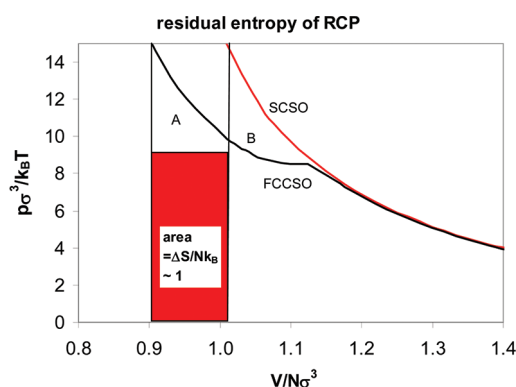


Figure 7. Residual entropy per sphere of the random close-packed state obtained from the SCSO model relative to the FCC crystal in the close-packed limit of the same temperature and pressure; the red area in the graph obtained by equalizing area A under the SCSO equation of state (black line) and area B below the FCCSO equation of state (red line). The full rectangular area shown is defined by the pressure (~ 15) above which the volume difference between SCSO and FCCSO becomes constant.

In the absence of any analytical theory for the RCP state density, another frequently asked question relates to the apparent coincidence between the value 0.6366 ± 0.001 and Buffon's constant $2/\pi$ ($= 0.6366192$) which occurs naturally as a factor in the solution to problems of statistical geometry. Since there is no exact analytical theory for the density of the RCP state, we can only speculate as to whether the thermodynamic state of RCP can be constructed analytically from mathematical operations to obtain the Buffon constant, as found, for example, in statistical geometry of randomly rotating needles, and even "noodles" or circles, on gridlines.²⁰

This suggestion arose from the earliest granular sphere experiments of Bernal¹ followed by Scott²¹ who obtained the value of 0.634 with 20 000 steel balls and copper cylinders. Scott and Kilgour²² later revised Scott's original RCP granular value to 0.6366, a result connecting this to the liquid state later confirmed by Finney⁸ by mathematical analysis of configurations of computer-generated liquid structures of 8000 atoms. Another three values from the present analysis may now be added to the list: Le Fevre interpolation from high-accuracy liquid-state MD pressures to $1/Z = 0$ ρ_{RCP} (Le Fevre) = 0.6375 (Figure 1); from the compressions via irreversible process at $k_1 = 10$ interpolated to $N = \infty$ which gives γ_{RCP} (isotropic compression) = 0.6360 (Figure 3); and finally, relaxation of RCP-SCSO to the unconstrained RCP amorphous ground state value 0.6365 (Figures 4–6).

All these values are collected in Table 1 together with the original granular shaking value of Scott and Kilgour²² with uncertainty estimates. Table 1 does not include the many

computer compaction "experiments" in the literature in a wide range of γ_{RCP} from 0.60 to 0.66 of various jammed RCP states that are not well-defined in a thermodynamic sense. The thermodynamic RCP amorphous ground state is well characterized, and as we see here, it can be also well-defined; however, at present, there is no analytic theory of RCP. A mean value from Table 1, 0.6366 ± 0.0005 , is essentially Buffon's constant within the bounds of numerical uncertainties, but without theory it remains a coincidence. While holding a suspicion, we cannot say that the packing fraction of this amorphous thermodynamic ground state for hard spheres is, or is not, $2/\pi$ until we have an analytic theory for RCP based upon principles of statistical geometry.

LIQUID–VAPOR COEXISTENCE

The hard-sphere fluid is the starting point for perturbation theories of the liquid state⁴ with a history that goes back to the van der Waals equation.² If the RCP amorphous ground state is a starting point for the hard-sphere high-density fluid equation-of-state beyond the percolation transition, it follows that in the limits of high temperature or very weak attractions RCP must also have a role in attractive-sphere models of critical condensation and the liquid state. In a recent paper,¹⁵ it is conjectured that the hard-sphere percolation transitions of available volume should also manifest itself in the origin of vapor–liquid coexistence when an attractive perturbation is added. The simplest such attractive hard-sphere molecular Hamiltonian is a "square-well" constant potential between pairs of spheres with a specific depth and range.

The pairwise additive model interaction between two square-well molecules i and j separated by distance r_{ij} is defined as

$$\begin{aligned}\phi_{ij}(r) &= 0 \text{ for } r_{ij} > \lambda\sigma \\ &= -\epsilon \text{ for } \sigma > r_{ij} > \lambda\sigma \\ &= \infty \text{ for } r_{ij} < \sigma\end{aligned}$$

where σ is the hard-sphere diameter; ϵ is the square-well depth; and $\lambda\sigma$ is the range.

The square-well model molecular fluid is the subject of an extensive literature of simulation studies and many theoretical investigations.²³

The critical points and thermodynamic liquid–vapor coexistence data have been obtained by Veda et al.²⁴ from Gibbs ensemble Monte Carlo (MC) calculations for five values of the square-well width relative to sphere diameter (λ) in the range $\lambda = 1.25$ – 2.0 . Elliott and Hu²⁵ also report critical point and coexistence properties of the same systems from molecular dynamics (MD) computations of liquid and vapor chemical potentials from equations-of-state data. Critical parameters for $\lambda = 3.0$ are reported by Benavides et al.²⁶ from simulations using direct methods of inhomogeneous MC computations. In all three studies,^{24–26} the uncertainties are quite large especially in the critical point densities. Another noteworthy observation is that all these simulation studies are unable to determine directly the coexistence properties at critical vapor densities well below their reported critical density.

