

# Pair connectedness functions and percolation in highly charged electrolyte solutions

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The structure of highly charged electrolyte solutions is investigated through a percolation approach. The systems, simulated by standard Monte Carlo methods, include several 2:2 aqueous solutions with concentrations ranging from 0.25 to 2 M and one 1:1 electrolyte at 1 M concentration. The ion-ion pair connectedness functions and related quantities have been computed. Two ions are considered connected if they are closer than a predefined distance. Besides this geometric criterion, an energetic condition (i.e., only particles with unlike charge signs are allowed to form directly connected links) has also been employed. The clusters obtained via the geometric and the energetic conditions are substantially different for the 1:1 electrolyte while the 2:2 solutions show a cluster structure almost independent on the criterion used. The percolation thresholds exhibit a nonmonotonic variation with concentration. A minimum in the percolation threshold has been observed at the higher concentrations investigated for the 2:2 systems; the shape of the curve and the limiting values for infinitely dilute solutions suggest the appearance of a maximum at concentrations lower than those studied in this paper. In addition, the critical exponents  $\alpha$ ,  $\gamma$ , and  $\tau$  have been computed. The result for  $\alpha$  significantly differs from the values reported for three dimensional lattices but it agrees with those obtained for the Lennard-Jones fluid. In contrast, the  $\gamma$  and  $\tau$  exponents for 3D lattice systems and for our electrolyte solutions seem to be coincident.

## I. INTRODUCTION

In the last years several works have been devoted to characterize the structure of electrolyte solutions. The ionic association phenomena have centered most of these efforts.<sup>1-5</sup> It is known that large aggregates are present in highly charged electrolytes at concentrations far from dilution. This fact has influence on conductivity and reaction rates because the encounter probabilities are then strongly influenced.<sup>6</sup> A new approach to this problem can be provided exploiting the idea of physical clusters first proposed by Hill.<sup>7</sup> Coniglio *et al.*<sup>8</sup> used this principle to derive an Ornstein-Zernike-like integral equation for the *pair connectedness function*,  $p(r)$ , which is related with the probability that two particles separated by a distance  $r$  are members of the same cluster, i.e., either exists a direct bond between them or they are connected by interparticle bonds via other particles. The pair connectedness is a natural function to study the cluster structure of systems with an important degree of aggregation.

Integral equations with different closure relations have been used to evaluate  $p(r)$  for models like permeable and adhesive spheres,<sup>9</sup> multicomponent systems of randomly centered and permeable spheres,<sup>10</sup> concentric shell models,<sup>11,12</sup> and square well systems, both pure fluids<sup>13</sup> and mixtures.<sup>14</sup> Computer simulations of these models have been reported as well.<sup>15-20</sup> Comparatively, less attention has been devoted to study systems modeled by continuum potentials.<sup>21</sup> As far as we are aware, the work done on the pair connectedness functions of electrolytes reduces to a paper by Given and Stell.<sup>2</sup> There,  $p(r)$  is obtained by solving the generalized MSA equation and then used to de-

velop a consistent (essentially analytic) theory for the thermodynamic properties of the restrictive primitive model. But, leaving aside the rather simplistic theoretical approximations, no further use of  $p(r)$  is made in order to investigate the cluster structure of electrolytes.

The pair connectedness function plays a main role in the theoretical study of continuum percolation problems. The main interest of percolation theory is the study of the number and structure of long range paths. If we consider such paths as clusters of particles, it is clear that percolation will provide a useful tool to study long-range connectivity. An interesting feature is that the percolative behavior suddenly changes at a point called *percolation threshold*,  $R_{th}$ , which is characterized by the formation of an infinite cluster of particles that spans the entire system. At this point some properties diverge, the behavior being defined by scaling laws closely related to that observed in thermal phase transitions.<sup>22</sup> Percolation theory has been successfully applied in systems whose properties are affected by the existence of an infinite cluster of particles; conductivity in random media,<sup>23</sup> sol-gel transitions,<sup>24</sup> nucleation,<sup>25</sup> and the structure of liquid water<sup>26</sup> are only some of the topics in which percolation theory has proved powerful.

