

Continuum theory of percolation

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Abstract. The development of a general theory of clustering, is sketched. The primary focus is on the use of the pair connectedness function in problems of correlated clustering and on the Ornstein-Zernike formalism that has been developed to evaluate this function and relate it to observed mesoscopic and macroscopic properties. The treatment stresses applications and potential applications that are directly relevant to colloid problems, especially percolation in microemulsions and gelation in polymer solutions.

1. Introduction

This contribution will be concerned with a general and quite abstract theory of clustering, but we shall emphasize here work that has already been found by colloid experimentalists such as S.H. Chen and his coworkers to be useful in interpreting microemulsion data, as well as some immediate extensions of that work that also promise to be of use to colloid and polymer scientists. This paper complements a recent article by the author [1] sharing the same theoretical approach but focused upon a somewhat different set of applications that have proved especially relevant to composite-media problems.

There is a well-developed and comprehensive theory of percolation going back to pioneering work of Broadbent and Hammersley and some others in the 1950's [2]. It describes

various aspects of connectivity on a regular lattice. But percolation, and more generally, clustering, is clearly not a notion that intrinsically requires the presence of a lattice structure in order to make sense. Moreover, there are significant features of real clustering phenomena that do not naturally lend themselves to a lattice description. There are important antecedents among earlier studies by physicists and chemists that already provide a basis for a lattice-free theory of percolation, beginning with the work in the 1930's of Bijl [3], Frenkel [4] and Band [5] concerning nucleation and condensation of gases into liquids. Subsequent work by Hill [6,7] to develop a general systematic treatment of the clustering of interacting particles and by Stillinger [8] to embed the earlier work of Frenkel and Band [4,5] in an exact statistical mechanical formalism were also carried out on a lattice-free basis as was some further work on percolation such as that of Essam, Coniglio, Zwanzig, and their coworkers [9-14]. In the 1980's the author and his colleagues developed a general lattice-free theory of percolation that began by extending the results of Coniglio et al. [11]. It is this theory that will be summarized here.

A great deal of the lattice-based research in percolation theory that followed the initial work of Broadbent and Hammersley (as well as some of the continuum work) has been concerned with what can be characterized as random percolation — this notion will be made more precise in the following sections — in which there are no interparticle forces acting to produce interparticle correlations with respect to position. On the other hand, most of the off-lattice work on condensation that we mentioned above has been focused on systems of particles that are assumed to be interacting with non-negligible interparticle forces, giving rise to non-negligible interparticle correlation. Such theories are concerned with correlated percolation, in the terminology of the subject. The theory given here has been applied to random [15-17] as well as *correlated percolation*, but it is the latter that will be stressed here, since it is correlated percolation that must be used to describe effects in colloids and other real systems of interacting particles. It is worth pointing out that the formalism developed here, although not lattice based, is immediately applicable to lattice models of percolating

systems, where it has already yielded new insights and approximations [14,18,19].

2. Theoretical Background

Much of our work centers upon the pair-connectedness function and the Ornstein-Zernike (OZ) formalism that has been developed to evaluate it and relate it to observed mesoscopic and macroscopic properties of real systems. The pair connectedness function can be thought of as being part of the pair-distribution function $g(12)$ that has long been used in liquid-state statistical mechanics. The OZ percolation formalism is correspondingly part of a more general OZ formalism that describes $g(12)$ and its relation to a direct correlation function $c(12)$. We therefore begin our theoretical development with a description of the family of correlation functions to which $g(12)$ and $c(12)$ belong and their relation to each other and to other key functions that describe the thermodynamics and structure of a many-particle system in thermal equilibrium. A key function is the pair probability density $\rho_2(12)$ associated with finding a particle in volume element dr_1 and r_1 and another particle in dr_2 at r_2 . This is one of a family of s -particle density functions $\rho_s(12\dots s)$ similarly defined, which includes $\rho_1(1)$, a local one-particle density that reduces to ρ , the expected number density, in a spatially uniform system. In [20] a general formalism relating these functions is discussed in great detail. Other treatments of ours, each emphasizing a special aspect or application of the formalism, are [21], [22], [23], as well as [1]. An early but still very valuable formal treatment of the ρ_s is found in [7].

When the distance r between particles at r_1 and r_2 becomes large, one expects $\rho_2(12)$ to approach $\rho_1(1)\rho_1(2)$ as long as a system is in a single thermodynamic phase. It is hence useful to introduce the difference between $\rho_2(12)$ and $\rho_1(1)\rho_1(2)$, sometimes referred to as the two-particle cluster function or Ursell function, as a measure of interparticle correlation

$$u_2(12) = \rho_2(12) - \rho_1(1)\rho_1(2). \quad (2.1)$$

Also useful are the pair-distribution function $g(12)$ and the pair-correlation function $h(12)$, which are dimensionless functions expressing intrinsic pair correlation, from which the one-

body effect of density inhomogeneities has been divided out,

$$g(12) = \rho_2(12)/\rho_1(1)\rho_1(2) \quad (2.2)$$

$$h(12) = u_2(12)/\rho_1(1)\rho_1(2) = g(12) - 1. \quad (2.3)$$

When ρ approaches zero, $g(12)$ approaches the two-particle Boltzmann factor

$$e(12) = \exp [-\beta\varphi_2(12)] \quad (2.4)$$

associated with the pair potential $\varphi_2(12)$. Here β is $1/kT$, with k Boltzmann's constant and T absolute temperature. Two other important functions are the Mayer f -function associated with $e(12)$,

