Percolation Transitions and Fluid State Boundaries

L.V. Woodcock

Department of Physics, University of Algarve
Faro 8005-139, Portugal

E-mail: lvwoodcock@ualg.pt

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Abstract: Percolation transitions define gas- and liquid-state limits of existence. For simple model fluids percolation phenomena vary fundamentally with dimensionality (d). In 3d the accessible volume (V_A) and excluded volume ($V_E = V - V_A$) percolation transitions occur at different densities, whereas in 2d they coincide. The region of overlap for 3d fluids can be identified as the origin of a supercritical mesophase. This difference between 2d and 3d systems vitiates the hypothetical concept of "universality" in the description of critical phenomena. Thermodynamic states at which V_A and V_E, for a spherical molecule diameter σ, percolates the whole volume of an ideal gas, together with MD computations of percolation loci for the penetrable cohesive sphere (PCS) model of gas-liquid equilibria, show a connection between the intersection of percolation loci, and the 1$^{\text{st}}$-order phase-separation transition. The results accord with previous findings for square-well and Lennard-Jones model critical and supercritical fluid equilibria. Percolation loci for real liquids, e.g. CO_2 and argon, can be determined from literature thermodynamic equation-of-state data, and exhibit similar supercritical gas- and liquid-state bounds. For these real fluids the mesophase bounds extend to low density and pressures and appear to converge onto the Boyle temperature (T_B) in the low-density limit.

Key words: percolation, phase transition, critical point, liquid phase, gas phase

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I. INTRODUCTION

In 1863 J.W. Gibbs introduced the concept of a thermodynamic state function to describe physico-chemical equilibria. Gibbs' treatise [1] first explained how various thermodynamic states, can be defined by points on surfaces. Every state point, for example, of a one-component ($C = 1$) fluid volume pressure-temperature surface $V(p, T)$, as illustrated in Fig. 1, can be defined by the intersection of two lines. A state with two degrees-of-freedom ($F = 2$) is defined by the intersection of an isotherm and an isobar. For states with 2-phases ($P = 2$) where $F = 1$, either an isotherm or an isobar crosses a coexistence line. A coexistence line can be defined where two lines cross on Gibbs' energy surface. The triple point, whereupon $F = 0$, is where two coexistence lines cross in the p, T plane, etc.

Also shown in Fig. 1 is the point, labeled "critical state", that has not been defined thermodynamically, i.e. where two property loci cross. Its postulated existence has been based upon a hypothesis regarding the form of the p-V-T equation-of-state, first advanced in the PhD Thesis of van der Waals [2]. Above a critical temperature", there is deemed to be "continuity of liquid and gas". This implies that there can be no distinction between gas and liquid phases, i.e. no phase bounds along any supercritical isotherm.

In 150 years since Andrews' discovery of a critical temperature (T_c), however, nobody has reported a direct measurement of a liquid-gas "critical volume" [3]. Moreover, empirically parameterized cubic equations-of-state, in the spirit of van der Waals, have required ever-increasing numbers of adjustable parameters to reproduce the thermodynamic state functions with 5-6 figure numerical accuracy along critical and supercritical isotherms [3, 4]. This progressive inadequacy of cubic equations-of-state is indicative that the hypothesis of supercritical "continuity of gas and liquid" may be suspect.

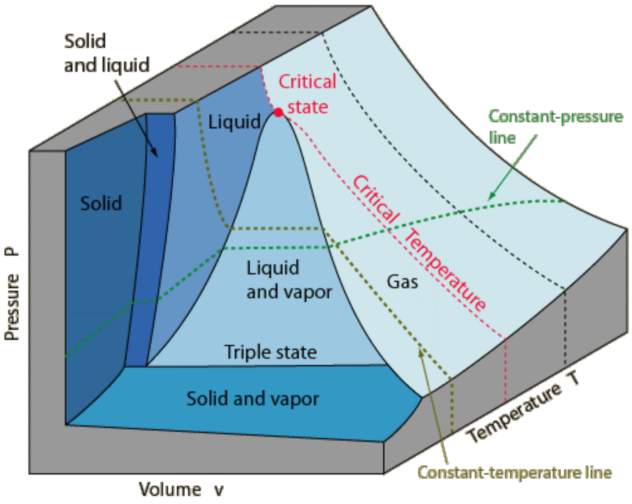


Fig. 1. Illustration of a Gibbs surface [1]: $p(V, T)$ for a simple fluid showing a hypothetical "critical volume" postulated by van der Waals (1873) [2]

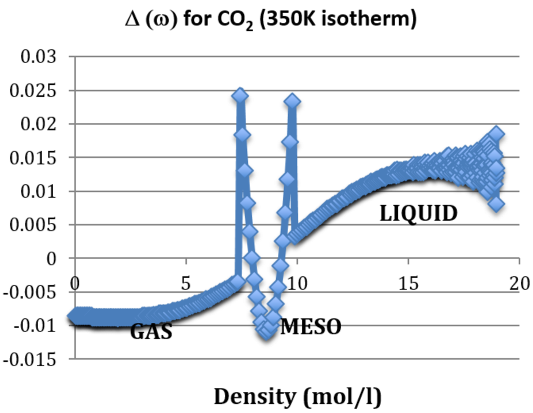


Fig. 2. Difference between rigidity, $(\mathrm{d}p/\mathrm{d}\rho)_T$, as calculated from NIST Thermophysical Properties equation-of-state [4] for CO_2 isotherm $T/T_c = 1.25$ by a numerical differentiation, and that obtained from the velocity of sound (c) tabulation using the thermodynamic identity $\omega = Mc^2 C_v/C_p$ (M is the molecular weight and C_v/C_p is the heat capacity ratio)

There is a 140-year history and an extensive literature of cubic equations-of-state, from van der Waals 2-parameter [2] to current research and compilations with 20+ parameters [4]. As the thermodynamic experimental measurements have improved in accuracy, to 5 or 6 figures, over the decades, these sophisticated cubic equations, that are extensively used for modern thermodynamic property data banks require an ever-increasing complexity and more fitted parameters [1].

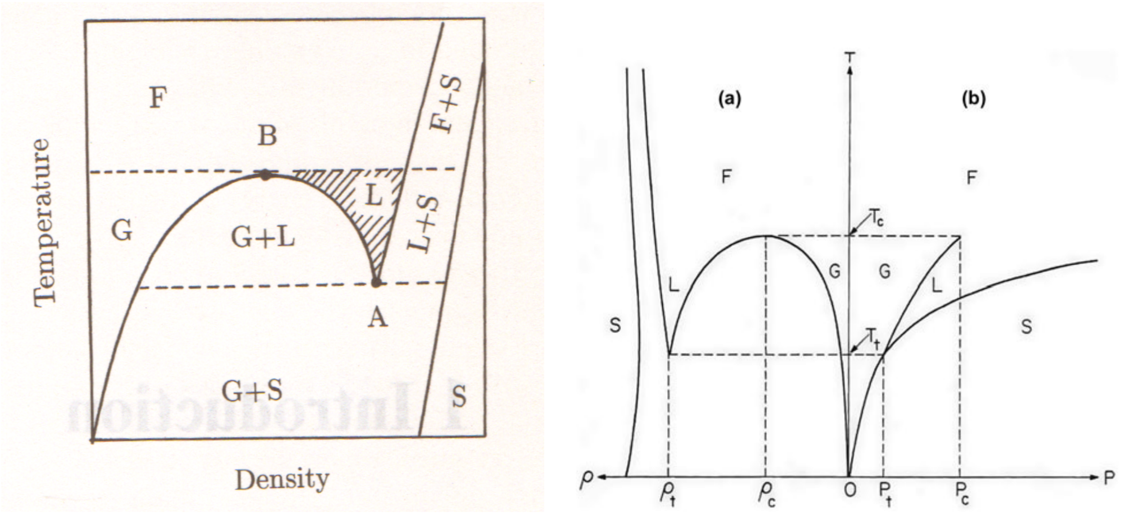
One reason for this progressive inadequacy is that the continuous cubic functional forms are fundamentally inappropriate in the vicinity of T_C and in the supercritical mid-range between gas and liquid phases. A mesophase, confined within percolation loci that bound the gas and liquid phases by higher-order discontinuities, can readily be identified. A simple numerical differentiation of NIST equations-of-state, for example, can demonstrate the existence of the supercritical mesophase and observe the phase bounds, along any isotherm, of any fluid (e.g. CO_2 at $T/T_c = 1.25$: see **Fig. 2**) for any of the 200 fluids in the NIST Thermophysical Property data bank [4]. These boundaries are smoothed over by the equations-of-state used to parameterize the original p-V-T experimental data.