The aim of this work is to investigate the effect of the concentration and charge on the ionic association from the point of view of  $p(r)$  and percolation properties. The electrolyte solutions have been obtained via Monte Carlo simulation of systems modeled with soft potential interactions. In continuum (off-lattice) models, it is necessary some criterion to decide when two particles are connected. The natural way to do this is to choose a fixed distance, the

clustering distance,  $R_{cl}$ , so that two particles are considered connected if the separation between them is smaller than  $R_{cl}$ . Besides, it is possible to impose additional criteria. Recently, Abascal and Turq<sup>1</sup> made a cluster analysis of electrolyte solutions and used two different connectivity requisites. The geometric criterion is just the clustering distance cutoff without any additional condition; the energetic one incorporates the restriction that the electrostatic interaction between the particles must be negative, i.e., the ions must carry different charges. Similar criteria have been recently used by other authors.<sup>3</sup> In this paper we report the pair connectedness functions (for several clustering distances) and percolation thresholds computed using both criteria. To study the scaling behavior of the percolation clusters several critical exponents have been determined. Even though we have not attempted a systematic investigation of this question, it seems that some of the exponents obtained are in agreement with those computed for lattice systems but others do not. Interestingly, our results for the latter are coincident with those reported in previous works<sup>21</sup> for continuous potential models.

In the next section, the model potential and the simulation details are briefly outlined. The results for the pair connectedness and other derived quantities follow. Section IV presents the percolation thresholds while in Sec. V we report the values of some critical exponents for these systems. Final remarks and the main conclusions close the paper.

## II. MODEL POTENTIAL AND SIMULATIONS

The electrolyte systems have been obtained via standard Monte Carlo simulation. The interionic potentials are given by the expression<sup>27</sup>

$$u_{jj'}(r) = B[(\sigma_j + \sigma_{j'})/r]^{n_c} - e_j e_{j'} / \epsilon r, \quad (1)$$

where  $e_j$  is the charge and  $\sigma_j$  the Pauling radius of the ion  $j$ . The parameter  $n_c$  modifies the slope of the repulsive forces and  $\epsilon$ , the relative dielectric constant of the solvent, the strength of the Coulombic interactions. The coefficient  $B$  is

$$B = A |z_j z_{j'}| e^2 / n_c (\sigma_j + \sigma_{j'}), \quad (2)$$

where  $A$  is the ratio of the Madelung's constant to coordination number for the crystal,  $z_j$  the electrovalence of  $j$  and  $e$  is the electron charge. Minimum image convention is used together with periodic boundary conditions. Negligible differences have been observed from the results presented in this paper and the same calculations done for systems obtained by stochastic dynamics using the Ewald summation method to account for the long range electrostatic interactions with the replicated boxes.<sup>5</sup> For all runs  $n_c = 9$ , and the ionic radii  $\sigma_+ = \sigma_- = 1.4214 \text{ \AA}$ . The sample consisted of 216 particles (108 anions and cations) at 298.16 K. The number of attempted moves in the production phase of the simulations was around seven million. Following this scheme, most of this paper is concerned with the results for several 2:2 aqueous solutions in the concentration range 0.25–2.0 M and a single 1:1 solution at 1.0 M concentration. The study of the percolation thresholds prompted us to simulate a new 2:2 system at a higher concentration, specifically 4.0 M. A 512 particles sampling was used in this case.

## III. PAIR CONNECTEDNESS FUNCTIONS

The pair connectedness function,  $p(r)$ , is similar to the pair distribution function,  $g(r)$ , but  $p(r)$  counts only those pairs that are part of the same cluster. To build the clusters, two different criteria have been used. The simplest one is to connect a particle to a cluster when the ion is closer to any of the components of the cluster than a fixed distance,  $R_{cl}$ . Hence the name of *geometric* criterion. It has been observed that this condition can lead to rather unphysical clustering.<sup>1</sup> Hence the convenience of ensuring that the pair interaction is low enough to consider the ions "bonded." The *energetic* condition is just the geometric rule with the additional restriction that only distances between unlike-charged ions are taken into account. (Note that the unlike-charge pair connectedness function is identical to the unlike-charge pair distribution function at distances  $r < R_{cl}$  irrespective of the criterion used; the same does not apply to the like-charge functions.) In this work three different values of connectivity distances have been considered:  $R_{cl} = 0.6, 0.75$ , and  $0.9$ . Lengths are given in