$$f(12) = e(12) - 1, \quad (2.5)$$

and the "cavity function" $y(12)$ associated with $g(12)$,

$$g(12) = e(12)y(12). \quad (2.6)$$

The $y(12)$ is the pair distribution between two particles that each interact with a full φ_2 with respect to all other particles that are ideal with respect to each other [i.e., $\varphi_2(12) = 0$]. In other words, they behave as cavities with respect to each other. Another two-particle function that will play a crucial role in our development is the direct correlation function $c(12)$, related to $h(12)$ and $\rho_1(1)$ by the Ornstein-Zernike (OZ) equation

$$h(12) = c(12) + \int h(13)\rho_1(3)c(32)d3 \quad (2.7)$$

Here $\int d3$ represents the volume integral $\int dr_3$. In the case of a uniform system, $\rho_1(3) = \rho$, and (2.7) simplifies to

$$h(12) = c(12) + \rho \int h(13)c(32)d3. \quad (2.8)$$

In this uniform-system case, the OZ equation is of very simple form in 3-dimensional Fourier space. Introducing $a(\mathbf{k})$, the 3-dimensional Fourier transform of $a(\mathbf{r})$,

$$a(\mathbf{k}) = \frac{1}{(2\pi)^3} \int d\mathbf{r} a(\mathbf{r})e^{-i\mathbf{r}\cdot\mathbf{k}} \quad (2.9)$$

we can write (2.8) in Fourier space as

$$h(\mathbf{k}) = c(\mathbf{k}) + \rho h(\mathbf{k})c(\mathbf{k}) \quad (2.10)$$

If $a(\mathbf{r})$ depends upon \mathbf{r} only through $|\mathbf{r}|$, denoted here as r , then $a(\mathbf{k})$ depends upon \mathbf{k} only through $|\mathbf{k}| (= k)$ and $a(k)$ can be expressed as a scalar integral

$$a(k) = \frac{4\pi}{(2\pi)^3} \int_0^\infty dr r^2 a(r) \left(\frac{\sin kr}{kr} \right) \quad (2.11a)$$

so

$$ka(k) = \frac{1}{2\pi^2} \int_0^\infty dr r a(r) \sin kr \quad (2.11b)$$

In terms of the structure factor $S(k)$ and its inverse, $X(k)$,

$$S(k) = 1 + \rho h(k), \quad (2.12)$$

$$X(k) = 1 - \rho c(k) \quad (2.13)$$

the OZ equation (2.8) becomes

$$S(k) = 1/X(k). \quad (2.14)$$

In real space, $\rho S(r)$, the transform of $\rho S(k)$, is the function $\rho\delta(r) + \rho^2 h(r)$ or $\langle \Delta\rho(r)\Delta\rho(0) \rangle$, where $\rho\delta(r)$ is the "self" or "ideal" part of $\rho S(r)$.

For given ρ , (2.8) represents one equation with two functions, h and c , to be determined. A second independent relation is needed in a full theory. One such relation can be written as

$$c(12) = -\beta\varphi_2(12) + R(12) \quad (2.15a)$$

where $R(12)$ is a functional of h and a function of ρ . There is a local part of $R(12)$ expressible in terms of h at r and a nonlocal part $b(12)$, expressible in terms of an infinite series of cluster integrals over products of h -functions

$$R(12) = h(12) - \ln[h(12) + 1] + b(12), \quad (2.15b)$$

$$b(12) = \frac{\rho^2}{2} \int d3d4 h(13)h(23)h(34)h(32)h(42) + \dots \quad (2.15c)$$

The integral exhibited here is of order β^5 and ρ^2 . This is the lowest-order contribution to $b(12)$ with respect to order in both ρ and β .

Alternatively $c(12)$ can be expressed as a functional of $f(12)$ and a function of ρ by means of a sum of cluster integrals over products of f functions, which can in turn be written in terms of $y(12)$ and a cluster sum $d(12)$ [21],

$$c(12) = f(12)y(12) + d(12), \quad (2.16a)$$

or equivalently, as

$$c(12) - f(12)[g(12) - c(12)] + e(12)d(12) \quad (2.16b)$$

where $d(12)$ is of order β^4 and ρ^2 :

$$d(12) = \frac{\rho^2}{2} \int d3d4 f(13)f(14)f(32)f(42) + \frac{\rho^2}{2} \int d3d4 f(13)f(14)f(34)f(32)f(42) + \dots \quad (2.16c)$$

In order to introduce some appropriate approximations, it is necessary to first consider the form of $\varphi_2(12)$ we shall be using in our molecular modelling. When introduced to describe solute-solute correlation the functions introduced above are typically used in a solvent-averaged (McMillan-Mayer) description [24] in which the solute-solute potential φ_2 is actually a solute-solute potential of mean force at infinite solvent dilution. In particular this is true in discussing colloid-colloid interactions. The resulting φ_2 will in general be β dependent as well as ρ dependent, and in the case of colloid interactions these dependencies can be very pronounced.

In principle, n -particle potentials of mean force at infinite solvent dilution for $n \geq 3$ should be taken into account as well as φ_2 . This can be accomplished through the introduction of n -particle f functions associated with such potentials [20,25], but often the continuum-solvent approximation is made (although sometimes not explicitly) in which the solvent is regarded as a structureless continuum. For such a solvent $f_n = 0$ for $n \geq 3$. When one is not making the continuum-solvent approximation, the f_n , $n \geq 3$, can be incorporated into φ_2 , an effective φ_2 that carries further state-dependence as a result of the effects of the

f_n , $n \geq 3$, being projected into its behavior via an additional averaging procedure. This can be effected systematically through a comparison the one-species solute-solute OZ formalism we have introduced here (with the f_n , $n \geq 3$ included) and the multi-species OZ formalism given in terms of the true solute-solute, solute-solvent and solvent-solvent pair interactions, rather than mean-force quantities. The resulting formalism — a marriage of McMillan-Mayer and OZ theory — was first considered systematically by Adelman for non-ionic fluids [26] and discussed more recently for ionic systems by Høye and the author [27].