To parametrize the critical and coexisting density data, Veda et al.²⁴ found that square-well fluids obey the law of rectilinear diameters (LRD) within the region of their computations. They

Table 1. Values Obtained from Various Sources for the RCP Amorphous Ground State Packing Fraction

RCP pathway	packing fraction	reference
granular shaking	0.6366 ± 0.0005	Scott and Kilgour ²²
$pV/Nk_B T$ extrapolation	0.6375	Le Fevre ⁶
laboratory construction	0.6366 ± 0.0004	Finney ⁸
equations of state	0.6372 ± 0.008	Woodcock ⁹
irreversible compaction	0.6360 ± 0.002	Figure 3
reversible SCSO/relaxed	0.6365 ± 0.0005	Figure 6

parametrized the coexisting curves of density of liquid and vapor phases using the equations

$$\rho_L = \rho_c + C_2(1 - T/T_c) + 1/2B_0(1 - T/T_c)^\beta \quad (6)$$

$$\rho_V = \rho_c + C_2(1 - T/T_c) - 1/2B_0(1 - T/T_c)^\beta \quad (7)$$

for liquid and vapor phases, respectively. The results for the critical density (ρ_c) and critical temperature (T_c) and also the three constants C_2 , B_0 , and β are reported in Table 6 of the paper by Veda et al.²⁴ When the temperature goes to absolute zero, the constant mean density in the law of rectilinear diameters (ρ_m) is

$$\rho_m = \rho_c + C_2 = 1/2B_0 \quad (8)$$

where B_0 is the density of the coexisting “liquid phase” extrapolated to absolute zero. Taking the average values of C_2 and B_0 in columns 7 and 8, respectively, of Table 6 in the paper by Veda et al.,²⁴ the value of B_0 averaged over the 5 values of λ for which data are available is 1.13 ± 0.09 , and the average value of $\rho_c + C_2$ is 0.704 ± 0.20 . Both these average values are, to within the rather wide and irregular uncertainty range, the RCP densities ρ_{RCP} ($= 1.216$) and $\rho_m = \rho_{\text{RCP}}/2$ ($= 0.608$), the LRD mean-density constant at $T^* = 0$, respectively, for square-well fluids.

The coexistence curves for the various values of the well width (λ) are shown in Figure 8 parametrized to within the

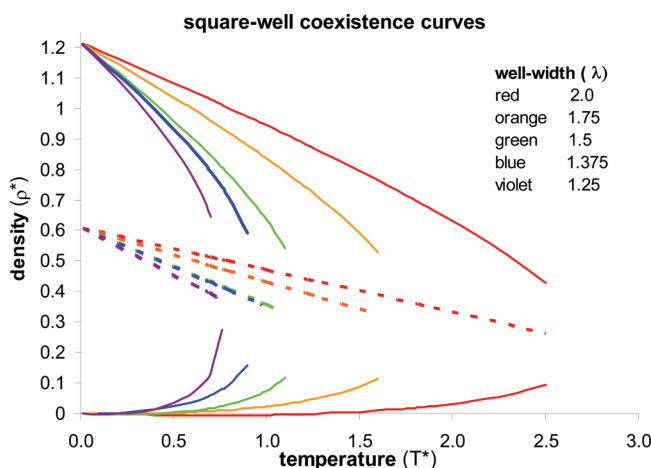


Figure 8. Thermodynamic liquid vapor coexistence lines of Veda et al.²⁴ parametrized according to the law of rectilinear diameters using the RCP amorphous ground-state LRD constant. The mean density constant at $T^* = 0$ is half of the limiting amorphous ground state which is the RCP density as shown, whereupon the vapor-phase density goes to zero.

uncertainties quoted by Veda et al.²⁴ using the present known value of RCP, i.e., $\rho_{\text{RCP}} = 1.216$, but retaining the critical exponent (β) values fitted by Veda et al. We see (Figure 8) that, to within the simulation uncertainties, the limiting amorphous ground state is the RCP state of hard spheres. We further observe that the liquid coexistence lines, insofar as the simulations permit, terminate at limiting coexisting density around the region of the hard-sphere percolation transition density (0.54). One can make similar observations from other molecular dynamics simulation results, for example, in Figure 2 of the paper by Elliott and Hu.²⁵

It has been suggested that a limiting critical density will originate at the available volume percolation transition reported recently for the hard-sphere fluid.¹⁵ First we examine the evidence for this relationship and consider the critical-point temperature in the limit $\lambda \rightarrow 1$, which can be referred to as the “sticky-sphere” limit. Theoretical estimates of the limiting critical temperature T_c^* put it as high as 0.8,²⁷ but reliable recent estimates from simulation data estimate it between 0.1 and 0.2.²⁸ Largo et al.,²⁸ moreover, quote a value for the critical density (ρ_c) at the limit $\lambda = 1$ of 0.552 ± 0.001 ; the hard-sphere percolation transition density is reported to be¹⁵ $\rho_{\text{pa}} = 0.537 \pm 0.05$. Thus, further evidence for a relationship between percolation transitions and critical phenomena is established; next we investigate the thermodynamic nature of this connection.