It is also known that at T_c there is a range of densities along which the meniscus between a gas and liquid in coexistence can be observed to disappear as temperature is increased. Experimentally, a minimum coexisting liquid density is observed in coexistence with a maximum coexisting vapor density at T_c. The difference is 15-20%. Presumed "critical densities" have hitherto been obtained by using a universal critical exponent to obtain T_c, in conjunction with the law of rectilinear diameters, which defines a mean density of coexisting gas and liquid [3] and enables tabulations of "critical densities" at T_c [4].

The boundary separating the liquid state from the crystal phase and subcritical gas is clearly defined by Gibbs criteria for first-order phase transitions. The boundary separating the liquid phase from the supercritical fluid phase however, are *ad hoc* in modern texts on the liquid state. (see e.g. **Fig.3**). Heyes [5], for example, defines the boundary of both the "liquid" and "gaseous" states by a critical isotherm. In Hansen and McDonald [6], the "gas phase" is bounded by a critical isotherm, whereas the "liquid phase" is bounded by an isobar! Since these lines have no thermodynamic status, where does the liquid state begin and end one may reasonably ask? This question, "What is liquid?" [7], has remained unanswered.

The van der Waals theory of a gas-liquid critical point is based upon the assumption of "continuity"; this implies that there are no discontinuities in thermodynamic state functions of density or their derivatives along the critical and supercritical isotherms. Van der Waals moreover postulated that a fluid has an equation-of-state for which the first two derivatives of pressure with respect to changes in density or volume go to zero at a singular point on the Gibbs density surface. "Universality", embodied in renormalization group theory of Wilson [8], is another fashionable concept used to describe all critical phenomena from Ising models, spin glasses and ferro-magnetic systems in both two and three dimensions.

There is an abundance of theoretical and experimental evidence, however, going back at least 70 years, to the original cluster theory of Mayer [9], that the nature of criticality expected, i.e. when the Mayer cluster integrals diverge for the supercritical fluid states, is inconsistent with van der Waals hypothesis and Wilson's theory [8] (for $d = 3$). Modern computational facilities have enabled the virial coefficients in the expansion of pressure in powers of density of model systems up to order 12. The virial equations for hard-



(a) (b)

Fig. 3. Textbook phase diagrams of a typical monatomic fluid showing the boundaries between the solid, liquid and gas phases: the supercritical fluid is assumed to be a continuous single phase that spans all states above either T_c or p_c. (a) the projection in the ρ-T plane from Heyes [5] , and (b) from Hansen and McDonald [6] showing the density-(a) and pressure-(b) temperature planes respectively

sphere model molecular Hamiltonians may now be closed analytically, essentially exactly. Comparisons with thermodynamic pressures from MD simulations show a divergence of the virial equations from the thermodynamic equation-of-state at fluid densities below the freezing point [10, 11].

In the following sections, we will present further arguments that reaffirm a previous conclusion [12], i.e. that there are higher-order percolation transition loci that bound the gaseous and liquid states. These percolation transitions can be associated with the divergence of terms in Mayer cluster integrals along supercritical isotherms. Intersection of two percolation loci defines a ‘critical point’ in the p-T plane, or a ‘critical line’ on Gibbs density surface $\rho(T, p)$. Percolation thresholds define state bounds that vitiate the hypothetical concept of “continuity of gas and liquid” for simple atomic and molecular fluids.

II. MAYER CLUSTER EXPANSION

The starting point for an exact statistical treatment of the molecular theory of fluids is the expression for the partition function for a classical model pairwise molecular Hamiltonian. The configurational factor (Q) of the partition function can be expressed as an integral over phase space of the Boltzmann probability function [5, 6]

$$Q(V,N)=\int\ldots\int\exp(\Phi(\boldsymbol{r}_N)/k_BT)\mathrm{d}\boldsymbol{r}_1\ldots\mathrm{d}\boldsymbol{r}_n \tag{1}$$

For a pairwise Hamiltonian, Mayer [9] defines a function

$$f_{ij}=\exp(-\phi_{ij}/kT)-1 \tag{2}$$

then the Boltzmann probability of any configuration of N molecules is

$$\exp(-\Phi(\boldsymbol{r}_N)/k_BT)=\prod_{j>i}(1+f_{ij}) \tag{3}$$

$$=1+\sum f_{ij}+\sum\sum f_{ij}f_{kl}+\sum\sum\sum\text{etc.} \tag{4}$$

The n-th virial coefficient is then defined by a sum of all possible cluster integrals, but which go to zero if any molecule of the defined “cluster” is far away from all the other, accordingly the total number of contributing clusters of size n always decreases with n, but the integrals over all space are of ever increasing dimensionality

$$\begin{aligned}b_n=(n!\,V)^{-1}\int\ldots\int\\ \times\sum(n>j>i>1)\prod f_{ij}\mathrm{d}\boldsymbol{r}_1\mathrm{d}\boldsymbol{r}_n\end{aligned} \tag{5}$$

and the pressure equation of state is the simple summation provided the number of molecules in any cluster is finite for a system in the thermodynamic limit, or alternatively, the largest cluster is much smaller than the volume of the system. Equation (1) and hence the derived thermodynamic properties can be expected to exhibit higher-order thermodynamic phase transitions at a sufficient density if the size of contributory clusters to b_n, for example, diverges at a percolation transition.

For the hard-sphere fluid, the pressure is then obtained

$$Z=\sum_{n=1}^{\infty}b_n\rho^{n-1}, \tag{6}$$

where $Z = pV/Nk_BT$ and density $\rho = N/V$. For real molecules with attractive forces b_n is a function of temperature. Van der Waals obtained an equation-of-state resembling criticality and phase coexistence, by simply adding an attractive mean field, proportional to the square of density, to an "excluded volume" hard-sphere equation-of-state for the thermodynamic pressure of N spheres of diameter s in volume V at temperature T.

$$Z_{VW}(HS) = \frac{V}{V - Nb_2} = \sum_{n=0}^{\infty} (b_2\, \rho)^2 \tag{7}$$

The second virial coefficient $b_2 = 2ps^3/3$, and represents an excluded volume (V_e/N) based only upon collision of only two spheres. Only the first two terms of van der Waals hard-sphere equation are correct in describing the exact virial equation-of-state at low density. Virial coefficients beyond $n = 2$ depend upon the size of the cluster n, and can be computed by integrating over all space, the excluded volumes of clusters of spheres of ever-increasing size n using Mayer's equation (5).

