Journal of Statistical Physics, Vol. 52, Nos. 5/6, 1988

Is the Percolation Transition of Hard Spheres a Thermodynamic Phase Transition?

Karl W. Kratky[1]

Received March 11, 1988

In hard-sphere systems, there is a fluid–solid transition, but no gas–liquid transition. In the fluid region, however, one can find a purely geometric percolation transition, which is studied in detail. The van der Waals model of hard spheres is treated. In this model, a uniform negative background potential is added. This modification does not change the structure, but induces a gas–liquid transition. In fact, percolation and the gas–liquid transition can be related to each other.

KEY WORDS: Statistical mechanics; phase transitions; percolation; hard spheres; extended spheres; van der Waals model.

1. INTRODUCTION

Simple model systems like hard spheres have been studied for many years in the attempt to understand the structure and dynamics of real fluids.(1) It has turned out that for the most part purely geometrical considerations are sufficient to understand the hard-sphere properties.(2,3) An early attempt to attack this problem was scaled particle theory.(4) Howard Reiss was one of the inventors of this theory(5) and is still interested in the hard-sphere problem.(6)

In recent years, interest in geometrical condiderations has increased due to the study of percolation,(7) especially in the continuum case.(8) The first paper that directly combined percolation with hard-sphere systems was published a decade ago.(9) This will be the starting point for the present considerations.

In the following, I consider N spheres in a large volume V (density $\rho = N/V$). The diction refers to the three-dimensional case ("volume,"

---

[1] Institut für Experimentalphysik der Universität Wien, A-1090 Vienna, Austria.

"spheres"), but for the most part the general D-dimensional case will be treated. Hard-sphere systems exhibit a fluid–solid transition (for $D > 1$), but no gas–liquid transition, due to the absence of attractive forces:

$$\exp(-u_{ij}/kT) = \begin{cases} 1: & r_{ij} > \sigma \\ 0: & r_{ij} < \sigma \end{cases} \tag{1}$$

The interaction potential u_{ij} between two spheres i and j makes it impossible for the spheres to come closer than $r_{ij} = \sigma$, where σ is the hard-sphere diameter.

Now consider a sphere i enclosed in the cage built up of its neighbors. The volume where the center of sphere i may move (with the neighbors held fixed) is the *free volume* $v_f(i)$. It can be calculated in the following way. Spheres of *radius* σ (diameter $d = 2\sigma$) are drawn around the centers of the neighbors. The small space left open by these spheres is the free volume. The large spheres (diameter d) are called *exclusion*, *intersection*, or *collision* spheres. They are partly penetrable with a hard core of diameter $\sigma = d/2$.

At very high density, each particle is confined in a small free volume which varies from particle to particle and fluctuates in the course of time. If the density decreases, the average free volume increases, and the cages open up in more and more cases. The density where the first free volume $v_f(i)$ spanning the total system occurs (e.g., from top to bottom) is the *percolation* density of *free* volume ρ^{pf}. The corresponding particle i may wander around the whole system. Thus, an important dynamical feature of *hard* spheres is given by the behavior of the *exclusion* spheres.

At very low density, the exclusion spheres are isolated. With increasing density, more and more exclusion spheres overlap, and overlapping spheres form *clusters*. At percolation density ρ^{pe} the first spanning cluster of exclusion spheres occurs. The total volume covered by the overlapping exclusion spheres is the *excluded volume* V_e. No additional hard sphere could be inserted there, only $V_a = V - V_e$ being accessible for the center of such a sphere. V_a is called the *accessible*, *available*, or *spare* volume,$^{(2)}$ or, misleadingly, also the free volume. At low density, separate pieces of excluded volume (namely the exclusion spheres) move in a connected "sea" of accessible volume. At high density, it is just the other way around: small pieces of accessible volume are surrounded by a connected excluded volume. These pieces are sometimes called cavities, holes, vacancies, pores, or voids, depending on the main interest of the respective author. The corresponding density of percolation of accessible volume is ρ^{pa}.