PERCOLATION TRANSITIONS

Postulates of thermodynamic percolation transitions relating to critical phenomena go back 25 years,^{29–31} but the determination of this property for the hard-sphere fluid is only recent. Values for the densities of available-volume (V_a) percolation transition in the hard-sphere fluid and the excluded volume (V_e) have been reported.¹⁵ The available volume of an equilibrium configuration is the volume accessible on the insertion of an additional sphere, then excluded volume $V_e = V - V_a$, i.e., the volume of the existing spheres plus the inaccessible zone of radius 1σ around each sphere that excludes the center of an incoming sphere.

We can predict qualitatively the direction of the effect of a square-well perturbation on the percolation transition density. Any kind of cohesive attraction, added to the equilibrium hard-sphere fluid at a given density and finite temperature, makes the spheres cluster together more. Hence, we expect the available-volume percolation threshold density (ρ_{pa}) to increase with square-well attraction strength, $\epsilon/(k_B T)$. Accordingly, the excluded-volume percolation density (ρ_{pe}) will decrease to some extent with $\epsilon/(k_B T)$.

The percolation density ρ_{pa} for square-well fluids can be determined using the method of single-particle diffusivity (D_i).¹⁵ Results obtained for D_i in Figure 9, for example, illustrate how this percolation density point has been computed. For the square-well system $\lambda = 1.005$, at a state point close to T_c^* , the percolation transition density is increased slightly above the hard-sphere value. Starting with the hard-sphere limit, $T^* = \infty$, ρ_{pa} increases from 0.537 to near 0.569. This is close to, but slightly above, the estimated critical point density $\rho_c = 0.552 \pm 0.001$ in the sticky-sphere limit computed by Largo et al.²⁸ From the combined observations, we find that in square-well fluids the RCP density (ρ_{RCP}) at $T = 0$ K and the available volume percolation (ρ_{pa}) at $T = T_c$ are the originating thermodynamic limits of liquid-state coexistence in equilibrium with a vapor.

Next, consider what happens to the percolation transition when an attractive perturbation is added in the wide-well limit of large, but finite, width λ . In particular, what is the limiting critical point density? There seems to be some confusion in the literature. The augmented van der Waals equation-of-state for the pressure

$$p = p_{\text{HS}} - a\rho^2 \quad (9)$$

defined simply by adding a constant mean-field attractive perturbation to an essentially correct hard-sphere equation-of-

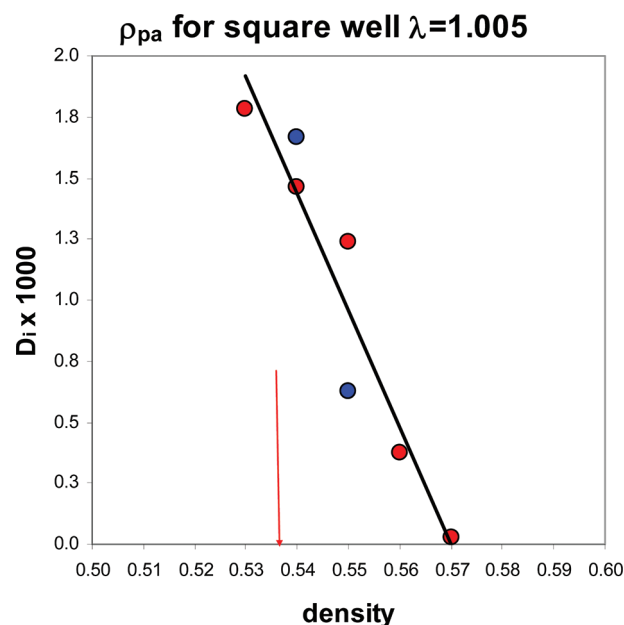


Figure 9. Determination of the available volume percolation transition density for the square-well fluid $\lambda = 1.005$ near the critical temperature $T^* = 0.2$. The circles are the values of single particle diffusion coefficient (D_i) as defined and described previously:¹⁵ blue circles, $N = 864$; red circles, $N = 6912$. The percolation transition density corresponds to $D_i \rightarrow 0$, i.e., at $\rho_{pa} = 0.569 \pm 0.01$; the red arrow shows ρ_{pa} for hard spheres.

state for the pressure²³ predicts the same limiting critical density $\rho_c = 0.25$ for all van der Waals fluids, but this is not “exact” for square-well fluids of finite well-width. No molecular Hamiltonian corresponds to $\lambda = \infty$, whereupon λ would become of the order of system size or made to be state-dependent as in the Kac limit,³² a mathematical contraption which has no real counterpart. Beyond the available-volume percolation, moreover, the mean-field linear dependence of attractive energy upon density, leading to the $-a\rho^2$ term in the pressure equation-of-state, becomes inapplicable. At the percolation density, the correction relative to the hard-sphere pressure ($p - p_{HS}$) begins to decrease, as density fluctuations begin to diminish more rapidly, and compressibility $(dV/dP)_T$ decreases.