Modern theories of simple liquids [6] are based upon the assumption that the thermodynamic hard-sphere fluid equation-of-state can be represented by equation (6), i.e. by an expansion of the phase integral into the excluded volume of small clusters of order n. A formal expression for the excluded volume, that takes account of all many-body correlations in a dense fluid, and which give the chemical potential and hence also correct equation-of-state for a system of N hard-spheres, was derived by Hoover and Poirier[13]. They considered the potential of mean force $\Psi(r)$ between two hard spheres in the equilibrium fluid as a function of separation (r). At zero separation, $\Psi(0)$ relates to the chemical potential, and for hard-spheres defines a "thermodynamic" excluded volume (V_e) which then defines the available volume $V_a (= 1 - V_e)$. For any equilibrium thermodynamic state, the available volume can be defined as the volume available for relocation of any one sphere i, anywhere in an equilibrium configuration, and is exactly related to the excess chemical potential (m), relative to the ideal gas for large N according to

$$\begin{aligned} -\frac{\mu}{k_BT} &= \log_e \frac{Q_{N-1}}{Q_N} = \log_e\left(1 - \frac{\langle V_e\rangle}{V}\right) = \\ &= \frac{\langle V_a\rangle}{V} =_{\rho\to 0} \sum_{n=1}^{\infty} \frac{n+1}{n} b_{n+1}\rho^n \end{aligned} \tag{8}$$

The Mayer cluster expansion, equations (6) and (8), is strictly only rigorous for thermodynamic properties at low density where the ratio (V/n) for large cluster size must be larger than the volume of cluster size n. Nonetheless, it has been widely assumed in liquid state theory to represent the thermodynamic state functions over the whole equilibrium fluid range up to high liquid densities [6], although the assumption is a dubious hypothesis. Equation (8) is often used in MD computations to calculate the chemical potential. It is often referred to as the "Widom method", although published by Hoover and Poirier [13] two years before Widom [14].

As higher virial coefficients have become known through advances in the power of modern computers, they begin to follow a trend. For the hard-sphere fluid, the coefficients up to b_{12} are now known following the recent computations of b_{11} and b_{12} by Wheatley [15]. When the coefficients are expressed in powers of density relative to close packing, i.e. $B_n = b_n\,(\rho/\rho_0)^{n-1}$, B_n decreases linearly with n for large n and the difference $B_n - B_{n-1} (= \Delta B_n)$ becomes constant. Consequently, the hard-sphere virial equation-of-state can be expressed analytically in a closed form, which is formally exact, albeit with explicit numerical coefficients up to B_m [10, 11].

$$Z = 1 + \sum_{n=2}^{m} B_n {\rho^*}^{n-1} + {\rho^*}^m \left[\frac{B_m}{1-\rho^*} - \frac{V_0}{(1-\rho^*)^2}\right] \tag{9}$$

$V_o = \sqrt{2}$ (empirically: this is the close-packed volume per sphere) and is the constant is the linear relationship between n and ΔB_n Equation (9) may be the most accurate equation to date for the hard-sphere virial equation of state. However, it may not represent the hard-sphere fluid thermodynamic equation of state with high precision at liquid-like densities. When comparison of equation (9) is made with high-precision MD pressures of the hard-sphere fluid, with 6-figure accuracy, a diversion is indicated at the density on or below a percolation transition (PA) of the accessible volume (11).

III. IDEAL GAS PERCOLATION TRANSITIONS

Hoover et al. reported the first determination of a percolation transition [15]. For an impenetrable hard-disk fluid, they obtained a value of the percolation transition density $\rho_{\mathrm{PA}} s^2 = 0.4$. For hard disks, this density of the accessible volume (PA) coincides with the percolation of excluded volume (PE). For d = 2, $\rho_{\mathrm{PE}} = \rho_{\mathrm{PA}}$; this is not so when d = 3. Relationships between dimensionality and percolation transitions can be summarized:

- d = 1 no percolation
- d = 2 PE and PA coincide $\rho_{\mathrm{PE}} = \rho_{\mathrm{PA}}$
- d = 3 there is an inequality and $\rho_{\mathrm{PE}} < \rho_{\mathrm{PA}}$

It is important to note that there is a fundamental difference between 2 and 3 dimensions. For 2d, there are two regions, 'gas-like' $\rho^* < \rho^*_{\mathrm{PE}}$ and "liquid-like" $\rho^* > \rho^*_{\mathrm{PE}}$, whereas for 3d fluids there are three regions with a mesophase, $\rho^*_{\mathrm{PE}} < \rho^* < \rho^*_{\mathrm{PA}}$ between gas and liquid phase bounds. In the mesophase, both the pockets of availability and clusters of exclusion sites percolate the system. The mesophase is neither gas-like nor liquid-like. For spheres,

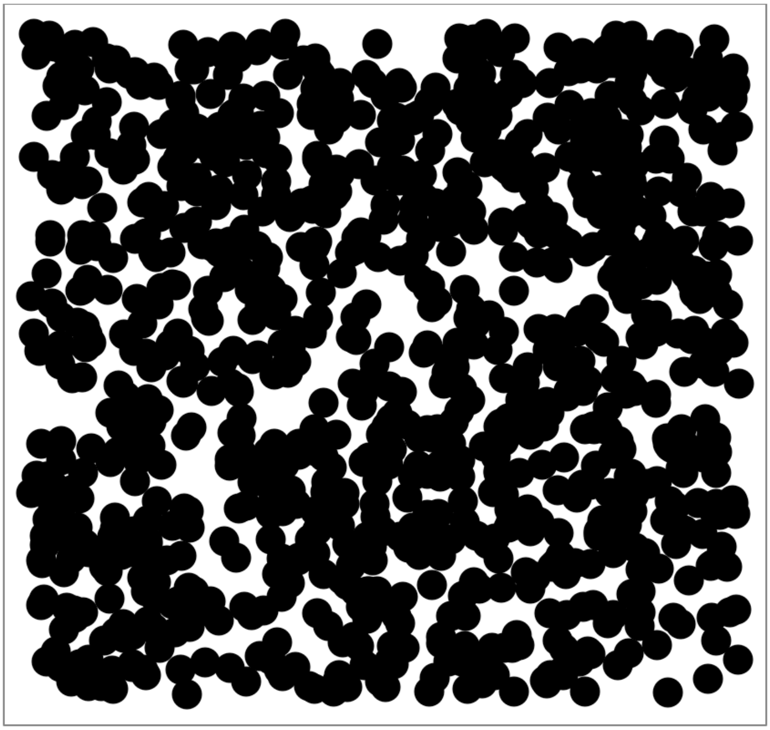


Fig. 4. Excluded and accessible areas (black and white respectively) of penetrable spheres for a configuration of a two-dimensional ideal gas close to the percolation transition

there are two percolation transitions associated with the excluded and available volumes. The V_A-percolation transition can equally be defined as the density at which the mean "accessible" configurational integral of a single sphere in the static field of all j (sometimes referred to as "Hoover's free volume" V_f), within the equilibrium ensemble, changes from being extensive at low density to intensive at high density. Above the percolation density ρ_{PA}, only the available volume in the immediate vicinity of sphere-i is "accessible". It is the percolation of this property that may be identified with the higher-order discontinuities predicted by the analysis of the coefficients in the Mayer cluster expansion equation (5) [9].

The ideal gas exhibits percolation transitions in both 2d and 3d of the volume excluded and available to an additional hard-sphere molecule of diameter s. This exclusion sphere diameter defines a reduced thermodynamic pressure $p^* = p\sigma^3/k_B T$ and a reduced temperature $T* = 1/p* = V* = 1/\rho^*$. We designate the percolation transition reduced densities, for example, as ρ^*_{PE} and ρ^*_{PA} respectively. Estimates of $\rho^*_{\mathrm{PE\ and\ PA}}$ for d $= 2$ ideal gas can easily be obtained pictorially using an EXCEL spreadsheet. For example, **Fig. 3** shows a typical configuration, 2000 random numbers from a uniform distribution 0-1, ($N = 1000$) in the vicinity of the percolation transition. In sections IV and V below we show that the percolation transitions of the ideal gas can be directly related to the critical point coexistence and a supercritical mesophase in the simplest model fluids to exhibit gas-liquid criticality and liquid-liquid upper critical consolute temperature (UCCT).