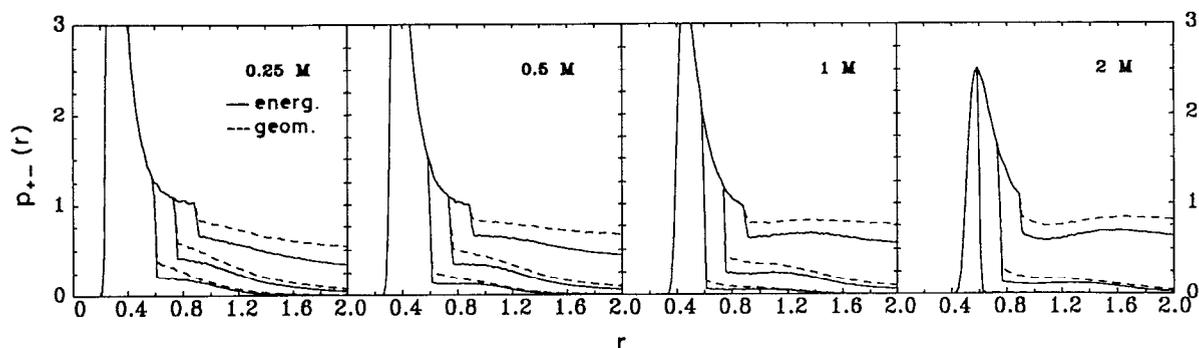


FIG. 1. Unlike-charge pair connectedness function for 2:2 electrolytes at different concentrations. Full lines: results using the energetic clustering criterion; dashed lines: geometric condition. From top to bottom the curves are obtained for the clustering distances  $R_{cl} = 0.9, 0.75$ , and  $0.6$ , respectively.

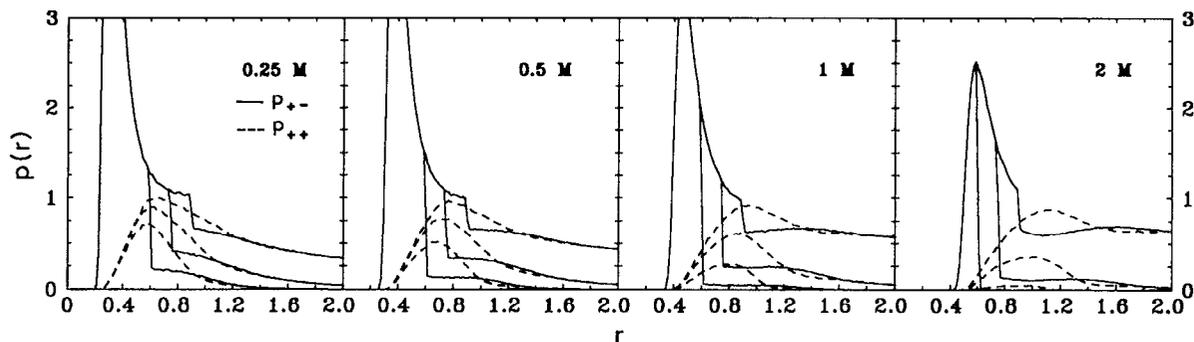


FIG. 2. Dashed lines: like-charge pair connectedness function for 2:2 electrolytes (energetic criterion);  $p_{+-}$  (full lines) is also included for comparison. In descending order the curves are for  $R_{cl}=0.9, 0.75,$  and  $0.6,$  respectively.

reduced units, i.e., expressed in terms of the distance between nearest neighbors in an halite lattice with the same number density

$$r = r_a / \sqrt[3]{10^{27} / (2N_A c)}, \quad (3)$$

$r_a$  being the absolute distance in Ångstroms,  $c$  the molar concentration, and  $N_A$  the Avogadro's number.

For the identification of the clusters several methods have been reported.<sup>15,18</sup> The essence is to assign each particle a label so when two particles belong to the same cluster both have the same label. The cluster size is then obtained by counting the number of particles with a given label. To properly account for the cluster size distribution, the periodic boundary conditions (with minimum image convention) have been used. The clustering procedure was applied to 2000–3000 configurations from the set obtained in the simulation depending on the charge and concentration of the system under study.

Figures 1 to 4 display the results for the pair connectedness functions of the simulated solutions. The comparison of the unlike-charge pair connectedness function,  $p_{+-}(r)$ , when different clustering criteria (either geometric or energetic) are used, is made in Fig. 1 for the 2:2 systems at different concentrations and connectivity distances. There are only small differences between the functions computed with the geometric and the energetic conditions; the departures are almost independent of  $r$  for  $R_{cl}$

$= 0.9$  and vanish at high  $r$  for smaller connectivity distances. In other words, few particles would join to the clusters formed with the energetic prescription if links between ions of the same charge were allowed. This fact is not obvious; actually, it is a specific feature of solutions containing highly charged ions (or, equivalently, ions in solvents with a low dielectric constant) as can be seen in Figs. 3 and 4 where the results for a 1:1 electrolyte are depicted.