In the thermodynamic limit of high temperature, the properties of the hard-sphere fluid must be recovered, including the percolation transition. For finite supercritical temperatures, i.e., $T_c < T < \infty$, the weak second-order percolation transition will remain with different perturbations on either side of the transition. On the low-density gas-like side, fluctuations in density are enhanced by the attractive well due to incipient clustering. At present, there is no supercritical thermodynamic data for square-well fluids. For subcritical temperatures, the only values of λ for which reliable critical constants have been evaluated by simulation are in the range $\lambda = 1.25$ – 3.0 .^{24–26}

The result²⁶ for $\lambda = 3$ has wide error margins. In the absence of any reliable simulation results beyond $\lambda = 2$, we decided to investigate the SW fluid $\lambda = 5$ by MC simulation to glean more evidence for the behavior of the coexisting densities of wide-well fluids in the vicinity of T_c . Scholl-Passenger et al.²⁷ found that cubic equation for the dependence of the square-well

critical temperature on well-width. If we reformulate their expression in terms of $\lambda - 1$ ($= x$)

$$T_c^* = a - bx + cx^2 + dx^3 \quad (10)$$

then the constants are $a = 0.838$, $b = 0.552$, $c = 2.415$, and $d = 0.070$ whence the critical temperature of the square-well fluid for higher values of λ may be estimated; eq 10 predicts a value $T_c^* = 41.8$ for $\lambda = 5$. Monte Carlo (N, V, T) calculations for the thermodynamic pressures, along a near-critical isotherm, $T^* = 40$, have been carried out for $\lambda = 5$, to obtain more insight into wider-well critical properties. The resulting average pressures for systems of $N = 864$, $N = 4000$, and $N = 6912$ are plotted in Figure 10. Each state point reduced pressure (p^*) is calculated

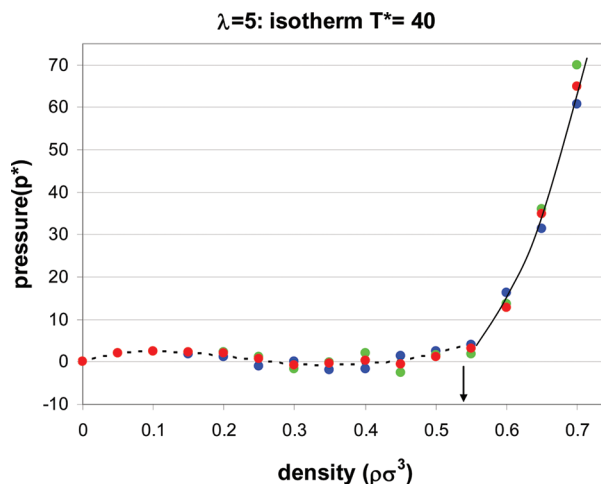


Figure 10. Monte Carlo pressures on a near-critical isotherm $T^* = 40$ of the square-well fluid $\lambda = 5$ for a range of system sizes with periodic boundary conditions; red, $N = 6912$; blue, $N = 4000$; green, $N = 864$; the dashed line is the best-fit trendline in the critical pressure region; the arrow shows ρ_{pa} for hard spheres.

from the pair distribution function $g(r)$, at the three contact points, $g(\sigma)$ and $g(\lambda+)$ and $g(\lambda-)$, by

$$p^* = 2\pi\rho k_B T [g(\sigma) + \lambda^3 \{g(\lambda+) - g(\lambda-)\}] / 3 \quad (11)$$

from $g(r)$ sampled from 1000 configurations from runs of 10 million MC trial moves with approximately 50% acceptance. The fluctuations are still rather large in the two-phase region close to the critical point, but the pressure data, particularly for the largest system $N = 6912$, shows a dense liquid phase at the percolation density, apparently coexisting with a very low density gas phase. When this preliminary result for $\rho_c(\lambda = 5)$ is plotted alongside the existing values of $\rho_c(\lambda)$ ^{24–26} (Figure 11), we see the critical-point density is approaching a limiting value which is about half of the percolation transition density ρ_{pa} of hard spheres.

The effect of a square-well perturbation on the hard-sphere percolation transition, starting at $\beta\epsilon = 0$ (where $\beta = 1/k_B T$), is to increase the density of the percolation threshold; this can simply be understood since attraction implies more clustering and hence more accessible volume, hence higher ρ_{pa} . The minimal effect of any finite attraction of nonzero range is to increase it, in the case of sticky spheres, very slightly from the hard-sphere ($T^* = \infty$) value 0.537 to 0.57 at $T^* = 0.2$. For the case $\lambda = 2$, at the supercritical temperature $T^* = 5$, a value of the percolation transition density as high as $\rho_{pa} = 0.61$ has been obtained. In the limit of very large λ and high T^* , the