Until the present computations, PA has not been previously investigated or determined for the d $= 3$ ideal gas. The transition density ρ^*_{PA} is known to be 0.537 ± 0.05 for the hard-sphere fluid [12]. We have used the same methods, and criteria for percolation, as described previously for the hard-sphere fluid. Both ρ^*_{PE} and ρ^*_{PA} have been computed for a range of finite size systems of N particles. Thermodynamic limiting values ($N \to \infty$) have been obtained from the linear trendlines.

A MD program solves equations of motion of a binary mixture $N_A + N_B$. PA density values are obtained by the mean-squared displacements of B average over many frozen random configurations of ideal gas A. As the B particles do not interact with themselves, we average over all N_B in the same MD simulation run. Plotting the point of zero diffusivity, $D_i(\rho, N) \to 0$, against N (N_A in MD run) gives a linear trendline with the result $\rho^*_{\mathrm{PA}}(N \to \infty) = 0.908 \pm 0.01$.

Every configuration either has a percolating cluster or it does not. Clearly, for small finite systems, there will be equilibrium configurations that percolate, and some that do not, in the vicinity of PE. The percolation threshold in the computations of Heyes et al. [17] was defined when 50% of configurations have a percolating cluster. Here, we define PE using an ensemble average definition of a percolation density [12]; i.e. ρ^*_{PE} is the saddle-point density above which the cluster size probability distribution $P(n)$ is bimodal. This

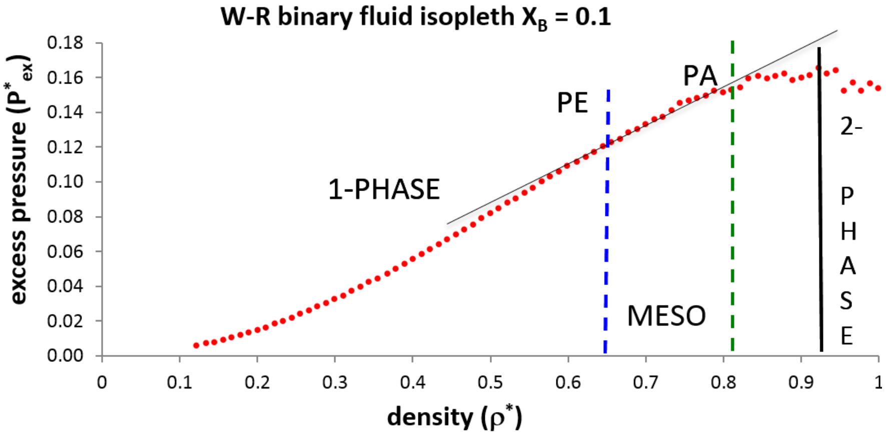


Fig. 5. Excess pressures of the Widom-Rowlinson binary fluid mixture along the isopleth $X_B = 0.1$ from a MD simulation of $N = 10000$ particles: the percolation transition densities indicated by dashed lines are computed directly using the methods as described previously [11] and in the text

is the normalized probability of a site belonging to a cluster of size n. Below $\rho^*_{\mathrm{PE}} P(n)$ is a monotonic gas-like distribution, for densities above ρ^*_{PE} it is bimodal. Using the saddle-point definition of $\rho^*_{\mathrm{PE}}(N)$ we have obtained the result $\rho^*_{\mathrm{PE}}(N \to \infty) = 0.668 \pm 0.01$ which is consistent with previous literature values [18, 19].

IV. PENETRABLE SPHERE BINARY FLUID

The Widom-Rowlinson (W-R) model fluid [20] can be regarded as a simple model of a binary fluid mixture; at a lower temperature or, equivalently, higher pressure, it exhibits a demixing phase transition similar to liquid-liquid criticality. This model belongs to the general class of symmetric binary non-additive hard-sphere fluid mixtures defined by collision diameters

$$\sigma_{\mathrm{AA}} = \sigma_{\mathrm{BB}} = (1+\alpha)\sigma_{\mathrm{AB}}, \tag{10}$$

where α is a dimensionless non-additivity, that varies from -1, for the W-R penetrable-sphere model binary fluid, via zero for one-component hard spheres, to infinity. Positive α relates to ionic liquids and ionic crystal structures when mole fraction $X_B = 0.5$ [21].

We have determined the percolation pressures p^*_{PE} along selected isopleths of the binary W-R model fluid. MD simulations have some advantages over Grand Canonical Monte Carlo [22] (GCMC). Not least is the direct extraction of transport properties for determination of r^*_{PA} loci. These are obtainable by "freezing" component A whilst allowing B to diffuse. The cluster distributions that determine r^*_{PE} also yield accurate values for coexisting X_B by integrating the solute cluster probability distribution $P(n)$ which decreases monotonically, from a maximum at n =1, to zero for clusters of B in solution of A, or vice-verser. Accurate MD pressures are calculated from A-B collision frequencies. Changes in pressure slopes can be observed from the MD excess pressures defined relative to the ideal gas.

$$p^*_{\mathrm{ex}} = p^* - \rho^*. \tag{11}$$

For example, the isopleth $X_B = 0.1$, shown in **Fig. 5**, has four distinct regions. At high density, in the two-phase region, the MD pressures averaged over 100 million A-B collisions still show fairly large uncertainties. The maximum pressure along any isopleth coincides with the first-order mixing-demixing transition. This reflects the thermodynamic equilibrium condition of minimal Gibbs energy (G) (since $\mathrm{d}G_T = \rho^{-1}\mathrm{d}p$) for equilibrium on either side of the transition. At the mole fraction $X_B = 0.1$ in the mesophase region pressure increases linearly with density. In the one-phase region, the MD data is sufficient to observe that the percolation loci appear to be associated with changes in slope that could reflect higher-order thermodynamic phase transitions. The present data is not sufficiently accurate to establish the order or strength of discontinuities. The vertical dashed lines in **Fig. 5** correspond to the percolation transition densities computed explicitly: they coincide with apparent changes in the slope of the excess pressure. The change in the slope of p^*_{ex}, and hence also p^*, is more pronounced. The rigidity function $\omega = (\mathrm{d}p/\mathrm{d}\rho)_T$ appears constant in the mesophase.

The connection between percolation loci and the phase transition is clear from **Fig. 6**. Equation (8) exactly relates V_A or V_E to chemical potentials, which determine equilibrium between phases. The essential result is that for the percolation of V_A i.e. p^*_{PA} in 3d (**Fig. 6**) which is around 35% greater than the already known $p^*{}_{\mathrm{PE}}$ for the ideal gas, i.e. when ρ^*_B in **Fig. 6** is zero. Between these transition temperatures both V_E and V_A percolate. The mesophase only exists