The analysis of the dependence of the pair connectedness functions on the clustering distance reveals the changes in the structure of the 2:2 electrolytes as the concentration increases (Fig. 2). Since positive and negative ions have identical radii there is a single like-charge ion-ion pair connectedness function which will be represented as  $p_{++}(r)$ . Because of the comments made in the preceding paragraph, only the results obtained with the energetic criterion are shown. The first point to note is that the unlike- and the like-charge functions are coincident at large distances. This is because at such distances the ions are joined through a chain of several  $+ -$  links. As the “bonds” are not kept to a fixed length, different types of clusters—both from the topological and from the spatial distribution points of view—are possible for a large separation between any two ions. Thus the sign of the charges of the concerned ions becomes unimportant. Let us focus our attention in this large  $r$  region for which the behavior

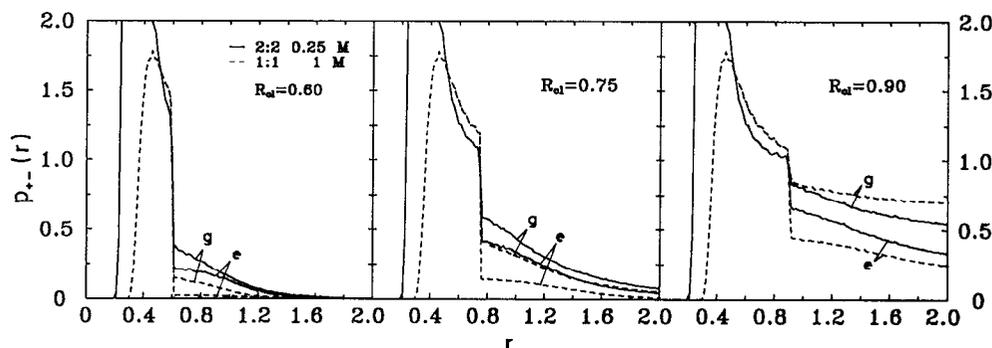
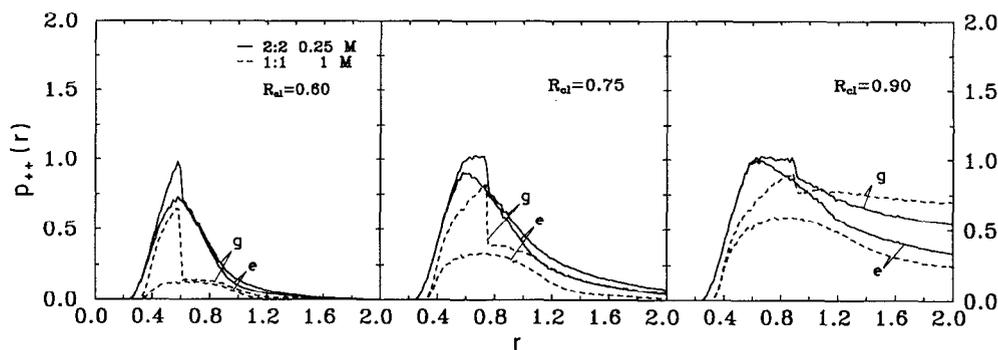


FIG. 3. Unlike-charge pair connectedness function for systems at the same ionic strength: 2:2 electrolyte at 0.25 M concentration (full lines) and 1:1 1 M (dashed). Each graph correspond to a different clustering distance. Top curves: geometric clustering; bottom lines: energetic condition.

FIG. 4. Same as Fig. 3 but for  $p_{++}$ .

is essentially common to both  $p_{++}(r)$  and  $p_{+-}(r)$ . The curves at different clustering distances are closer in the systems at lower concentrations. In these electrolytes it is difficult to link together a relevant proportion of the ions by increasing  $R_{cl}$  so that the pair connectedness functions decay with distance even when a large  $R_{cl}$  is used. The opposite situation is found for the system at 2 M concentration. In fact, it has appreciable maxima and minima for the higher clustering distance considered,  $R_{cl}=0.9$  with an asymptotic value close to unity at large  $r$  meaning that at such separations the majority of ions are connected in a unique cluster (recall that this  $R_{cl}$  is still a 10% lower than the distance between nearest neighbors in a perfect lattice). Indeed, this indicates that the system is already beyond the percolation threshold (see Sec. IV). In the more concentrated solution, there is an abrupt dependence of the pair connectedness functions on  $R_{cl}$  as indicated by the small values obtained when  $R_{cl}$  diminishes to 0.75 which become almost null at every distances greater than the clustering one for  $R_{cl}=0.6$ . Conversely, in the low concentration regime, changes happen continuously showing a system structured from shorter (reduced) distances.