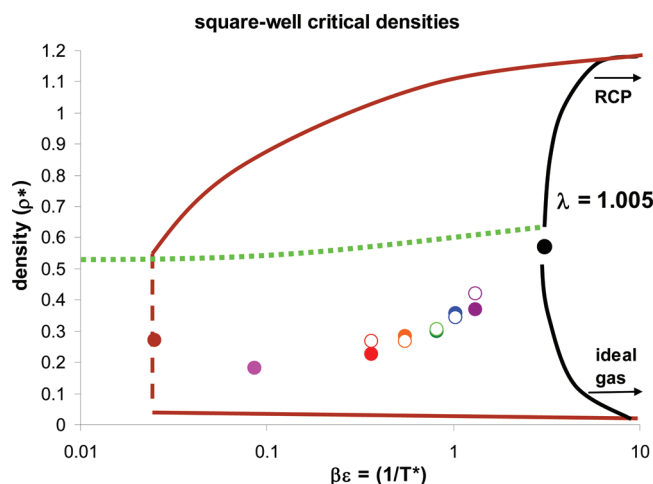


Figure 11. Critical densities of square-well fluids. The brown solid line is the current critical-density estimate for $\lambda = 5.0$ with tie-line (dashed) and liquid–vapor coexistence lines (solid). The other critical densities are solid and open colored circles from refs 24 and 25, respectively: violet ($\lambda = 1.25$), blue ($\lambda = 1.375$), green ($\lambda = 1.5$), orange ($\lambda = 1.75$), red ($\lambda = 2.0$). The solid black circle is the present critical density for $\lambda = 1.005$ [see also ref 28] together with coexistence lines; also shown (dotted blue line) for the system $\lambda = 1.005$ is the locus of the available volume percolation transition from the high-temperature limit to the critical temperature.

perturbation of the hard-sphere fluid structure again becomes negligible, whereupon both the square well ($\lambda = \infty$) percolation transition and critical-point liquid density will coincide with the hard-sphere ρ_{pa} .

This percolation transition of the hard-sphere fluid is a very weak second-order thermodynamic phase transition that occurs as the fluctuations in either number density, or equivalently available volume, change at the percolation threshold. The transition is so weak that, until recently,¹⁵ it has been imperceptible from the equations-of-state. The effect of any square-well attraction as a perturbation, however, is to strengthen the percolation transition, yielding larger discontinuities in fluctuation-related second-order properties, heat capacity, and compressibility, with decreasing temperature. Eventually, with sufficient cooling, at the critical temperature, this second-order phase transition becomes one of first order. At this point a liquid state at the density of the available-volume percolation transition coexists in thermodynamic equilibrium with a vapor state at lower density.

■ EXTENDED-VOLUME PERCOLATION

We have found a role of the hard-sphere available-volume percolation threshold density (ρ_{pa}) in describing square-well liquid–vapor coexistence phenomena. We also know that the coexisting vapor must have the same Gibbs chemical potential. Kratky³¹ conjectures that there is also a role of the excluded-volume percolation transition (ρ_{pe})^{15,31} in determining the coexistence vapor densities. While we here find no evidence to support Kratky's conjecture, we note that the excluded-volume percolation transition ρ_{pe} for hard spheres^{15,31} is the high-temperature limit of a percolation transition in a square-well fluid, for the special case when $\lambda = 2$, i.e., at the density when a bonded cluster first spans the system. We will refer to this as the “extended-volume” percolation transition and retain the same symbol as used previously, $\rho_{pe}(\lambda)$, note now with a λ -dependence.

There is no evidence of a thermodynamic phase transition at ρ_{pe} for the hard-sphere fluid, but it seems likely that, when the square-well perturbation is added at finite temperature, it will appear as a weak second-order discontinuity. At this density one expects the Mayer virial expansion^{4,5} equation-of-state for square-well fluids to deviate from the thermodynamic pressure. In the high-temperature limit, the values of λ corresponding to any density of the hard-sphere fluid, for which the square-well particles would percolate as a system-sized cluster, can be estimated from the results of Heyes et al.³⁴

This gas-phase discontinuity may be imperceptible well above the critical temperature but will strengthen with reduction of temperature, i.e., as $T \rightarrow T_c$. We therefore anticipate a second-order phase transition with a similar role in the thermodynamic description of the coexisting vapor when two-phase coexistence first appears. Preliminary results show that the square-well percolation transition density $\rho_{pe}(\lambda = 2)$ decreases slightly from the hard-sphere result¹⁵ (0.0785) to 0.0625; we have also obtained preliminary results for $\rho_{pe}(5) = 0.0067$ and $\rho_{pe}(1.005) = 0.48$, and an intermediate value $\rho_{pe}(1.1) = 0.30$. These are used to estimate the loci of $\rho_{pe}(\lambda)$ alongside the loci of available volume percolation transitions $\rho_{pa}(\lambda)$ for a range of values of λ at critical points taken from the literature (Figure 12).