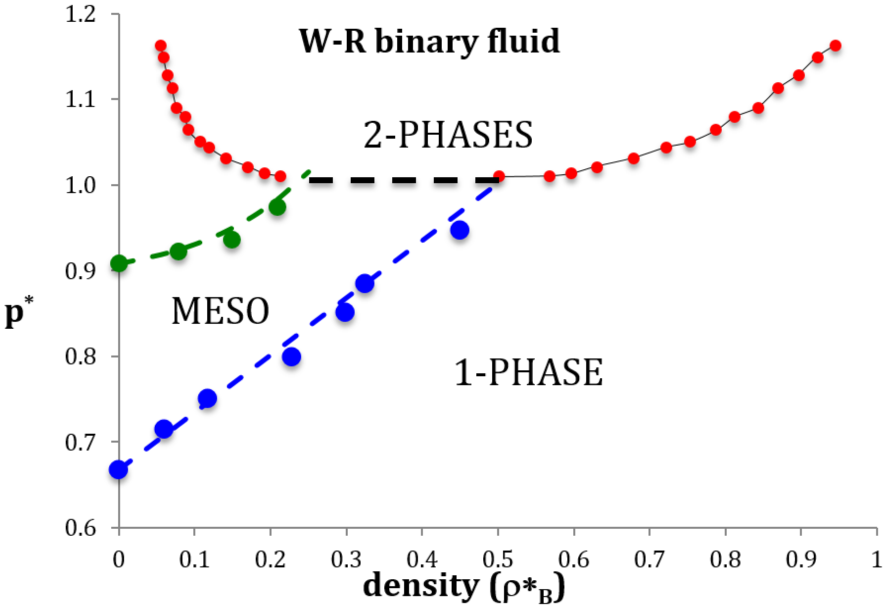


Fig. 6. Phase diagram of the W-R binary fluid in the pressure-density projection: p^*_{PE} (blue) and p^*_{PA} (green) are the percolation transition pressure data points from MD simulations showing the ideal gas percolation pressures at $\rho^*_B = 0$; two-phase coexistence pressure points are red circles; the dashed black line is the critical divide

in 3d liquid-liquid or liquid-gas fluids. This result for the ideal gas and W-R binary fluid is the verification of a connection between percolation loci and the critical demixing transition in the penetrable sphere binary fluid mixture.

As solute concentration (X_B) increases, the pressure difference between the two percolation temperatures decreases until it's the same. From thermodynamic considerations, this intersection triggers a first-order phase transition, with the two different phases having the same T, p and chemical potential. It is this fundamental property of percolation in 3d that does not exist in 2d that vitiates the hypothetical concept of universality, and confirms an alternative interpretation of criticality for both one-component liquid-gas [12, 23], and now also two-component liquid-liquid equilibria [24].

Along any isopleth, the pressure is a maximum at the two-phase boundary to comply with the thermodynamic requirement of minimum Gibbs energy. However, we have also determined the coexistence line directly from the results for the $X_B = 0.5$ equimolar isopleth by a more accurate method than GEMC [22], by accumulating the ensemble average cluster size probability distribution $P(n)$. From all MD runs at densities of the phase separation ($\rho^* = 0.75$) and higher this determines the coexistence mole fractions as shown for the density 0.8 in **Fig. 7.** The cluster size distribution is bimodal in the mesophase and monomodal in the one-phase region. In the two-phase region it is bimodal with a hiatus. Notice that the cluster size has begun to diverge at the density 0.68, which is just inside the mesophase (**Fig. 6**).

From the coexistence pressures, and from direct computations of PA and PE, we can obtain a phase diagram for the W-R binary fluid. The reduced pressure loci of the percolation transitions fit the trendlines (dashed lines in **Fig. 6**)

$$p^*{}_{PE} = 0.661 + 0.617\rho^*_B,$$

$$p^*{}_{PA} = 0.908 + 0.0171\rho^*_B + 1.47{\rho^*_B}^2,$$

thereupon establishing the connection between percolation phenomena and the demixing phase transition. **Fig. 6** shows a horizontal dividing line at the critical pressure p^*_c rather than an Ising-like or van der Waals singular critical point. We also note that the high-density fluid states at high pressures are two immiscible fluids both of which obey the ideal gas law.

The W-R binary fluid may be regarded as a simple model of partially miscible dissimilar liquids, e.g. cyclohexane and methanol. Many such binary liquid mixtures, just as seen here for the W-R fluid, separate into two coexisting phases at low enough temperatures. On heating, compositions of the two phases become more and more similar and at a critical temperature there is a single phase. This is the UCST. At higher temperature there is just one liquid phase. It is possible to define various percolation thresholds for clusters of solute molecules in the single liquid phase by analogy with clusters of molecules in a gas phase. The present evidence suggest that percolation loci that delimit the solution will give rise to a mesophase and a coexistence line at the UCST. Our simulation results for the W-R mixture suggest that the phase diagram of real partially miscible binary liquids will be determined by the intersection of percolation loci. The present results for the W-R mixture should stimulate further laboratory experimental research into percolation loci and the critical divide at T_c in binary mixtures.

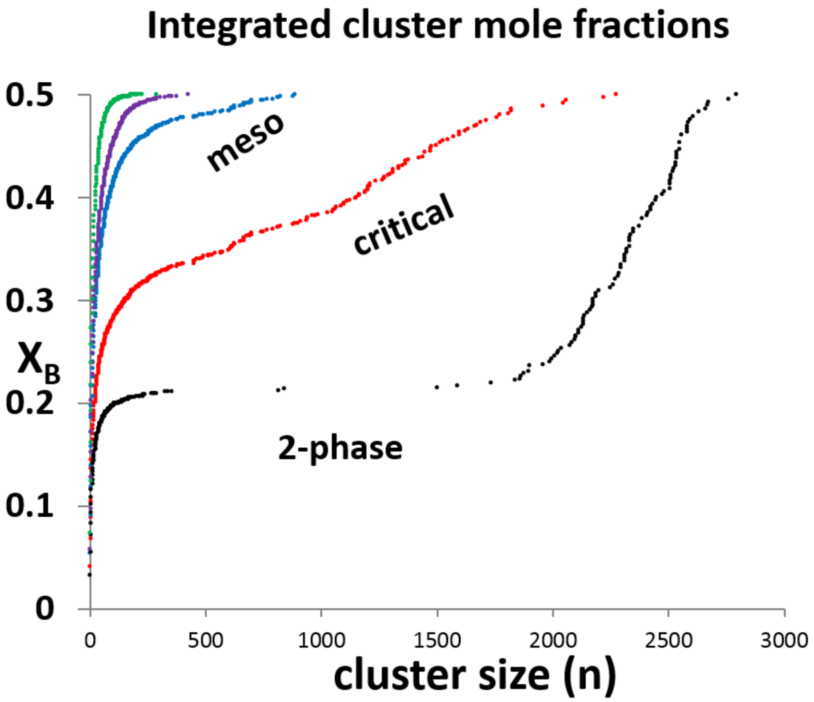


Fig. 7. Integrated mole fractions of cluster size distributions for W-R binary fluid $X_A = X_B = 0.5$ for 5 state points: density $\rho^* = 0.60$ green, 0.66 purple 0.68 blue, 0.75 red, 0.8 black, showing how the cluster size diverges in the mesophase, and how the coexistence mole fraction is obtained in the 2-phase region. For the density $\rho^* = 0.8$ (black points) the coexistence mole fraction is $X_B = 0.214 \pm 0.01$

V. PENETRABLE SPHERE GAS-LIQUID CRITICALITY

Probably the simplest 3D model Hamiltonian of a molecular fluid, which is continuous in phase space, and exhibits liquid-gas criticality and two-phase gas-liquid coexistence, is the penetrable cohesive-sphere (PCS) fluid [20, 22]. The internal energy (U) is simply

$$U = 3Nk_BT/2 + \epsilon(\langle V_E/v_0\rangle - N), \tag{12}$$

where k_B is Boltzmann's constant and T is temperature (K); the angular brackets denote a configurational average. Equation (12) defines an attractive molecular energy complementary to the volume of overlapping clusters, i.e. V_E as defined above for an ideal gas, of a configuration of N penetrable spheres, and $v_0(= 4\pi\sigma^3/3)$ is the volume of a sphere. At low temperatures, this model exhibits the exact properties of an ideal gas in both the low-density (gas phase) and high-density (liquid-phase) limits. Hence we note that there exists a liquid-like state with the properties of the ideal gas law.