We now discuss the short range behavior of the like- and unlike-charge pair connectedness functions (computed with the energetic criterion) for 2:2 electrolytes (Fig. 2). In this region there are significant differences between  $p_{+-}(r)$  and  $p_{++}(r)$  and, curiously, it is  $p_{++}(r)$  the function that provides more information about structural features. This is because  $p_{+-}(r)$  is identical to  $g_{+-}(r)$  for  $r < R_{cl}$ . Besides, for  $r > R_{cl}$ , the use of an energetic criterion requires the presence of at least *two* ions with opposite charges between the + and - ions under consideration:

The simplest cluster contributing to  $p_{+-}$  would be a tetramer in which the successive ions have alternating charges (hence the significance of the small maximum appearing at distances about 1.6 in the 2 M solution). The analysis of  $p_{++}(r)$  in the vicinity of  $R_{cl}$  gives information about the indirect correlations between like charged particles through *one* ion with opposite sign charge (as commented earlier at larger distances the contributions would be due to complex ion-ion correlations). Consequently,  $p_{++}(r) > p_{+-}(r)$  for distances higher than (but close to)  $R_{cl}$ . It is to be stressed that  $p_{++}(r)$  has a maximum in every 2:2 electrolytes treated in this work irrespective of the connectivity distance used. At the lower concentration, the peaks appear at  $r < R_{cl}$  and their heights are somewhat independent of the clustering distance (see Table I) while in the concentrated solutions they appear at distances greater than the connectivity ones and the heights are extremely dependent on  $R_{cl}$ . The picture of our 2:2 0.25 M electrolyte solution as can be drawn from the pair connectedness functions consists of ions tightly linked in small clusters at short distances (note that the short range of  $p_{++}(r)$  is not dependent upon  $R_{cl}$ ). These ions are in turn surrounded by others with (preferably) opposite charge but this occurs in a wider range of distances: for large  $r$ ,  $p_{++}(r)$  is already dependent on  $R_{cl}$ . However, even if this "diffuse" layer were taken into account the clusters would barely span the overall system since at large distances the pair connectedness functions show a slow decay as can be seen in Fig. 2(a).

The structure of the 2 M solution looks rather different. We have already cited some features supporting the existence of a unique cluster. Probably the more significant

TABLE I. Positions and heights at the maximum of the like-charge pair connectedness function for 2:2 electrolyte solutions. The energetic criterion (with  $R_{cl}=0.6, 0.75$ , and  $0.9$ ) is used. Distances are in reduced units (numbers in brackets are the corresponding values in  $\text{\AA}$ ).

$c/M$	$r$			$p_{++}(r)$		
	0.60	0.75	0.9	0.60	0.75	0.9
0.25	0.57(8.5)	0.60(8.9)	0.66(9.9)	0.72	0.91	1.00
0.5	0.68(8.1)	0.72(8.5)	0.77(9.1)	0.52	0.78	0.97
1	0.80(7.5)	0.86(8.0)	0.91(8.5)	0.27	0.61	0.92
2	0.91(6.8)	1.01(7.5)	1.11(8.3)	0.06	0.36	0.88

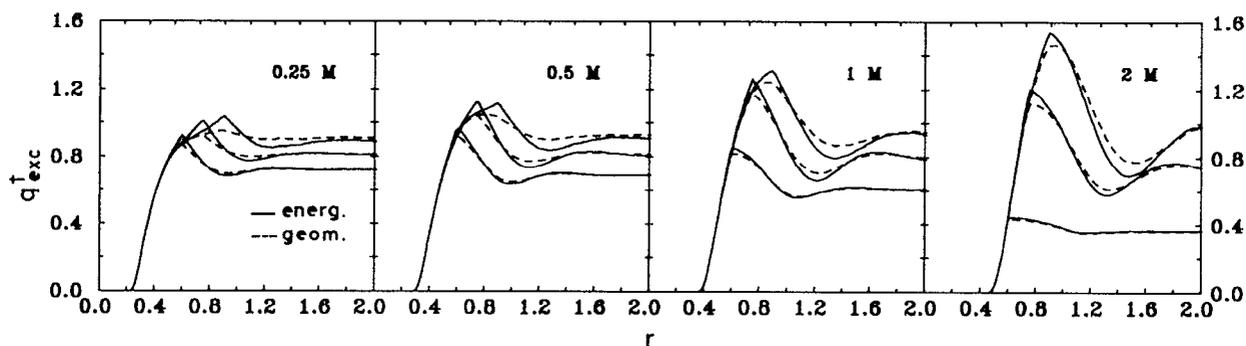


FIG. 5. Excess connected charge in 2:2 electrolyte solutions at different concentrations. Full lines: energetic clustering criterion; dashed lines: geometric condition. From top to bottom the curves are obtained for the clustering distances  $R_{cl}=0.9, 0.75$ , and  $0.6$ , respectively.