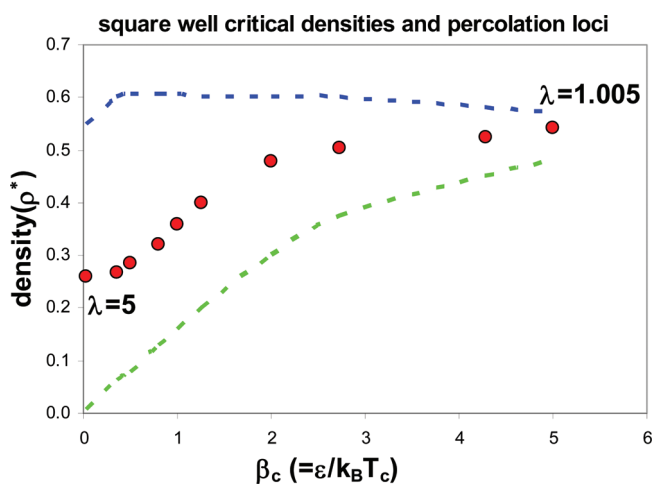


Figure 12. Loci of percolation transition densities for values of λ at a range of critical temperatures: available volume ρ_{pa} (dashed blue line) and square-well extended-volume percolation density ρ_{pe} (dashed green line). The values of λ that correspond to the critical mean densities (red circles) from left to right are 5.0 (present), 2.0, 1.75, 1.5, 1.375, 1.25 (refs 24 and 25), 1.1, 1.05, and 1.005 (ref 28).

From Figure 12, we see that there is a connection between two coexisting phases at the critical point and the percolation transition, but no evidence, for square-well fluids generally, for the role of the hard-sphere excluded-volume percolation (ρ_{pe}) as envisaged by Kratky.³¹ Rather, the coexisting vapor density follows the loci that one expects, not for the hard-sphere excluded-volume percolation but for the extended-volume bonded cluster percolation transition of the square well. The critical-point densities, within the rather wide uncertainty that they have been obtained, are intermediate of the two percolation transitions. At the critical temperature and pressure, the vapor at, or close to, ρ_{pe} and the liquid at ρ_{pa} must have the same chemical potential as the gradient in chemical potential (dp/ρ) approaches zero for densities between ρ_{pe} and ρ_{pa} as the

density fluctuations diverge. For large well-width, e.g., $\rho_{pe}(\lambda = 5)$, the vapor is a low density gas; at very narrow well-width, in the sticky sphere limit, $\rho_{pe}(\lambda = 1)$ and $\rho_{pa}(\lambda = 1)$ are quite close, and the tie-line is narrow.

This raises the question “what is the thermodynamic description of critical densities of real liquids, such as liquid argon?”. The argon–argon pair potential has a rather small vibrational amplitude at liquid temperatures, i.e., an effective width, below T_c , of the order 0.1σ to 0.2σ . This would correspond to a narrow square well and hence may be expected to behave as such. Perturbation theories⁴ indicate the available-volume percolation transition transfers from hard spheres to soft spheres, hence Lennard-Jones liquids, with a locus of the second-order discontinuity extending from the high-temperature limit to the critical T_c . At this point, the discontinuity in the second derivatives of chemical potential becomes first-order, with a discontinuity in the first derivatives, with respect to T and p , i.e., entropy and volume, respectively, and a horizontal two-phase tie-line, still in accord with Gibbs “phase rule”. The available-volume percolation is described by the insertion probability, as for hard spheres.¹⁵ The thermodynamic description of the coexisting-vapor density percolation remains unclear, as we do not have a definition of $\lambda_{eff}(T)$ to obtain $\rho_{pe}(T)$ for Lennard-Jones fluids.

CONCLUSIONS

We conclude by addressing further unanswered questions beginning with RCP and its role in the description of liquid-state equilibria. Is RCP fraction a minimum or a maximum is a frequently asked question.¹⁰ RCP is definitely not a minimum density for homogeneous amorphous close packing. Alternative compaction processes and athermal algorithms lead to homogeneous amorphous “jammed states” with lower densities.^{11,18} The present results indicate a local maximum in density and entropy provided nucleation is prohibited. For thermal metastable states in the vicinity of RCP, thermodynamics requires that small displacements must increase the Helmholtz free energy, i.e., $dA = -TdS = pdV \geq 0$; hence, the amorphous ground state RCP is a local, but not global, minimum in free energy and a local maximum in entropy and density.

Since RCP is a local maximum entropy in amorphous phase space, systems of spheres with kinetic energy, albeit generated simply by shearing or shaking, will obey laws of random choice and must always gravitate in a direction toward this metastable equilibrium given the opportunity. To obtain the RCP ground state, however, local relaxation must be allowed, and crystal nucleation must be disallowed, in any irreversible compaction process. This answers the question “Why is RCP reproducible?”.¹²

Thermodynamic state functions of any equilibrium liquid, e.g., $V(T,p)$ or $S(T,p)$, are continuous in all their derivatives, with respect to T and p , within phase bounds. If a model Hamiltonian, e.g., square-well potential, has a reversible path to ground state RCP, albeit metastable below freezing, then so also will real liquids. There must therefore exist a thermodynamically well-defined amorphous ground state at temperatures approaching absolute zero for all liquids if we extrapolate the liquid–vapor coexistence pressure line from the region of obedience to LRD to 0 K. The density at 0 K, for any liquid, should be obtainable from equilibrium experimental liquid–vapor coexistence data, when the LRD constants are known. For liquids that the linear law suffices, it is simply the

constant $2\rho_m$ where ρ_m is the LRD mean density constant. This experimental law has been known for over 100 years, but the significance of the limiting density constant appears not to have been recognized as being related to an amorphous ground state having a thermodynamic status.