Thus, there are three percolation densities: ρ^{pf}, ρ^{pe}, and ρ^{pa}. Before we consider these densities further, the difference between free volume and accessible volume needs to be stressed: V_a/V, sometimes called the porosity, is the probability that a random insertion of an additional sphere can take place. It is a rapidly decreasing function of density.(3) V_a is directly connected with the excess chemical potential of hard spheres.(2,3) On the other hand, the free volume $v_f(i)$ is generated by taking away sphere i (centered at $\mathbf{r}_i$). Accordingly, the total V_a increases. $v_f(i)$ is just the part of the increased V_a that is connected to $\mathbf{r}_i$. If $V_a = 0$, all $v_f(i)$ are separated from each other. Each particle is enclosed in the cage of its neighbors. If $V_a \neq 0$, the spheres bordering a connected piece of V_a (*cavity*) have this cavity as common part of their free volumes. Thus, the occurrence of a spanning cavity means that the free volumes of all bordering spheres are also spanning. This means

$$\rho^{\mathrm{pf}} \geqslant \rho^{\mathrm{pa}} \tag{2}$$

On the other hand, there is only one possibility that a spanning free volume $v_f(i)$ occurs, but no spanning cavity: Sphere i interrupts the otherwise spanning cavity. For large systems, the influence of a single sphere on the density difference $(\rho^{\mathrm{pf}} - \rho^{\mathrm{pa}})$ is negligible, the equality sign in (2) being valid. Thus, we have only to consider ρ^{pe} and ρ^{pa} in the following.

In the one-dimensional case of hard rods, a single exclusion rod interrupts the accessible volume. Equivalently, a single cavity interrupts the cluster of exclusion rods. Thus,

$$D = 1: \qquad \sigma\rho^{\mathrm{pe}} = 1, \qquad \sigma\rho^{\mathrm{pa}} = 0 \tag{3}$$

Thus, in the whole interesting region $0 < \sigma\rho < 1$, neither the excluded nor the accessible volumes percolate. $D = 1$ is exceptional in many respects and will not be considered further. In two dimensions,(9)

$$D = 2: \qquad \rho^{\mathrm{pe}} = \rho^{\mathrm{pa}} \equiv \rho^{\mathrm{p}} \tag{4}$$

Above ρ^{p}, the accessible volume breaks up into pieces; below ρ^{p}, the same is the case for the excluded volume. For increasing D, $D \geqslant 3$, there is an increasing density region where both accessible and excluded volumes are spanning:

$$D \geqslant 3: \qquad \rho^{\mathrm{pe}} < \rho^{\mathrm{pa}} \tag{5}$$

This may be compared with the "coexistence" of the spanning blood and nervous systems. Furthermore, they do not break the human body into pieces. This would not work in less than three dimensions.

The above considerations may be compared with site percolation on the triangular lattice ($D = 2$) and fcc lattice ($D = 3$), (see Ref. 7, p. 17). The lattice points are randomly occupied with probability p (black points), the others remaining white. Neighboring points of the same color form clusters. From the symmetric definition it follows that

$$p^{\mathrm{pb}} = 1 - p^{\mathrm{pw}} \tag{6}$$

for the percolation densities of black (b) and white (w) clusters. The actual values are(7)

$$D = 2: \qquad p^{\mathrm{pb}}/p^{\mathrm{pw}} = 1 \tag{7}$$

$$D = 3: \qquad p^{\mathrm{pb}}/p^{\mathrm{bw}} = 0.247 \tag{8}$$

in accordance with (4) and (5).

2. COMPUTER EXPERIMENTAL VALUES OF HARD-SPHERE PERCOLATION DENSITIES

Determination of ρ^{pe} for hard disks yielded(9)

$$D = 2: \qquad z^{\mathrm{pe}} \equiv \rho^{\mathrm{pe}}/\rho_0 = 0.245 \pm 0.020 \tag{9}$$

where z is the density relative to regular (triangular) close packing ρ_0. Before we proceed, it should be mentioned that the different dimensionless density definitions used in the literature are quite confusing. Besides z, also $y = v_\sigma \rho$, $b\rho$, and $\sigma^D \rho$ can be found. v_σ is the volume of the hard sphere (diameter σ), y (also termed η or ϕ) is the packing fraction, the fraction of the total volume filled by the spheres. $b = B_2 = 2^{D-1} v_\sigma$ is the second virial coefficient for hard spheres. The relations between the different densities are

$$D = 1: \qquad y = b\rho = \sigma\rho = z \tag{10}$$

$$D = 2: \qquad 2y = \mathrm{b}\rho = \tfrac{1}{2}\pi\sigma^2\rho = 3^{-1/2}\pi z \tag{11}$$

$$D = 3: \qquad 4y = b\rho = \tfrac{2}{3}\pi\sigma^3\rho = \tfrac{2}{3}2^{1/2}\pi z \tag{12}$$

In the hard-sphere case, the corresponding exclusion spheres automatically have diameter $d = 2\sigma$. But one may generalize this relation, $d/\sigma \geqslant 1$. This results in the model of *extended* spheres.(8) They have diameter d and a concentric hard core of diameter σ. The cores are not allowed to overlap. Again, the overlapping extended spheres define V^{e}, the remaining $V^{\mathrm{a}} = V - V^{\mathrm{e}}$ not being covered by them. However, the original meaning (the volume "excluded" or "accessible" for the insertion of a further particle) only holds if the fictitious additional particle is a sphere with a hard core of diameter $d - \sigma$.