is the existence of a maximum and minimum in  $p_{++}(r)$  coincident, respectively, with the minimum and maximum in  $p_{+-}(r)$  [Fig. 2(d)]. The cluster is thus formed by ions with alternating charges and likely spans the overall system. Because of the ions mobility, the local fluctuations must be important and the asymptotic value of the pair connectedness functions is slightly less than unity. Essentially, the results for  $p_{+-}(r)$  and  $p_{++}(r)$  provide a picture of the structure of highly charged electrolytes which is in agreement with previous findings.<sup>5</sup>

Figures 3 and 4 display the pair connectedness functions for systems at the same ionic strength (a 2:2 0.25 M and a 1:1 1 M solutions). Note the important departures between the results with the geometric and the energetic prescriptions in the case of the 1:1 electrolyte. The differences for  $p_{++}(r)$  below the clustering distance are specially revealing. There, the unrestricted use of a geometric condition would include a large amount of ions that from an energetic point of view would not contribute to the clusters meaning that no real correlations exist between ions with like sign charge. Both the unlike- and the like-charge pair connectedness functions obtained with the energetic criterion are considerably higher in a 2:2 system than in a 1:1 at the same ionic strength for any of the clustering distances used in this work. However, the results using the geometric rule indicate that the same is not fulfilled for  $R_{cl}=0.9$ . In such a case, the pair connectedness functions obtained with the geometric and the energetic criteria differ very much in the system with valence 1; in fact, both functions bracket the corresponding ones for the 2:2 aqueous solution. This feature seems to be brought about by the weakness of the ionic forces in the 1:1 system since the same behavior is observed in a two-component mixture of randomly centered spheres.<sup>28</sup> At longer  $r$  the differences between the 1:1 and the 2:2 electrolyte solutions at the same ionic strength decline in importance. This is in agreement with previous works<sup>5</sup> where it was concluded that for dilute highly charged systems the strong Coulombic interactions play a dominant role in organizing the short range structure, whereas at long distances a mean field effect is adequate to explain the observed behavior.

A further insight into the cluster structure can be obtained via the excess charge

$$q_{exc}(r) = n_{+-}(r) - n_{++}(r), \quad (4)$$

which represents the charge canceled by the ions within a distance  $r$  of a particle  $j$  in  $z_e e$  units. The excess charge can be easily computed from the running coordination numbers obtained through the integration of  $g_{+-}(r)$  and  $g_{++}(r)$ . We can go further and define the *excess connected charge* as

$$q_{exc}^\dagger(r) = n_{+-}^\dagger(r) - n_{++}^\dagger(r), \quad (5)$$

where

$$n_{ij}^\dagger(r) = \rho_j \int_0^r 4\pi r'^2 p_{ij}(r') dr', \quad (6)$$

$\rho_j$  being the bulk number density of species  $j$ . This function gives the cancellation of the charge of a particle due to other ions belonging to the same cluster. In Fig. 5  $q_{exc}^\dagger(r)$  is depicted for 2:2 systems as a function of concentration and connectivity distance. The cusp in the  $q_{exc}^\dagger(r)$  computed with the energetic criterion is due to the restrictions induced by imposing a *selective* connectivity condition between two different types of particles and not to the interactions between them: The cusps also appear in a system made of two differently labeled noninteracting particles.<sup>28</sup> Another consequence of the selective clustering is the existence of oscillations in  $q_{exc}^\dagger(r)$  despite the absence of interactions. Interestingly, in 2:2 systems, the oscillations are also present when the selective criterion is removed: Again, no significant differences exist between the results obtained by imposing either the energetic or the geometric condition. It is to be stressed that, for  $R_{cl}=0.9$ ,  $q_{exc}^\dagger(r) \approx q_{exc}(r)$ <sup>5</sup> thus indicating the physical relevance of the aggregates obtained with such clustering distance. Figure 5(a) shows that the charge of the average ion in a 2:2 0.25 M solution is mostly canceled at low distances. Besides, an increase in the connectivity distance does not induce large changes in the function. This is another evidence of a structure in which small aggregates appear at short distances (in reduced units) producing a fast compensation of the ionic charge; however, a large region of space is needed to completely neutralize each ion. When the concentration increases the curves for different  $R_{cl}$  come apart from each other and charge oscillations are more evident. As for the