Every state of the PCS fluid corresponds to a transcribed state of the W-R binary model fluid. The exact equations for the transcription from the W-R binary percolation and coexistence pressures (**Fig. 6**) to the PCS one-component gas-liquid pressure **(Fig. 8)** are

$$\text{pressure}\quad [\text{PCS}]p^* = [W-R](p^* - Z_A^*/v_0)k_BT/\epsilon \tag{13}$$

$$\text{density}\quad [\text{PCS}]\rho^* = [W-R]\rho_B^*, \tag{14}$$

where Z_A* is the thermodynamic activity of a component defined as $\ln Z* = m/k_BT$ and m is Gibbs chemical potential relative to the ideal gas. Gibbs energy change, hence Z^*, can be obtained by integrating the excess pressure loci at constant T, with respect to density.

$$\mu/k_BT = \int (p^* - \rho_{\text{id}}^*)\mathrm{d}\log_e(\rho_B^*) \tag{15}$$

The PCS fluid is the simplest imaginable continuous Hamiltonian model to exhibit liquid-gas coexistence and a critical temperature. There is a coexistence line at the intersection of percolation loci in the p-T plane. This is consistent with what we have observed for square-well [12, 23], Lennard-Jones [26, 27] model fluids, and also real fluids [28]. Above a liquid-gas critical coexistence line there is supercritical mesophase. The liquid state extends to a low density and pressure limit that will obey the ideal gas equation-of-state. This raises the question: could there exist a high temperature limit of the percolation transition loci in real fluids in the dilute gas limit? Various evidence suggests this may indeed the case. Next, we report experimental evidence

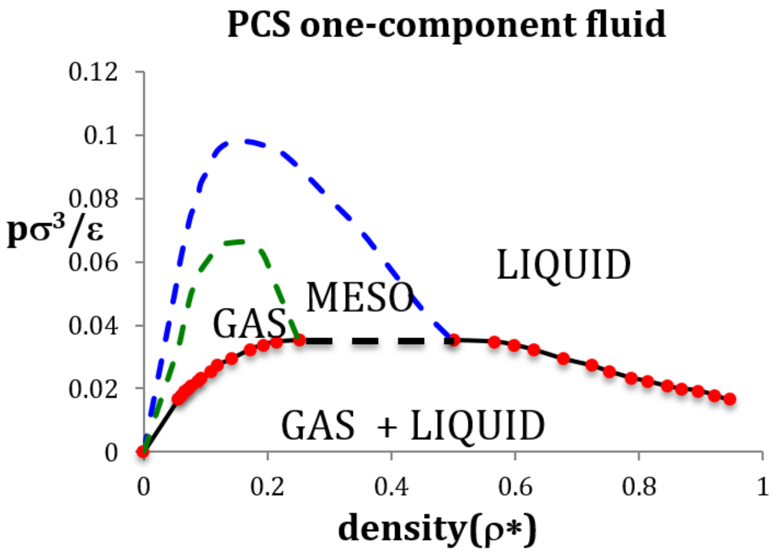


Fig. 8. Phase diagram of the one-component PCS liquid-gas system obtained by transcription of two-component W-R pressures $p^*(r_B^*)$

from thermodynamic properties of real fluids, gleaned from our knowledge of percolation transitions in model fluids.

VI. REAL FLUIDS

Although lacking a molecular-level definition, for any real fluid, for which the Hamiltonian is generally unknown, the percolation loci can be defined and obtained phenomenologically along any thermodynamic equilibrium isotherm by the rigidity inequalities [28]. In the case of real fluids with attractive potentials, the percolation transition bounding the gas phase, i.e. the counterpart of PE for impenetrable spheres, has been designated PB, as it is essentially a percolation of 'bonded clusters'. For real intermolecular forces, definition of a "bonded cluster" for percolation transitions is a more nebulous mathematical contraption of Mayer integrals lacking the precise definition of hard spheres and square wells. A contributing "cluster" is not necessarily the same as our physical concept of a small cluster of molecules, for example, that characterize a low temperature gas phase. At higher temperatures, as the configurational integral in equation (1) approaches zero, and contributing clusters may be more diffuse in configuration space.

Rigidity (ω_T) is the work required to isothermally and reversibly increase the density of a fluid; with dimensions of a molar energy (**Fig. 9**). This simple state function relates directly to the change in Gibbs energy (G) with density at constant T according to

$$\omega_T = (\mathrm{d}p/\mathrm{d}\rho)_T = \rho(\mathrm{d}G/\mathrm{d}\rho)_T \tag{16}$$

Inequalities that distinguish gas from liquid are:

$$\text{gas} \quad \rho < \rho_{\text{PB}} \qquad (\delta\omega/\delta\rho)_T < 0, \tag{17}$$

$$\text{meso} \quad \rho_{\text{PA}} < \rho < \rho_{\text{PA}} \qquad (\delta\omega/\delta\rho)_T = 0, \tag{18}$$

$$\text{liquid} \quad \rho > \rho_{\text{PA}} \qquad (\delta\omega/\delta\rho)_T > 0. \tag{19}$$

It is clear from eqn. (16) that $\omega \geq 0$, i.e. rigidity must always be positive: Gibbs energy cannot decrease with pressure when T is constant. From these definitions, moreover, not only can there be no "continuity" of gas and liquid, but the gas and liquid states are fundamentally different in their thermodynamic description. Rigidity is determined by number density fluctuations at the molecular level, which have different but complementary origins in each phase, hence the symmetry [28]. There is a distribution of many small clusters in a gas with one large void, there is a distribution of unoccupied pockets in the liquid with one large cluster.

The rigidity isotherm data, from the NIST Thermophysical Properties [4], for CO_2 is shown in **Fig. 9.** If inequalities (17 to 19) thermodynamically define the percolation loci, then it follows that at low density r_{PA} must approach the Boyle temperature (T_B) by definition. This is the temperature above which the second virial coefficient is positive and below which it is negative. In the pressure-density plane the percolation loci show maxima and approach the ideal dilute gas limit. The same behavior is seen for other liquids, such as liquid argon **(Fig. 10)** showing the critical isotherm ($T_c = 151$ K) and 7 supercritical isotherms

The initial slope of the percolation loci in the pressure plots **(Fig. 10)** corresponds to the intercept temperatures obtained from percolation loci (shown in **Fig. 9** for CO_2) at low density, as $\omega = Nk_BT$ for an ideal dilute gas. This result suggests that all fluids will exhibit characteristic percolation

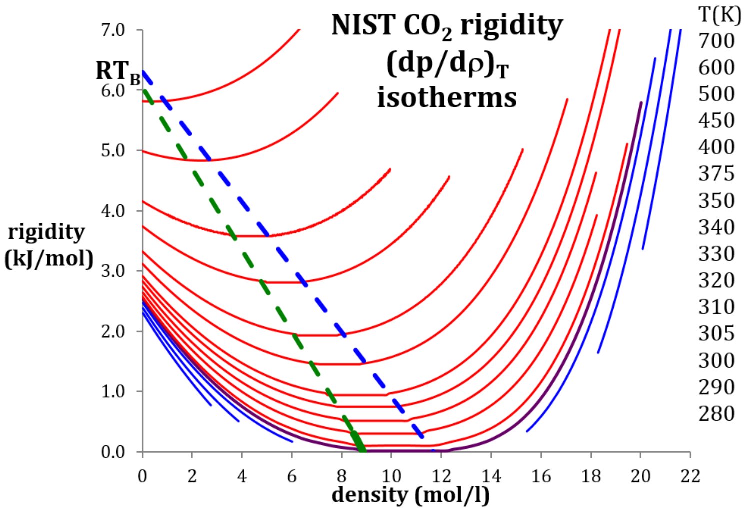


Fig. 9. Isotherms for the rigidity of fluid phases of carbon dioxide from NIST thermophysical tables [4]: the loci of gas and liquid phase bounds according to empirical criteria equations (17 to 19) are green and blue respectively: red lines are supercritical isotherms, blue lines are sub critical isotherms, the purple isotherm is T_c (305K): the Boyle temperature $T_B = 725$ K corresponding to a rigidity (RT_B) 6.03 kJ/mol where R is the gas constant

loci stemming from the constitutive Boyle temperature T_B whereupon the second virial coefficient $b_2(T)$ changes sign. It becomes negative at lower temperatures due to clustering in the gas phase arising from the attractive strength of intermolecular forces relative to k_BT.