Regarding future objectives, we need to find a theory for the RCP state based upon statistical geometry and hence resolve the conundrum of Buffon’s constant. Perhaps theory should also find a simple explanation of the residual entropy of RCP which is approximately equal to Boltzmann’s constant per sphere. A subsequent priority requires an application of high-performance computing to determine accurately the entire equations-of-state and phase diagrams of all square-well fluids, not least to consolidate the present findings.

Turning to real liquids, for even the simplest such as liquid argon, however, there are problems in determining the amorphous ground state. Not least is the intervention of a glass transition at a finite temperature before any thermodynamically metastable ground state can ever be accessed near $T = 0$ K. Moreover, the residual entropies and volumes can be small, compared to square-well cases, where the freezing transition is strong first order. The law of rectilinear diameters is empirical and inexact; it is actually a slight curve for most liquids, with some evidence of prefreezing phenomena. There may even be nonanalytic behavior of functions of state in the equilibrium prefreezing region as fluctuations involving a different symmetry or incipient nucleation appear. Also, the extrapolation from the triple point to absolute zero may exaggerate any errors arising from the deviations of real coexistence densities in the equilibrium range from LRD.

Verification for real liquids, of the originating percolation limits, however, is easier than the amorphous ground state because we are dealing with fluids in thermodynamic equilibrium. The experimental literature of p – V – T data for liquid argon, up to and beyond the critical temperature, is extensive and relatively accurate. A preliminary inspection of the pressure–density isotherms plotted in Figure 1 of the paper by Gilgen et al.³⁵ appears to support the present findings. The second-order percolation discontinuities in dp/dV for supercritical isotherms can be seen and are well represented by vertical loci lines at the two densities 455 and 625 kg/m³. If the argon–argon pair potential is taken to be the Lennard-Jones form, and the pair potential minimum is the effective hard-core diameter,⁴ i.e., $3.405 \times 2^{1/6} \times 10^{-10}$ m, we calculate the reduced number densities of the percolation transitions on the critical isotherm (150.7 K) to be $\rho_{pe} = 0.383$ and $\rho_{pa} = 0.526$, respectively. The critical liquid density is extremely close to the hard-sphere available volume percolation transition density¹⁵ (0.537), and the vapor density at T_c according to Heyes et al.³⁵ would correspond to an effective attractive diameter of $\lambda_{eff} = 1.20$, i.e., in the anticipated range. This is evidence that the role of the percolation transitions in describing limiting critical coexistence applies to real liquids.

More complex molecular liquids should also exhibit both supercritical higher-order percolation transition phenomena coincident upon a coexisting liquid-state critical density and also an amorphous ground state. Pertinent to the present study may be the recently reported discovery of a higher-order structural phase transition, described by the authors as a “percolation transition” in supercritical water.³³ These authors refer to a supercritical “percolation line” accompanied by a “change of symmetry”, dividing “gas-like” and “liquid-like” structures, respectively. That is precisely what we are seeing

here, starting right at the beginning with the reference hard-sphere fluid in Figure 2 with a “gas-like” and a “liquid-like” phase, either side of the percolation transition, and likewise for square-well fluids in Figures 10–12. We conjecture that all liquids, including water, will have a thermodynamic liquid phase, ranging from a metastable amorphous ground state all the way to an available-volume percolation transition at T_c , which will then become second-order above T_c , and extend to high temperature well into the supercritical region until it may eventually become imperceptible.

Thus, we reach the remarkable conclusion that a liquid–gas critical “point”, as hypothesized and parameterized by van der Waals,² and accepted by the physics community for 140 years,^{4,23–27} does not exist as such. There is no universality of critical phenomena that spans the dimensions.^{4,32} Rather, in the $V(T,p)$ surface, we find a line of uniform chemical potential at the critical temperature and pressure, above which there exists a supercritical mesophase bounded by the second-order percolation transitions, and below which there is the familiar liquid–vapor coexistence region. Physical condensation requires a weak external or gravitational field; the otherwise thermodynamically homogeneous states on the critical line would then phase separate at the liquid–vapor densities of the respective percolation transitions.

For the statistical thermodynamic theory of simple liquids, both the hard-sphere percolation transitions and the amorphous ground state, or RCP of hard spheres, should become the starting points for theoretical equations-of-state. We envisage further developments in the general theory, based more on principles of the statistical geometry of random packing, as originally suggested by Bernal.¹

AUTHOR INFORMATION

Corresponding Author

*E-mail: les.woodcock@manchester.ac.uk.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Helpful preprint comments by Professor John Finney and Dr. John Maguire are gratefully acknowledged. This paper was completed with the support of the Korean Ministry of Education in Science and Technology (KMEST) and the Korean Federation of Universities of Science and Technology (KFUST); we thank hosts Professor Sangrak Kim and the Department of Physics, Kyonggi University.