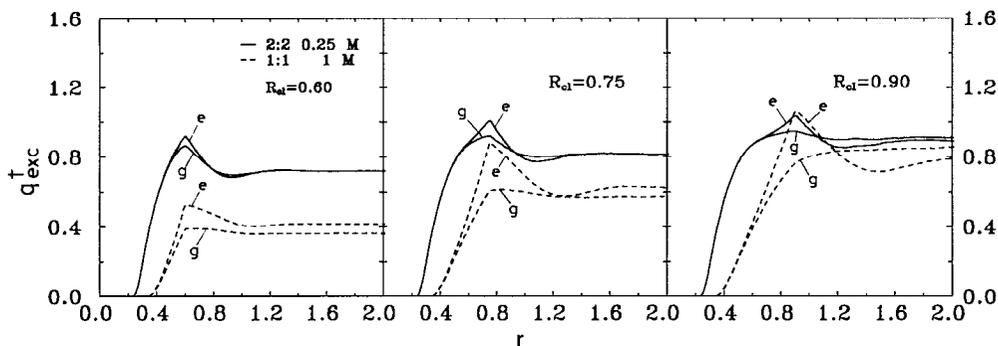


FIG. 6.  $q_{exc}^{\dagger}(r)$  for systems at the same ionic strength.

2 M solution, the large oscillations—which can reach values well above the neutralization of the reference ion—denote a long range structure in layers of alternating charge signs.

Figure 6 displays  $q_{exc}^{\dagger}(r)$  for systems with the same ionic strength. The excess connected charge enhances the departures already seen for the pair connectedness functions of these solutions. The 1:1 1 M system exhibit important differences between the  $q_{exc}^{\dagger}$  computed by both criteria. Let us recall that the cusp as well as the minimum in the excess connected charge computed with the energetic prescription are consequences of the restrictions inherent to the selective nature of the clustering criterion and not indicative of a structured system. In fact,  $q_{exc}^{\dagger}(r)$  for the 1:1 electrolyte is rather close to that for a mixture of noninteracting particles using selective particle connectivities.<sup>28</sup> Curiously, since the effect of the strong Coulombic forces in the 2:2 0.25 M electrolyte is just to reduce the presence of like-charged neighbors, the increase of structural features results in a damping of the cusp and the oscillations of  $q_{exc}^{\dagger}(r)$  computed with the energetic rule.

#### IV. PERCOLATION THRESHOLDS

The results for the pair connectedness functions give strong indications about the existence—in several 2:2 electrolytes—of large clusters which might span the whole system. It seems then appropriate to investigate the appearance of percolating clusters. In a system with periodic boundary conditions, a cluster is considered as percolating if it is possible to reach a particle from one of its images in another replica by moving along links between particles.<sup>18</sup> Usually, in continuum (off-lattice) systems, the connectivity distance is kept fixed and then the density is scanned looking for the value at which a percolating cluster is present for the first time. As the structure changes with density, a number of points need to be simulated to get the percolating threshold for a given binding distance. The inverse procedure is less expensive; for a given density (concentration) we look for the connectivity distance at which a percolating cluster would appear. Of course, with this procedure, the existence of a percolating cluster is assumed at any concentration so the physical significance of the percolating clusters must be assessed. In this work the fixed

parameter is then  $c$ , the concentration, and the scanning of the variable  $R_{cl}$  allows the computation of the percolation threshold  $R_{th}$ . This is not more arbitrary than the usual method; indeed, both must lead to the same results. We have confirmed this question for a system of randomly centered spheres.<sup>28</sup>

Since the simulation box is finite, each configuration has its own percolation distance  $R_p$ . The percolation threshold can be approximated for finite systems through the percolation probability function  $f(R_p)$  defined as the fraction of configurations for which the percolation distance is  $R_p$ . Plots of these probabilities are displayed in Fig. 7. In an infinite system the percolation probability is a step function, zero for  $R_p < R_{th}$  and 1 for  $R_p > R_{th}$ . The finite size effect appears as a deviation of this critical behavior. The shape of the curves are thus indicative of how