Almost all molecules and ions have highly repulsive intermolecular cores as do their constituent atoms. We can model such core terms with a hard-sphere interaction

$$\varphi^{HS}(12) = \infty \text{ for } r < \sigma, 0 \text{ for } r > \sigma \quad (2.17)$$

For some systems of interest, the attractive part of $\varphi_2(12)$ outside the core term can be reasonably modelled by a Yukawa term,

$$\varphi(12) = \varphi^{HS}(12) - A\sigma e^{-\alpha(r-\sigma)}/r, \quad (2.18a)$$

or a linear combination of Yukawa terms. We shall refer to (2.18a) as the Yukawa-sphere potential. In certain colloid problems (one of which is discussed in Section III), it seems equally reasonable to approximate the Mayer f function by a hard-sphere f plus a Yukawa term

$$f(12) = f_{(12)}^{HS} - B\sigma e^{-\alpha(r-\sigma)}/r, \quad (2.18b)$$

or a linear combination of Yukawa terms. We shall call (2.18b) the hard-core Yukawa f -function potential.

Another form that has been found to be useful in approximating potentials with strong short-range attraction is the Baxter sticky-sphere potential [28], which is most conveniently expressed in terms of its Boltzmann factor

$$e(12) = e^{HS}(12) + \frac{\sigma}{12\tau} \delta(r - \sigma) \quad (2.19)$$

where $\delta(r - \sigma)$ is a Dirac delta function loaded at $r = \sigma$. The sticky-sphere $e(12)$ can be regarded as an limiting case of the $e(12)$ for a square-well potential, in which the well width w goes to zero as the well depth goes to infinity. When the square-well $e(12)$ is written as

$$e(12) = e^{HS}(12) + e^{SW}(12) \quad (2.20)$$

$$e^{SW}(12) = \frac{w + \sigma}{12\tau w} \text{ for } r < \sigma + w ; 0 \text{ for } r > \sigma + w$$

the sticky-sphere limit is $w \rightarrow 0$. Because of its analytic convenience, (2.19) has come to be widely used as an approximation to (2.20) [29], but it turns out that (2.19) is problematic if taken literally. As the author showed some time ago [30], a monodisperse system of sticky-sphere particles has no state of thermal equilibrium — the free energy per particle is not finite. We shall return to this point at the end of this section. We note that one can *also* regard the sticky-sphere limit as a limiting case of (2.18) with βA or $B \rightarrow \infty$, $\alpha \rightarrow \infty$ with $\beta A/\alpha$ or B/α constant [31].

Ionic solutions are often modelled as fluids of charged hard spheres in a structureless medium of dielectric constant ϵ . One has for the potential between ions of species α and species β

$$\varphi_{\alpha\beta}(12) = \varphi_{\alpha\beta}^{HS}(12) + q_{\alpha}q_{\beta}/\epsilon r \quad (2.21)$$

where q_{α} is the charge of an ion. For a binary mixture of ions, $\alpha = +, -$ and $\beta = +, -$. This $\varphi_{\alpha\beta}$ is often referred to as the primitive-model potential. The restricted primitive model (RPM) refers to the symmetric case $q_{\alpha} = -q_{\beta}$ with all core diameters equal, $\varphi_{\alpha\beta}^{HS}(12) = \varphi^{HS}(12)$.

For the sorts of $\varphi_2(12)$ just listed, the formally exact results embodied in (2.15) and (2.16) immediately suggest some approximations. Consider the form of $c(12)$ exact through first order in β or, equivalently, the strength of $\varphi_2(12)$ — this defines a linear-response theory in potential strength. From (2.15) one has simply

$$c(12) = -\beta\varphi_2(12) \quad (2.22)$$

This is a useful approximation outside the repulsive interparticle core over a broad range of thermodynamic states for which β times the potential strength is relatively small. It becomes increasingly accurate as r increases since the magnitude of $\beta\varphi_2$ decreases. But in the core region, where $-\beta\varphi_2(12)$ is huge, Eq. (2.22) is wildly inaccurate. There, however, the condition $g(12) = 0$ is nearly exact. In our hard-core models, it is fully exact, so we can set

$$c(12) = -\beta\varphi(12) \text{ for } r > \sigma, \quad g(12) = 0 \text{ for } r < \sigma \quad (2.23a)$$

Used with the OZ equation (2.8) or (2.10) these boundary conditions define the mean spherical approximation (MSA). Although exact through first order in β , (2.23a) is not an exact low-density limit, given by

$$c(12) = f(12) \text{ for } r > \sigma, \quad g(12) = 0 \text{ for } r < \sigma, \quad (2.23b)$$

which represents an approximation that is exact when $\rho \rightarrow 0$ as well as being exact through $O(\beta^2)$. We denote this approximation the *f function mean-spherical approximation* (FMSA).