Several papers(8,10,11) consider ρ^{pe} as a function of the ratio σ/d using the model of extended spheres. Unfortunately, this yields a further set of densities based on d instead of σ, [cf. Eqs. (10)–(12)]. For instance,

$$y_d = v_d \rho = (d/\sigma)^D \, y \tag{13}$$

The conversion factor $(d/\sigma)^D$ holds for the other density definitions, too. The following considerations are restricted to y. Thus, the hard-disk value (9) becomes

$$D = 2, \text{ ref. 9:} \qquad y^{\mathrm{pe}} = 0.222 \pm 0.018 \tag{14}$$

From the literature considering *extended* spheres, it can be deduced for *hard* spheres ($d = 2\sigma$) that

$$D = 2, \text{ ref. 10:} \qquad y^{\mathrm{pe}} = 0.213 \pm 0.009 \tag{15}$$

$$D = 2, \text{ ref. 11:} \qquad y^{\mathrm{pe}} = 0.217 \pm 0.006 \tag{16}$$

This may be compared with the results of parallel extended squares,(12) which yield the same dependence of y^{pe} as a function of σ/d up to high density. For the case $D = 2$,

$$D = 2, \text{ ref. 12:} \qquad y^{\mathrm{pe}} = 0.21 \pm 0.01 \tag{17}$$

which is consistent with (14)–(16). In the three-dimensional case,(8,11)

$$D = 3, \text{ ref. 11:} \qquad y^{\mathrm{pe}} = 0.042 \pm 0.002 \tag{18}$$

is the estimate for extended spheres, $d = 2\sigma$. As to the *accessible* volume, so far an estimate of the two- and three-dimensional y^{pa} can be made only indirectly. Speedy(2) obtained a simple hard-sphere equation of state by estimating the cavity distribution in hard-sphere systems. The result for the compressibility factor $Z \equiv P/\rho kT$ was

$$D = 2, 3, \text{ ref. 2:} \qquad Z - 1 = \tfrac{1}{5} D \exp 5z \tag{19}$$

where P is the pressure, k is Boltzmann's constant, and T is the temperature. For the medium and dense fluid region, the relative deviation of expression (19) from the correct $Z - 1$ lies within 2%. Going to smaller densities, the deviations explode due to the percolation transition of accessible volume, the assumption of isolated cavities no longer being valid. It follows that

$$D = 2, \text{ ref. 2:} \qquad y^{\mathrm{pa}} = 0.20 \pm 0.02 \tag{20}$$

$$D = 3, \text{ ref. 2:} \qquad y^{\mathrm{pa}} = 0.24 \pm 0.04 \tag{21}$$

the relative deviation of (19) from the correct $Z-1$ being in the range 3–10%. Equation (20) is consistent with (14)–(17), reflecting the identity $y^{\mathrm{pa}} = y^{\mathrm{pe}}$ for $D=2$, Eq. (4). Combination of (18) and (21) yields

$$D=3: \qquad y^{\mathrm{pe}}/y^{\mathrm{pa}} = 0.18 \pm 0.04 \tag{22}$$

which may be compared with the lattice result 0.247, Eq. (8).

A further hint concerning y^{pa} (hard spheres, $D=3$) can be found in ref. 13. There it is mentioned that diffusion, viscosity and the velocity autocorrelation function change from "gaslike" to "liquidlike" at a packing fraction around 0.25. Since these dynamic quantities are connected with percolation of excluded volume (see the Introduction), this means that