The percolation loci in **Fig. 10** are seen to extend to low density. However, the NIST equations-of-state for argon is not as precise as the data for CO$_2$, and it is not as clear from the derivatives of the NIST argon isotherms that the mesophase extends to the Boyle temperature at a very low pressure. When the raw data from Gilgen et al. [29, 30] are used to obtain the supercritical phase bounds for argon, as shown in the T-ρ phase diagram (**Fig. 11**), it is not as convincing as the case of CO$_2$, but within the experimental un-

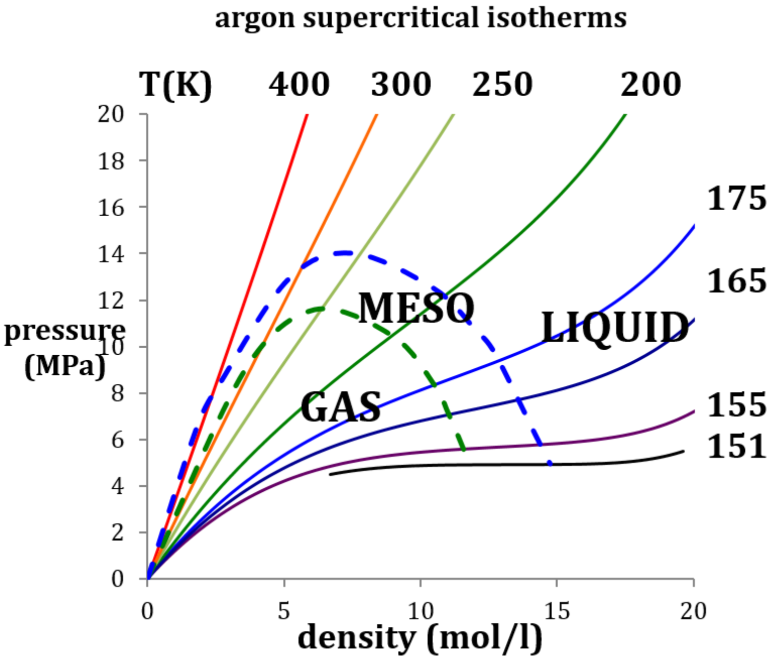


Fig. 10. Supercritical pressure isotherms of fluid argon: the data are plotted from NIST Thermophysical Property Tables [4] showing the loci of PB and PA (green and blue respectively) defined by the linear mesophase region bounds equation (18)

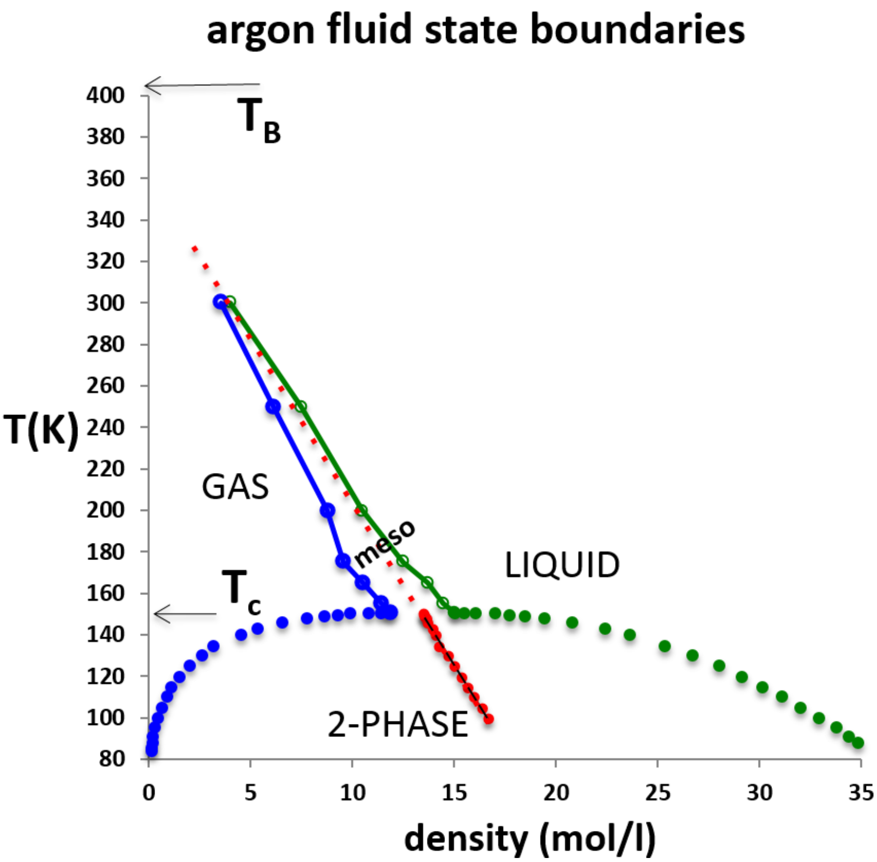


Fig. 11. T-ρ phase diagram for fluid argon using only data points obtained from Gilgen et al. [29, 30] indicating the percolation loci that bound the liquid and gas states: the blue-green filled circles are the gas-liquid (respectively) coexistence densities; open circles are the gas-liquid percolation bounds from equations (17 to 19); solid red circles are the LRD data points; the dotted red line is the extrapolated LRD equation trendline

certainties, the percolation loci approach the Boyle temperature but appear to merge at a lower temperature. More accurate p-V-T measurements for supercritical argon in this low-density region would be helpful.

This raises the question: "if the percolation loci describe long-range connectivity of sites in a gas and holes in a liquid, how can they extend to dilute gas densities obeying the ideal gas law ?". The answer may be that the exact concept of free volumes and available volumes, for hard-sphere and square-well fluids do not have the Mayer mathematical percolation properties of real molecules with continuous intermolecular potentials. Also, for real fluids, the concept of a physically "bonded cluster" of occupied sites in a gas, or the complimentary unoccupied pockets in a liquid, are only the same as Mayer's clusters in equation (5) at low temperatures. As the temperature increases above the critical temperature, the mathematical clusters of Mayer will become larger and more nebulous, and hence percolate at a lower density, as the configurational integral (Q) equation (1) approaches zero at the Boyle temperature.

To understand the percolation properties of clusters of real molecules, therefore, we will need to analyze the formally exact resolution of the partition function into Mayer cluster integrals that define the virial coefficients $b_n(T)$ in equation (5). A central assumption of the Mayer theory, which implies it may only be rigorous for gaseous states, is that the b_n are independent of the volume of the system. The b_n are sums of multi-dimensional integrals whose integrands have near total cancellation between positive and negative terms. Hence, miniscule contributions from continuous pair potentials at low density and higher temperatures could divergent. Mayer's mathematical clusters [9] are not the same as our mental concept of physical clusters of the gas phase sitting in potential minima at a low temperatures, and can diverge to large distances at low densities and exhibit percolation transitions where very weak, relative to k_BT, repulsive and attractive interactions may be influential.