A widely used approximation that is exact outside the core through the first four orders in the strength of $\beta\varphi_2$ is the hypernetted chain (HNC) approximation, obtained by neglecting $b(12)$ in Eq. (2.15b). Another widely used approximation can be motivated by considering (2.16). Whenever there is a discontinuity in $\varphi_2(12)$ (or, equivalently, in $f(12)$) the discontinuity in $c(12)$, $\Delta c(12)$, is given exactly by

$$\Delta c(12) = [\Delta f(12)]y(12) \quad (2.24)$$

where $\Delta f(12)$ is the discontinuity in $f(12)$, since $y(12)$ is continuous, with $\Delta y(12) = 0$, through finite jumps in $f(12)$. One might therefore expect the expression that arises when the function $d(12)$ is neglected in (2.16a),

$$c(12) = f(12)y(12) \quad (2.25a)$$

to be good for potentials that change only discontinuously where they change at all (i.e., for hard-sphere and square-well φ_2). Equation (2.25a) is one way of expressing the Percus-Yevick

(PY) approximation, which has indeed been found particularly useful for such potentials. For the hard-sphere potential, $c(12) = 0$ for $r > \sigma$ in both the PY approximation and MSA, the two approximations yield identical expressions for g and c for a hard-sphere system.

It is worth noting that for hard-core potentials, Eq. (2.25a) will yield a very poor approximation to $y(12)$ for r near zero when used with the PY $c(12)$. As discussed by the author in detail elsewhere [21], it is better to regard the PY approximation as being given by the expression that follows from neglecting $d(12)$ *only* outside the core region, yielding

$$c(12) = f(12)[g(12) - c(12)] \quad (2.25b)$$

which is equivalent to (2.25a) outside the core region but reduces to $g(12) = 0$ inside the core. Equation (2.25b) is silent with respect to the value of $y(12)$ inside the core, in contrast to (2.25a). A similar pair of alternative formulations exists for the HNC approximations [21].

Approximations such as the MSA and the PY and HNC approximations are not accurate enough to give thermodynamic results from the relation for the isothermal compressibility K_T

$$\rho K_T / \beta = 1 + \rho \int h(12) d2 = [1 - \rho \int c(12) d2]^{-1} \quad (2.26)$$

that are fully consistent with the expression for internal energy per particle U/N

$$U/N = \frac{1}{2} \rho \int g(12) \varphi_2(12) d2 \quad (2.27)$$

or the virial-theorem expression for pressure ρ

$$\beta p = \rho - (2\pi\beta\rho^2/3) \int g(12) [\partial\varphi_2(12)/\partial r] r dr \quad (2.28)$$

The author and his colleagues have developed a family of more accurate self-consistent mean-spherical approximations (SCOZA) that insure self consistency in this regard [32-36].

The location of the coexistence curve and the values of the critical exponents associated with liquid-gas or liquid-liquid phase separation described by approximations that have

not been tailored to be self-consistent typically depend upon which of the equations (2.26)-(2.28) are used to describe the thermodynamics, as well as whether one is using a lattice-gas or continuum-fluid version of the approximation. For example, the continuum MSA and FMSA critical exponents are those of the spherical model ($\gamma = 2; \delta = 5, \beta = 1/2, \nu = 1, \eta = 0$) when the compressibility relation (2.26) is used, but mean-field-like ($\gamma = 1, \delta = 3, \beta = 1/2$) when the energy or virial-theorem routes are used. The latter routes yield different critical-point locations, too, at which $h(12)$ does not have the undamped critical-point form it has at the critical point defined by (2.26). For that reason correlation exponents like ν and η are not well-defined via (2.27) and (2.28). However, for a simple lattice gas, the MSA and FMSA exponents are those of the spherical model for *both* the compressibility and energy routes and they describe the *same* critical point. (In the lattice gas, there is no simple relation corresponding to (2.28) because of the spatial derivative of φ_2 that appears in that equation.) Somewhat surprisingly, the PY critical behavior is quite different when assessed via (2.26). For a rather broad class of models, it appears to be mean-field-like, with $\gamma = 1, \delta = 2, \beta = 1/2, \nu = 1/2, \eta = 0$, as a result of an artificial asymmetry in density about $\rho = \rho_c$, the critical density, which leads to different values for the critical amplitudes of $h(12), S(k)$, and K_T above and below ρ_c . The asymmetry was explicitly demonstrated by Baxter for the PY sticky-sphere solution [28] and by Parola and Reatto [37] for the PY solution for nearest-neighbor lattice gas. Reatto and his coworkers went on to demonstrate that the same asymmetry could be expected in the PY approximations for a broad class of fluid models [38]. If it were not for the asymmetry, the PY behavior would be spherical-model-like, because the PY approximation has both the core-condition (mean-spherical constraint) and short-ranged $c(12)$ that give rise [39] to spherical-model behavior in the absence of other special symmetries or constraints. The contrast between the MSA behavior for the Yukawa-sphere model and the PY behavior for the sticky-sphere model, discussed in Cummings and Stell [40], persists more generally for a wide variety of models when one compares PY behavior to MSA or FMSA behavior.

In the case of the sticky-sphere limit, approximate solutions of the PY or MSA type are artificial in a profound way that has to do with the singular nature of the square-well model as the sticky-sphere limit is approached. As discussed in [30], when one takes the sticky-sphere limit $w \rightarrow 0$ in Eq. (2.20), the energy per cluster necessary to break up clusters of twelve or more connected particles in three dimensions becomes infinite, causing the free energy per particle to diverge and the pair correlation function $h(r)$ to develop an infinite number of values of r at which it is nonintegrable. On the basis of exploratory studies [41], however, it appears that the energy per cluster only begins to be anomalously large for extremely small values of w/σ — probably very much less than 10^{-2} for all densities of interest, although a reliable assessment of this threshold value, w^*/σ , remains to be made. The PY, MSA or FMSA approximations for g and g^+ do not show any evidence of the singular nature of the $w \rightarrow 0$ limit and its consequential loss of thermodynamically stable states, because such approximations omit all of the highly connected cluster-integral contributions to g^- and g^+ that give rise to the singular behavior of g and g^+ . As a result, such approximate results and the exact result become more and more disparate as $w \rightarrow 0$.