$$D=3, \text{ ref. } 13: \qquad y^{\mathrm{pa}} \approx 0.25 \tag{23}$$

The estimates of percolation density may be contrasted to the density at the fluid–solid transition of hard spheres. The corresponding fluid densities are $y=0.69$ and 0.49 for $D=2$ and 3, respectively. Thus, it turns out that hard-sphere systems have a thermodynamic phase transition (fluid–solid) and a purely geometric transition (percolation, in the fluid region for both y^{pe} and y^{pa}). There is no evidence that the virial series shows any pecularity at y^{pe} or y^{pa}.(9,13) On the other hand, the *physical* clustering and the *mathematical* clusters yielding the virial coefficients depend on each other.(8,13) The old idea of Mayer relates the gas–liquid transition to the first occurrence of an infinite cluster. This indicates that y^{pe} should correspond to the gaseous density y^{g} at the transition, which, however, is suppressed for hard spheres. In analogy, one may conjecture that the liquid density y^{l} at the gas–liquid transition corresponds to y^{pa}. For $D=2$, $y^{\mathrm{pe}} = y^{\mathrm{pa}}$, thus giving the critical density $y^{g} = y^{l}$. In the following, this will be worked out in detail.

3. VAN DER WAALS MODEL

The only possibility to add some kind of attractive "force" to a hard-sphere system without changing the structure is a uniform negative background potential depending on density. This leads to the *van der Waals model* (ref. 1, p. 145) with the equation of state

$$P = P_{\mathrm{h.s.}} - Ay^2 \tag{24}$$

Since the structure does not change for given density, the percolation densities are not changed. Due to Maxwell's equal-area rule in the P–V diagram, the location of the fluid–solid transition slightly changes with A.(14)

For the present considerations, the most important point is the occurrence of a gas–liquid transition. We start with $D=2$. We determine the critical point and check to see if it is consistent with y^p, Eq. (4):

$$\mathrm{D}=2: \qquad y^{\mathrm{c}} \overset{?}{=} y^{\mathrm{pe}} = y^{\mathrm{pa}} \equiv y^{\mathrm{p}} \tag{25}$$

The critical point is given by

$$y = y^{\mathrm{c}}: \qquad dP/dy = d^2P/dy^2 = 0 \tag{26}$$

For the hard-sphere pressure $P_{\mathrm{h.s.}}$, Eq. (24), we insert the virial expansion for hard disks up to the seventh virial coefficient B_7,[15,16]

$$\begin{aligned} D=2: \qquad yZ_{\mathrm{h.s.}} &= v_\sigma P_{\mathrm{h.s.}}/kT = y + \sum_{n=2}^{\infty} B_n(2/B_2)^{n-1}\, y^n \\ &= y + 2y^2 + 3.12802y^3 + 4.25785y^4 \\ &\quad + 5.33690y^5 + 6.3626(3)y^6 + 7.35(3)y^7 \end{aligned} \tag{27}$$

Z is again the compressibility factor. The numbers in parentheses are the uncertainties of the last digits. Combining (24), (26), and (27) yields

$$y^{\mathrm{c}} = 0.21223 \pm 0.00001 \tag{28}$$

This in accordance with Eqs. (14)–(17) and (20). One can see that the contribution of B_7 to the pressure is already very small at this density. Taking into account the higher virial coefficients up to B_{10} which are approximately known, the detailed results are

$$\begin{aligned} D=2: \qquad & y^{\mathrm{c}} = 0.2115 \pm 0.0001, \qquad Z^{\mathrm{c}} = 0.366 \pm 0.001 \\ & (v_\sigma A/kT)^{\mathrm{c}} = 5.915 \pm 0.003 \end{aligned} \tag{29}$$

In the *three-dimensional* case, the same procedure as above yields

$$\begin{aligned} D=3: \qquad & y^{\mathrm{c}} = 0.13006 \pm 0.00005, \qquad Z^{\mathrm{c}} = 0.3592 \pm 0.0006 \\ & (v_\sigma A/kT)^{\mathrm{c}} = 10.614 \pm 0.004 \end{aligned} \tag{30}$$

using again the virial coefficients up to B_{10}.[17] Inclusion of further virial coefficients would not change the results (29), (30). Incidentally, the critical density and compressibility factor do not depend on temperature.