REFERENCES

- (1) Bernal, J. D. *Nature* **1959**, *183*, 141–147.
- (2) van der Waals, J. D. *Over de Continuïteit van den Gas-en Vloeistoofstand* (on the continuity of the gas and liquid state). *Ph.D. Thesis*, Leiden, The Netherlands, 1873.
- (3) Barker, J. A. *Lattice Theories of the Liquid State*. *International Encyclopedia of Physics and Chemistry*; Pergamon Press: Oxford, 1963.
- (4) Hansen, J.-P.; McDonald, I. R. *The Theory of Simple Liquids*, 3rd ed.; Academic Press: Oxford, 2006.
- (5) Mayer, J. E.; Mayer, M. G. *Statistical Mechanics*; Wiley: New York, 1940.
- (6) Le Fevre, E. J. *Nat. Phys. Sci.* **1972**, *235*, 20.
- (7) Bannerman, M.; Lue, L.; Woodcock, L. V. *J. Chem. Phys.* **2010**, *132*, 084507.
- (8) Finney, J. L. *Proc. R. Soc. (London)* **1970**, *A319*, 479–493.
- (9) Woodcock, L. V. *J. Chem. Soc., Faraday Trans. II* **1976**, *72*, 1667–1672; Also *Ann. N.Y. Acad. Sci.* **1981**, *371*, 274–298.
- (10) Berryman, J. G. *Phys. Rev. A* **1983**, *27*, 1053–1061.
- (11) Jodrey, W. S.; Tory, E. M. *Phys. Rev. A* **1985**, *32*, 2347–2354.
- (12) Kamien, R. D.; Liu, A. J. *Phys. Rev. Lett.* **2007**, *99*, 15501(4).
- (13) Torquato, S.; Truskett, T. M.; Debenedetti, P. G. *Phys. Rev. Lett.* **2000**, *84*, 2064–2067.
- (14) Woodcock, L. V. *LANL Cond. Mat. Stat. Mech.* **2008**, arXiv:1008.3872 [pdf].
- (15) Woodcock, L. V. *AIChE J.* **2011**, DOI: 10.1002/aic.12666.
- (16) Beris, A. Woodcock L. V. *LANL Cond. Mat. Stat. Mech.* **2010**, arXiv:1008.3872 [pdf]. See also APPENDIX I of reference 17.
- (17) Woodcock, L. V. *Nat. Sci.* **2011**, *3* (7), 622–632.
- (18) Analysis of the known virial coefficients (B_n) for 4D hard hyperspheres indicates that, in this case also, B_n become negative at B_7 ; a closure based upon $B_n - B_{(n-1)} = C_n + A$, where C is ~ -2 and A is ~ 13 , means the virial equation diverges from the thermodynamic pressure below the ordering transition in this system also.
- (19) Hoover, W. G.; Ree, F. H. *J. Chem. Phys.* **1968**, *49*, 3609–3619.
- (20) Ramaley, J. F. *Am. Math. Mon.* **1969**, *76*, 916–918. Also: Klain, D. A. Gian-Carlo, R. *Introduction to geometric probability*; Cambridge University Press: Cambridge, UK, 1997.
- (21) Scott, G. D. *Nature* **1960**, *188*, 910–911.
- (22) Scott, G. D.; Kilgour, D. M. *Brit. J. Appl. Phys.* **1969**, *ser.2* *2*, 863–866.
- (23) Gil-Villegas, A.; del Rio, F. *Rev. Mex. Fis.* **1993**, *39* (4), 526–541. See also the references in this paper to I to IV of this series.
- (24) Vega, L.; de Miguel, E.; Rull, L. F.; Jackson, G.; McLure, I. A. *J. Chem. Phys.* **1992**, *96*, 2296–2305.
- (25) Elliott, J. R.; Hu, L. *J. Chem. Phys.* **1999**, *110*, 3043–3048.
- (26) Benavides, A.; Alejandre, J.; del Rio, F. *Mol. Phys.* **1991**, *74*, 321–331.
- (27) Scholl-Passinger, E.; Benavides, A. L.; Castaneda-Priego, R. *J. Chem. Phys.* **2005**, *123* (234513), 1–9.
- (28) Largo, J.; Muller, M. A.; Sciortino, F. *J. Chem. Phys.* **2008**, *128*, 134513.
- (29) Woodcock, L. V. *Lect. Notes Phys.* **1987**, *277*, 113–123.
- (30) van Swol, F.; Woodcock, L. V. *Mol. Simul.* **1987**, *1* (1), 95–108.
- (31) Kratky, K. W. *J. Stat. Phys.* **1988**, *52*, 1413–1421.
- (32) Kac, M.; Uhlenbeck, G. E.; Hammer, J. *J. Math. Phys.* **1964**, *5*, 60–66.
- (33) Bernabei, M.; Botti, A.; Bruni, F.; Ricci, M. A.; Soper, A. K. *Phys. Rev. (E)* **2011**, *78*, 021505.
- (34) Heyes, D. M.; Cass, M.; Branka, A. C. *Mol. Phys.* **2006**, *104*, 3137–3146.
- (35) Gilgen, R.; Kleinrahm, R.; Wagner, W. *J. Chem. Thermodyn.* **1994**, *26*, 383–398.