In colloidal applications of the square-well potential, the w/σ that has been considered is typically greater than 10^{-2} , and it is possible that in all such applications, one will remain comfortably above the threshold value of w/σ . In colloidal applications there is another reason that the problem of thermodynamic stability may not be an important issue. Many colloids are polydisperse in size. As discussed in [30], a continuous distribution of hard-sphere sizes will prevent the formation of a finite concentration of the close-packed clusters that require infinite energy to decompose. Presumably, this would remove the divergence of the free-energy density. One has two natural length ratios in the problem, $w/\bar{\sigma}$ and the normalized dispersion $[\overline{(\sigma - \bar{\sigma})^2}]^{1/2}/\bar{\sigma}$, where a bar denotes an average value. If the $w/\bar{\sigma}$ is small compared to the dispersion, one would not expect the anomalous small- w behavior characteristic of the monodisperse case even if $w/\bar{\sigma}$ were below the threshold value w^*/σ of the monodisperse case. (It should be mentioned, however, that the results of an analysis

of this problem by J.S. Groeneveld leads him to believe [42] that the sticky limit may be pathological even in the polydisperse case.)

Although the HNC approximation has proven valuable in understanding the structure and thermodynamics of a number of the models that have been discussed here, it does not lend itself to sharp analysis involving closed-form expressions or simple quadrature. Moreover it has proven to be highly unreliable in describing phase boundaries between fluid phases [43,44,45].

All of the approximations that have been discussed are faithful to the core condition, $g(12) = 0$ when $\varphi_2(12) = 0$. Suppose the condition is relaxed — for example, by asking that

$$c(12) = -\beta\varphi_2(12) \text{ for } r > \sigma \quad (2.29a)$$

or

$$c(12) = f(12) \text{ for } r > \sigma \quad (2.29b)$$

but

$$c(12) = c^{HS}(12) \text{ for } r < \sigma \quad (2.29c)$$

where $c^{HS}(12)$ is the hard-sphere reference-system $c(12)$ that one has when $\varphi_2(12)$ is turned off outside the core, or, equivalently, when $\beta \rightarrow 0$. Then $g(12)$ for $r < \sigma$ will no longer be identically zero inside the core although it will approach zero there in the limit $\beta \rightarrow 0$, at which $c(12)$ given by (2.29) reduces to the the PY/MSA $c^{HS}(12)$. It is easy to show that the critical exponents from (2.29) will be mean-field-like. In fact, if the PY/MSA $c^{HS}(12)$ is used, Eq. (2.19a) and (2.19c) immediately yield, via (2.26), the van der Waals type equation

$$\begin{aligned} \beta p &= (\beta p)^{HS} - \beta a \rho^2, \\ 2a &= \int \varphi_2^{SOFT}(12) d(2) = \tilde{\varphi}_2^{SOFT}(0) \end{aligned} \quad (2.30)$$

where $\tilde{\varphi}_2^{SOFT}(12) = \varphi_2(12)$ for $r > \sigma$ and $\varphi_2^{SOFT}(12) = 0$ for $r < 0$. Via (2.13) and (2.14), (2.19a) and (2.19c) give the structure factor

$$S^{-1}(k) = X(k) = 1 - \rho \tilde{c}^{HS}(k) - \rho \tilde{\varphi}^{SOFT}(k) \quad (2.31)$$

while (2.19b) and (2.19c) yield the same set of relations with φ everywhere replaced by f .

There are both disadvantages and advantages to the use of (2.19) instead of (2.23). The major disadvantage is the violation of the core condition, but for some purposes, this will not be important. In particular, one would not expect it to degrade the small- k quality of $S(k)$ in a significant way, because the small- r error will be reflected primarily in some shifts that are pointwise small and distributed over all k . An advantage is analytic simplicity, which is obvious from (2.30) and (2.31). Compared to the PY approximation, an advantage is the absence of the artificial PY asymmetry about ρ_c . Compared to the MSA, an advantage for $\rho = \rho_c$ and $T > T_c$ is the somewhat more accurate temperature dependence of K_T and universe correlation length κ given by the mean-field behavior. On the other hand, the mean-field description of the critical isotherm and of the correlation length at $T = T_c$ is decidedly less accurate than their MSA description.

3. Connectedness and Clustering

A. A formalism induced by connectedness [1,46,47]

Suppose we introduce a connectedness probability $H(12)$ that defines the probability that in the $\rho \rightarrow 0$ limit, two particles are connected for a given r . (In this limit, any two particles can be regarded as isolated.) For *all* ρ , $H(12)$ will also define what we mean by two particles being *directly* connected. The form of H will be dictated by the connectedness process we are trying to model:

Example A

$$H(12) = 1 \text{ for } r < D, 0 \text{ for } r > D \quad (3.1)$$

Here we call two particles whose centers are closer than a distance D connected.

Example B

$$H(12) = Ae^{-\alpha r} \text{ or } Ae^{-\alpha r}/r \text{ or } \begin{cases} P & \text{for } r < D \\ 0 & \text{for } r > D \end{cases} \quad (3.2)$$

Here two particles are “connected in probability” rather than in an all-or-nothing way [47].

The first two forms are appropriate in modelling “hopping probabilities” of various sorts, in

which an excitation passes from one particle to another with a probability that increases as r decreases. The third is a generalization of the all-or-nothing criterion in Example A to a “something-or-nothing” criterion that retains a geometrically sharp notion of connectedness.