Now we turn to the three-dimensional gas–liquid transition away from the critical point and check the ansatz

$$D=3: \qquad y^{\mathrm{pe}} \overset{?}{=} y^{g} < y^{\mathrm{c}} < y^{l} \overset{?}{=} y^{\mathrm{pa}} \tag{31}$$

(see Section 2, last paragraph). y^g and y^l are the gaseous and liquid densities at the transition. Unlike the situation for the two-dimensional case, Eq. (25), y^g and y^l cannot be calculated uniquely without additional information. Thus, we assume

$$D=3: \qquad y^g = y^{pe} = 0.042 \pm 0.002 \tag{32}$$

[see Eq. (18)] and look for the corresponding y^l. According to (31), the question to consider is whether the resulting y^l is consistent with y^{pa} [Eqs. (21), (23)]. To calculate y^l, it is advantagous to use the analytical Carnahan–Starling expression,(18)

$$Z_{\text{h.s.}} = v_\sigma P_{\text{h.s.}}/ykT = (1+y+y^2-y^3)/(1-y)^3 \tag{33}$$

Using this expression yields $y^c = 0.13044$, which is very close to the correct critical density, Eq. (30). For given y^g, y^l and $B \equiv v_\sigma A/kT$ are determined by

$$y^l Z(y^l, B) = y^g Z(y^g, B) \tag{34}$$

$$\int_{y^g}^{y^l} y^{-1} Z(y, B)\, dy = Z(y^l, B) - Z(y^g, B) \tag{35}$$

Equation (34) means that the pressure is identical [cf. (33)]. Equation (35) is the appropriate version of Maxwell's equal-area rule. Using the Carnahan–Starling expression (33) in the van der Waals model (24), one has from Eqs. (34) and (35), respectively,

$$B\,\Delta(y^2) = \Delta[y(1+y+y^2-y^3)/(1-y)^3] \tag{36}$$

$$2B\,\Delta y = \Delta \ln y + \Delta[(4-4y+3y^2-y^3)/(1-y)^3] \tag{37}$$

where

$$\Delta X \equiv X(y^l) - X(y^g) \tag{38}$$

for any quantity X. Eliminating B yields y^l as a function of y^g. Inserting the value (32) for y^g, one gets

$$\begin{aligned} y^l &= 0.255 \mp 0.004, \qquad Z^l = 0.113 \pm 0.005 \\ B &= v_\sigma A/kT = 11.92 \mp 0.09 \end{aligned} \tag{39}$$

The $\mp$ instead of $\pm$ in the uncertainties of y^l and B means that increasing y^g induces decreasing y^l and B. The value obtained for y^l is in very good agreement with the estimates for y^{pa} [Eqs. (21), (23)].

According to the above results, the hypothesis connecting the percolation transition to the gas–liquid transition still holds. It predicts $y^{\mathrm{pa}} = y^{\mathrm{pe}}$ $(D = 2)$ and the connection between y^{pa} and y^{pe} ($D = 3$, Eqs. (36), (37)) much more precisely than these quantities are known. Thus, the hypothesis is open for further tests.

ACKNOWLEDGMENT

I am grateful to Prof. P. Weinzierl for continued interest in this work.

REFERENCES

1. J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic Press, 1986).
2. R. J. Speedy, *J. Chem. Soc. Faraday Trans. II* **77**:329 (1981).
3. K. W. Kratky and H. Drexler, *J. Stat. Phys.* **29**:449 (1982).
4. U. Landman, ed., *Statistical Mechanics and Statistical Methods in Theory and Application* (Plenum Press, New York, 1977).
5. H. Reiss, H. L. Frisch, and J. L. Lebowitz, *J. Chem. Phys.* **31**:369 (1959).
6. H. Reiss and A. D. Hammerich, *J. Phys. Chem.* **90**:6252 (1986).
7. D. Stauffer, *Introduction to Percolation Theory* (Taylor and Francis, 1985).
8. T. DeSimone, S. Demoulini, and R. M. Stratt, *J. Chem. Phys.* **85**:391 (1986).
9. W. G. Hoover, N. E. Hoover, and K. Hanson, *J. Chem. Phys.* **70**:1837 (1979).
10. G. E. Pike and C. H. Seager, *Phys. Rev. B* **10**:1421 (1974).
11. A. L. R. Bug, S. A. Safran, G. S. Grest, and I. Webman, *Phys. Rev. Lett.* **55**:1896 (1985).
12. E. T. Gawlinski and S. Redner, *J. Phys. A* **16**:1063 (1983).
13. L. V. Woodcock, *Lecture Notes Phys.* **277**:113 (1987).
14. H. C. Longuet-Higgins and B. Widom, *Mol. Phys.* **8**:549 (1964).
15. K. W. Kratky, *J. Chem. Phys.* **69**:2251 (1978).
16. K. W. Kratky, *J. Stat. Phys.* **29**:129 (1982).
17. K. W. Kratky, *Physica* **87A**:584 (1977).
18. N. F. Carnahan and K. E. Starling, *J. Chem. Phys.* **51**:635 (1969).