From the Mayer analysis, it would appear that whenever the number of contributing terms in the summation of the irreducible integrals in equation (5) diverges, there will be a higher-order phase change on the Gibbs density surface along the isotherm [9]. There may be a number of reasons for such a divergence in various model and real systems. At the Boyle temperature (T_B) the second virial coefficient

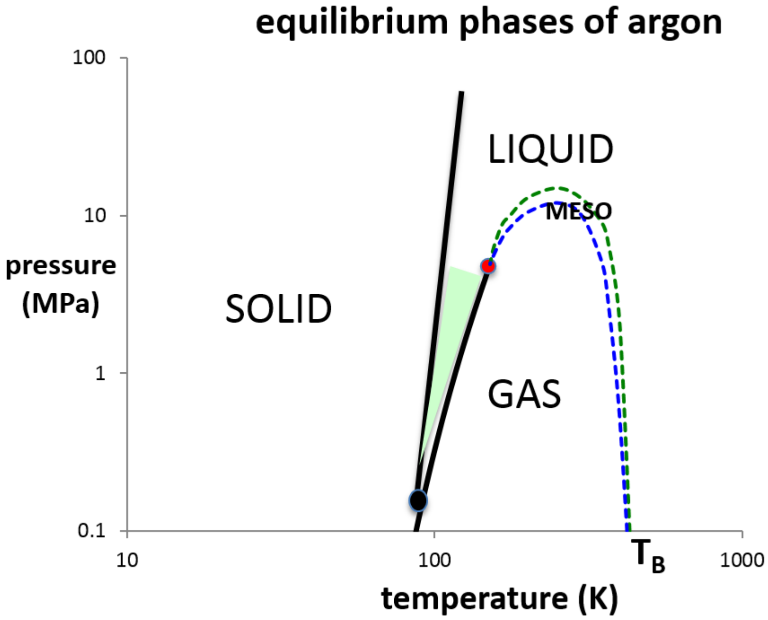


Fig. 12. Postulated p-T phase diagram for fluid argon showing the supercritical mesophase: the blue and green dashed lines are the gas and liquid supercritical state bounds; the red circle is the critical point black circle triple point; the tiny light greed shaded area is generally referred to as liquid "state" but the liquid "phase" appears to extend to high temperatures and to exist above the critical temperature, and at all pressures above the Boyle temperature (T_B)

changes from negative to positive, by definition and also the configurational partition function (Q) in equation (1) is equal to zero. Also, if a sum diverges at a given density, there will be a change in the analytical functional representation of the partition function. For simple model pair potentials, e.g. Lennard-Jones, b_2 can be obtained exactly, albeit semi-numerical [30]. At present, it is not known whether or not there is a non-analytic higher-order discontinuity in $b_2(T)$ at T_B for n-m potentials generally [31]. The presence of percolation loci, however, suggest $p(\rho)_T$ may become non-analytic, with a higher-order phase change, as it crosses zero at T_B for fluids at high dilution or when $pV/NkT \sim 1$.

VII. CONCLUSIONS

Results for the percolation transition loci comparing both real and model fluids have reaffirmed previous conclusions [12, 23-27] that there is no critical point singularity on Gibbs density surface for gas-liquid condensation. Rather, there is a horizontal dividing line at the critical temperature, above which there exists a mesohase between the percolation loci that bound the liquid and gas phases. Computer experiments have certain advantages over real laboratory measurements; not least is an absence of impurities, zero gravity, and periodic boundaries or no interfaces. One cannot blame the "flatness" at T_c, on these undesirable artifacts, as in historic rebuttals to evidence against van der Waals [32]. These commonly used excuses to disregard otherwise compelling laboratory p-V-T evidence, "gravity", "impurities", and "surfaces" are all absent in the computer simulations. Heyes (25,26), for example, concludes unequivocally, from his extensive computations of the L-J fluid in the vicinity of T_c, that the coexistence envelope has a flat top, i.e. that the van der Waals singularity is nonexistent.

Equation-of-state data are perhaps not the most reliable to decide this question of flatness as it is not easy to distinguish a low curvature region from one that is in fact a straight line in $p(\rho)_T$. The literature critical-point universality theory predicts that the temperature or pressure scales as $(\Delta\rho)^\delta$ along the critical isotherm [33], which could therefore be very flat anyway in that hypothesis. In fact a lot of p-V-T experimental results for real molecular fuids have required exponents $\delta = 3$ to 4, or even higher [33] in order to create a parabola with a singular maximum to within the limits of experimental uncertainty. These experimental results have been adversely prejudiced by prevailing theory. Fifty years ago, Rowlinson's opening first sentence in reference [33] reads: *"At a critical point the intensive properties of two coexisting phases become equal."* Since when did van der Waals hypothesis become scientific fact we ask?

On the universality hypothesis, and dimensionality dependence of the description of criticality, we conclude that for d $= 2$, since PE (or PB) = PA for all densities (or concentration X_B), the phase behaviour and criticality will be different with no mesophase. We conjecture, therefore, that the 2d percolation locus will intersect the equimolar isopleth with a critical singularity at $X_B = 0.5$ for the d $=$ 2 W-R model. Another consequence of the absence of a d $=$ 2 mesophase would be no metastability beyond the first-order phase boundaries, and, unlike d $=$ 3, no metastability and hence no spinodals within the subcritical bimodals. The existence of a mesophase and subcritical metastability is a property only of d $=$ 3 systems. This difference in the description of liquid-gas criticality between 2d and 3d vitiates the hypothetical 'universality' concept as applied to liquid-gas, and binary-liquid, criticality.

Results for various percolation loci suggest that all real atomic and molecular fluids will have a liquid state that is bounded only by a percolation transition that extends from the coexisting liquid state at T_c to the Boyle temperature (T_B). If state boundaries are defined phenomenologically by inequalities (17-19), the liquid-state boundary is seen to extend to low-density gas-like states. On the basis of these observations, it is the gas phase, i.e. as defined by the inequality eqn. (17), which exists in a limited area of the T-p plane rather than the liquid, as illustrated in **Fig. 12**.

We note, however, since there can be no zero of density or pressure for a real fluid, as they become logarithmic to high dilution, the ideal gas does not exist in reality. The sign of the second virial coefficient would determine the designated state, by the rigidity criterion. Thus, the 'liquid' area of existence may extend to infinite pressure and temperature, whereas the 'gas' phase extends to infinite dilution only below a certain temperature. This is contrary to what is hitherto generally believed to be 'liquid', and reopens the debate "What is Liquid" [7].

Finally, we conclude that there can be no "universality" [see some of the articles and discussions that gave recognition to this concept by M.S. Green, G.E. Uhlenbeck, J.S. Rowlinson, M.E. Fisher, J.V. Sengers in reference 33] in the description of criticality as applied to liquid-gas and liquid-liquid critical points. The mesophase is a fundamental property of bonded-molecule cluster percolation and complementary vacant-site cluster percolation loci only in 3d, which do not exist in 2d. Although there may well be Ising-like critical-point singularities on the density surfaces of 2d fluids, all the evidence we can see reaffirms the conclusion: there is a critical dividing line for real 3d liquid-gas thermodynamic equilibria, and no van der Waals critical point.

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Leslie Woodcock PhD London (1970): after a 40-year teaching career, and research into condensed matter thermodynamics, at the Universities of Cambridge, Amsterdam, Bradford and Manchester, Les Woodcock is Emeritus Professor of Chemical Thermodynamics at the University of Manchester and presently Catedratico Convivado Professor of Physics at the University of Algarve, Portugal. Current research projects are (i) investigations of percolation transitions in the description of critical and supercritical properties of liquids and gases, and (ii) the thermodynamics of rheology including a project on the non-equilibrium thermodynamics descriptions of of muscle as an engine.
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