Example C

$$H(12) = \begin{cases} 0 & \text{for } r \ni \varphi_2(12) > 0 \\ \Gamma[3/2, -\beta\varphi_2(12)]/\Gamma(3/2) & \text{for } r \ni \varphi_2(12) \leq 0 \end{cases} \quad (3.3)$$

Here $\Gamma[a, b]$ is an incomplete Γ function. This H is a function defined by the condition that the relative energy of the pair of particles is negative. (Relative energy is potential energy plus relative kinetic energy.) It was introduced systematically by Hill [6,7].

Given $H(12)$ we can introduce e^+ and e^* , the “connectedness” and “blocking” parts of $e(12)$ [6,7],

$$e^+(12) = H(12)e(12), \quad (3.4)$$

$$e^*(12) = e(12) - e^+(12), \quad (3.5)$$

The corresponding breakup of f into $f^+ + f^*$ with $f^+ = e^+$ and $f^* = e^* - 1$ enables one to decompose the f -bond, ρ -vertex cluster expansion of $u_2(12)$ into the subsum $u_2^+(12)$ in which there is at least one unbroken path of f^+ bonds between the vertices representing 1 and 2 and the remaining subsum, $u_2^*(1, 2)$,

$$u_2(12) = u_2^+(12) + u_2^*(12). \quad (3.6)$$

This immediately yields [11] a corresponding breakup of $h(12)$, $\rho_2(12)$, and $g(12)$, with $g^+ = h^+$ and $g^* - 1 = h^*$,

$$g(12) = g^+(12) + g^*(12). \quad (3.7)$$

In extending Hill’s terminology for e^+ and e^* , the g^+ has been called the pair-connectedness function and g^* the pair blocking function. More generally, however, one can think of g^+ as the intercluster part of g and g^* as the intracluster part.

In the case of $H(12) = [P \text{ for } r < D, 0 \text{ for } r > D]$ the notion of a cluster is geometrically sharp — it is a set of particles connected via directly connected pairs, where

two particles are directly connected if their centers are a distance less than D apart. In this case the decomposition of g into g^+ and g^* can be easily defined without recourse to the cluster-sum decomposition involving f^+ -bond paths. In the case of more general $H(12)$, however, a formal procedure such as the cluster-sum decomposition appears to be necessary to define g^+ and g^* precisely.

Given h^+ and H as well as g one can immediately find mean cluster-size S as well as g one can immediately find mean cluster size S and mean coordination number z . One has

$$S = 1 + \rho \int h^+(12)d2, \quad (3.8a)$$

$$z = \rho \int g(12)H(12)d2 \quad (3.8b)$$

Equation (3.8a) is closely analogous to the thermal relation (2.26). The decomposition of $1 + \rho h$ into an intercluster part ρh^* and intracluster part $1 + \rho h^+$ in Fourier space yields a corresponding decomposition of the structure function $S(k)$, which is a key function in the description of scattering from a sample of the system. The f^+ -bond, ρ -vertex cluster expansions of g^+ , g^* , immediately provide power-series representations in ρ of those functions and of S as well, through (3.8a), while the f -bond, ρ -vertex expansion of g yields the expansion of z in ρ through (3.8b).

There is an OZ equation for $h^+ [= g^+]$

$$h^+(12) = c^+(12) + \rho \int h^+(13)c^+(23)d3 \quad (3.9)$$

obtained by using the relations $h = h^+ + h^*$, $c = c^+ + c^*$ in (2.8). No correspondingly simple relation emerges between h^* and c^* . Instead the OZ equation for h^* is in terms of c^* and convolution integrals involving h^* , h^+ , c^* and c^+ . In analogy with (2.16) one also finds

$$c^+ = f[g^+ - c^+] + f^+[g^* - c^*] + e^+d^+ + e^+d^* + e^*d^+ \quad (3.10a)$$

$$c^* = f^*[g^* - c^*] + e^*d^* \quad (3.10b)$$

where

$$d = d^+ + d^* \quad (3.10c)$$

so that a formally exact OZ theory can be given through the f^+ -bond, f^* -bond, ρ -vertex expansions of d^+ and d^* . By setting $d^+ = 0$ and $d^* = 0$ one obtains PY-type approximations for g^+ and g^* as well as recovering the PY approximation for g . We shall refer to these as “PY approximations”. Equations (3.8a) and (3.10) were first derived by Coniglio et al. [11], who also introduced the f^+ -bond, f^* -bond, ρ -vertex expansions of h^+ , h^* , and c^* as well as the PY approximation for c^+ . Stell [46] extended the work to obtain the OZ equation for h^* along with (3.10).

B. Some models, approximations, and applications

In Section II we have already introduced a number of models pertinent to colloid modelling. We did not dwell on an ideal gas of point particles, because its thermal description is trivial, with $g = 1$, $h = 0$, and $c = 0$. Even for the simplest form of $H(12)$ given by Example A, Eq. (3.1), however, the clustering properties of the ideal-gas system are highly non-trivial and describing them accurately represents a theoretical challenge. In particular, the behavior of g^+ and c^+ is not known exactly, nor is that of the mean cluster size S . The ideal gas of point particles with the H of Example A is sometimes referred to as the *randomly-centered sphere* model, or just *random-sphere* model, which represents the simplest off-lattice example of uncorrelated percolation. This was solved in the PY approximation by Chiew and Glandt [48]. Using the same H of Example A along with the hard-sphere φ_2 gives rise to what has been called both the *extended-sphere model* and the *penetrable concentric-shell model*. In that model a PY approximation for h^+ can be given that reduces to

$$c^+ = 0 \text{ for } r > D, \quad h^+ = h^{PY} \text{ for } r < D \quad (3.11)$$

where h^{PY} is the PY approximation for h . This approximation was solved analytically by DeSimone et al. [49].

In work with L. Blum [50] and with J.J. Salacuse [51], the author introduced the *permeable-sphere* model defined by setting $\varphi_2(12) = 0$ for $r > \sigma$ with $\varphi_2(12)$ such that $g(12) = 1 - \epsilon$ for $r < \sigma$, where ϵ is a fixed permeability parameter. In the same references,

the permeable-sphere model was solved in the PY approximation. Chiew and Glandt [48] extended Stell's solution to the PY approximation for g^+ , using the H of (3.1) with $D = \sigma$. They also extended Baxter's solution of the PY equation for the h of a sticky-sphere fluid to the PY equation for g^+ , using the same H with $D = \sigma^+$ (i.e., $D = \sigma + \epsilon$ for ϵ arbitrarily small.)

The natural extension of the MSA to g^+ depends on the type of H (12) being considered. The MSA is defined in terms of a hard-core region, outside of which c is approximated and inside of which g is exactly prescribed. When H is given by the step function of (3.1) it is natural to regard $r > D$ as the "core region" appropriate to the clustering problem and to prescribe c^+ as zero outside this region (since $e^+ = 0$ there) as well as to require $g^+ = g$ for $r < D$, since this is an exact core condition. (For such H , the MSA and PY approximation for c^+ become identical, just as the MSA and PY approximation for c becomes identical for hard-sphere fluids.) Since g for $r < D$ is typically not known exactly in this case, it is also appropriate to use the MSA for g to complete the MSA approximation for g^+ . For H not given by (3.1) it is instead natural to use the hard-core diameter in formulating an MSA for g^+ by using the exact relation $g^+ = 0$ for $r > \sigma$. For $r > \sigma$ the approximation most directly analogous to the MSA statement $c = -\beta\varphi_2 = \ln e$ would be $c^+ = \ln e^+ = \ln f^+$. However, in percolation problems it is not the magnitude of $\ln f^+$ but of f^+ itself that is the most natural perturbation parameter, so that the appropriate linear-response approximation to use in completing the percolation MSA is $c^+ = f^+$ for $r > \sigma$. Hence, in the terminology of Section II, when the core region for g^+ is taken to be $r > \sigma$, the natural version of the MSA for g^+ is the FMSA. For models with such a percolation core, the PY and FMSA results are different, and the percolation-singularity description for g^+ might well be different in the two approximations, just as it is for g . However the PY approximation is not analytically solvable for such models and all PY results as yet considered for g^+ can equally well be regarded as MSA results.

For the Yukawa sphere system, Xu and Stell [47] solved the MSA/PY approximation

for g^+ for the step-function H of Eq. (3.1). They also obtained g and g^+ by setting

$$c = K\sigma e^{-z(r-\sigma)}/r \quad (3.12a)$$

$$c^+ = K^+\sigma e^{-z^+(r-\sigma)}/r \quad (3.12b)$$

for $r > 0$, which yielded a second set of results, Eq. (3.12a) can be used as a MSA for the Yukawa spheres of (2.18a) with $K = -\beta A$ or as an FMSA for the Yukawa f -function of (2.18b) with $K = -B$. Eq. (3.12b) can be used analogously with c^+ identified as either $-\beta\varphi^+$ or f^+ , respectively. Xu and Stell considered two sets of relations among K^+ , z^+ , K and z ; Korlipara and Stell [52] considered still another relation among these quantities.

For the RPM, the step-function H of (3.1) has been used in characterizing ionic clustering since the pioneering work of Bjerrum [53]. The RPM $g_{\alpha\beta}^+$ has been obtained in the MSA by Given and Stell [54], who also obtained $g_{\alpha\beta}^+$ in the more accurate generalized MSA developed earlier for the RPM $g_{\alpha\beta}$ by Stell and Sun [33]. The PY and MSA results for the random-sphere, permeable-sphere, sticky-sphere, and Yukawa-sphere systems all show a percolation transition at which the mean cluster size S computed through (3.6) becomes infinite. The PY, MSA, and GMSA critical percolation exponents that characterize the behavior of S , g^+ , and related quantities at the percolation threshold are not exact, but are quite accurate. In particular wherever the mean-field results deviate substantially from the best estimates of the exact values, the PY/MSA results are much closer to the exact values. In the standard notation of the subject, the PY/MSA values are $\gamma = 2$, $\eta = 0$, $\delta = 5$, $\beta = 1/2$ while the exact values are estimated to be $\gamma \approx 45/24$, $\eta \approx -1/21$, $\delta \approx 53/10$, $\beta \approx 5/12$. The mean-field values are $\gamma = 1$, $\eta = 0$, $\delta = 3$, $\beta = 1/2$.

Remarkably enough, when one scrutinizes the analytic structure of the exactly solvable approximations for g and g^+ that we have been discussing here one finds that the analytic solutions can be extended to the polydisperse case in which there is a distribution of hard-core radii and also a distribution of potential strengths found outside the core (e.g., a distribution of charge number in the case of charged spheres). Not surprisingly, the extent

to which the extension can be made in terms of explicit closed-form results depends upon the distributions chosen and also upon the assumed relation between potential strengths $\varphi_{ij}(12)$ and $\varphi_{ii}(12)$ found outside the core. The PY/MSA treatment of the distribution functions $g_{ij}(12)$ and structure factors $S_{ij}(k)$ of a hard-sphere system was initiated by Vrij [55] and independently by the author with Blum [50] and with Salacuse [51]. The Blum-Stell results for the structure factors were used by Griffiths et al. [56] to get explicit results for the gamma (Schulz) distribution of radii.

The Blum-Stell work exploited the technique developed in earlier work by Blum and Høye [57] on the MSA for a mixture of charged hard spheres. Although the Blum-Høye work was not couched in the language of polydispersity, it immediately yields the MSA solution for a polydisperse distribution of sphere sizes and sphere charges. Blum and his coworkers have continued to extend their MSA results for polydisperse systems, including a mixture of sticky charged hard-spheres and dipolar hard spheres [58], sticky charged hard spheres polydisperse in size, charge, and stickiness (with the stickiness treated in the PY approximation and the charge in the MSA) [59], and sticky Yukawa spheres (polydisperse in size, stickiness, and Yukawa strength) in the MSA [60] Robertues et al. [61] had earlier given the PY solution for sticky-sphere system polydisperse in size. Ginoza [62] gave an elegant MSA solution for Yukawa spheres polydisperse in Yukawa strength, and Blum et al. [63] subsequently considered linear combinations of Yukawa potential polydisperse in size and strength. Zhu and Rasaiah [64] have given a detailed analysis of a polydisperse mixture of charged spheres with a sticky interaction between particles of unlike charge, with a Coulomb interaction treated in the MSA and the stickiness treated in both the PY and HNC approximations.

All of the polydisperse work we have just mentioned has been concerned with approximations for $g_{ij}(12)$, $S_{ij}(k)$ and related thermodynamic approximations. As yet, little or no corresponding work on $g_{ij}^+(12)$ and associated percolation quantities has been published, although Høye and Stell have considered $g_{ij}^+(12)$ for polydisperse sticky spheres in

as-yet unpublished work.

The three-component water-in-oil microemulsion system consisting of AOT/water/decane is a good candidate for the application of the theory discussed here. Results for this system were recently reviewed and summarized by Chen et al [65]. Over a range of molar ratios of water to AOT the system consists of microdroplets of water coated by a layer of the AOT surfactant molecules immersed in an oil solvent. The surfactant gives rise to a short-ranged solvent-averaged attractive droplet-droplet interaction between the microdroplets. At the well-studied molar water/AOT ratio of 40.8, the droplets have an effective diameter of about 60 Å and a polydispersity of about 30 %. The system has become a laboratory in the investigation of correlated-percolation phenomena in a fluid; it shows both the phase coexistence and a locus of conductivity singularities that represent a percolation line. When the solvent-averaged interaction is modelled as a narrow-well square-well interaction, the effective ratio, $w/\bar{\sigma}$, has been found to be around 2×10^{-2} with the effective well depth of the f function, ϵ/kT , around 46. The effective solvent-averaged droplet-droplet interaction is extremely state-dependent (i.e., T and ρ dependent). Whereas a state-independent φ_2 (in the absence of φ_n , $n \geq 3$) with a repulsive core and short-range attractive tail would give rise to a $\rho - T$ diagram (ρ abscissa and T ordinate) with an upper critical point characteristic of simple fluids and a percolation line emergency with positive slope from a convex-up coexistence curve, the AOT/water/decane $\rho - T$ diagram shows temperature inversion — the coexistence-curve is concave up with a percolation line below it, emerging from the vicinity of its minimum with negative slope.

There are at least two independent factors that go into the pronounced state dependence of the effective $\bar{\varphi}_2$ found in the AOT/water/decane system. The first is the state dependence of the solvent-averaged pair potential between isolated microdroplets. The second factor stems from the fact that the system has been considered in the context of a treatment in which the solvent-averaged φ_n , $n \geq 3$, have not been explicitly taken into account. Formally speaking, this means that in making contact with experiment, the effects

of the φ_n , $n \geq 3$, are implicitly being projected into the effective $\overline{\varphi_2}$ considered by Adelman [26] that has state dependence beyond the McMillan-Mayer φ_2 .

Two of the approximations we have discussed have already been used in analyzing both the phase separation and the percolation line. Cametti et al. [66] have used the Xu-Stell results with Eq. (3.12a) as an approximation for Yukawa spheres and (3.12b) parameterized for a Yukawa f^+ . The temperature dependence of the K of (3.12a) was determined by the results of an earlier study [67] that had been made to find the substantial T -dependence of the effective solvent-averaged pair potential $\overline{\varphi_2}$. Agreement between theory and experiment was strikingly good.

A subsequent analysis of the same system was made more recently by Chen et al. [65] using the sticky-sphere approximation for a square-well system. In order to accommodate the state dependence of $\overline{\varphi_2}$, a temperature-dependent particle diameter was introduced. A simple relation between the inverse stickiness parameter τ and temperature T was determined that accommodates both the T dependence of $\overline{\varphi_2}$ and the effect of size polydispersity. The resulting theoretical description of the coexistence and percolation curves in the $\rho - T$ plane match the experimental results very well, providing a second theoretical model for the analysis of the $\rho - T$ results.

Another system that seems well suited to analysis using continuum percolation theory is the gelation/water/methanol system studied by Tanaka et al. [68]. In this system there is also phase separation and percolation. Here the percolation manifests itself as gelation accompanied by a singularity in viscosity. Tanaka et al. provided a Flory-type mean-field theory of the phase separation and gelation to analyze their experimental results; Coniglio et al. [69] also developed a comprehensive lattice-based mean-field theory to describe the polymer gelation and phase separation in such systems. However, the continuum theory we have discussed here does not seem to have been used yet in discussing the reversible gelation found in such systems.

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