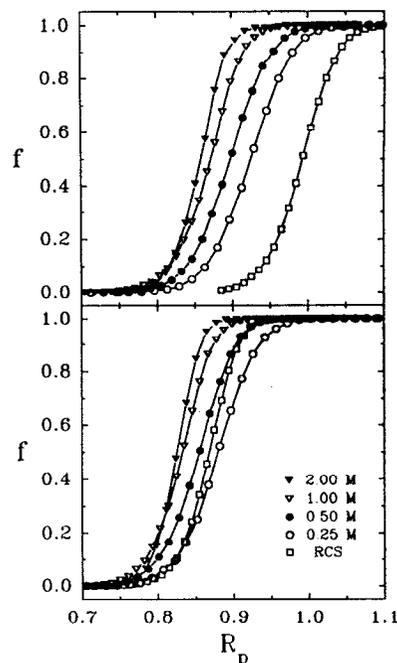


FIG. 7. Percolation probability for 2:2 electrolytes as a function of the percolating distance. Upper and lower plots are the results obtained using the energetic and the geometric clustering criterion, respectively.

TABLE II. Percolation thresholds for electrolyte solutions computed with geometric and energetic criteria. Ideal gas and perfect crystal limits are included for comparison.

System	Geometric	Energetic	Difference
RCS	0.868	0.994	0.126
1:1 1.0 M	0.847	0.927	0.080
2:2 0.25 M	0.879	0.925	0.046
2:2 0.5 M	0.855	0.898	0.043
2:2 1.0 M	0.833	0.872	0.039
2:2 2.0 M	0.826	0.859	0.033
2:2 4.0 M	0.855	0.885	0.030
Perfect crystal	1	1	0

sharp is the formation of the large clusters. In fact, the shape of the curves in Fig. 7 are similar to those obtained for the mean cluster size.<sup>5</sup> The curve closest to a step function is that of the 2:2 2 M solution confirming that a strong aggregation process occur in this system within a small range of distances.

The percolation thresholds can be estimated from the percolation probability function, either by looking for the value at which<sup>17,18,21</sup>

$$f(R_p=R_{th})=0.5, \quad (7)$$

or by calculating the first moment of the distribution,<sup>29</sup>

$$R_{th} = \int R_p \left[ \frac{df(R_p)}{dR_p} \right] dR_p. \quad (8)$$

We have computed the percolation thresholds by both methods. Nevertheless, the differences observed are within the statistical error. Numerical values of the percolation thresholds are given in Table II. For the sake of comparison the percolation thresholds for a perfect crystal and for the ideal gas system are also printed (the perfect crystal—irrespective of whether the energetic condition is required or not—has  $R_{th}=1$  since all the nearest neighbors of a given ion carry unlike charge signs and because of the definition of the reduced distance). Our computations of  $R_{th}$  in 2:2 electrolytes at concentrations in the range 0.25–2 M showed a monotonic decrease with concentration (Fig. 8). This behavior can be ascribed to a higher degree of aggregation which favors the appearance of large clusters in the more concentrated solutions. But, once the clusters span the whole system, an increase in the aggregation process leads to a more regular structure and the percolation threshold must rise. This is more easily seen if we imagine a perfect crystal and slightly distort the lattice. Some of the ions would become closer and a path between them leads to a percolating cluster thus decreasing the percolating distance. At the same time, the mean number of particles within that radius decreases. If the distortion continues the number of particles involved in the percolating cluster would diminish. Eventually, a situation arrives in which, for a significant proportion of the bonds, the removal of the link breaks the percolating cluster so the percolating distance increases. These arguments are essentially coincident with those given by Bug *et al.*<sup>30</sup> who computed the percolation thresholds for square-well systems and found that

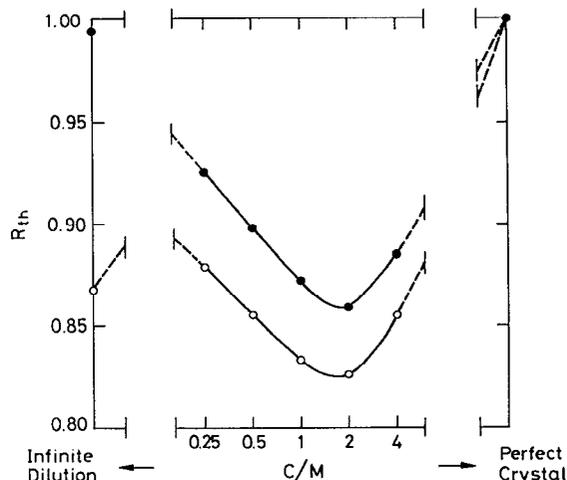


FIG. 8. Percolation thresholds in 2:2 electrolyte solutions. Full lines are a guide to the eye. Dashed lines represent roughly the speculated behavior outside the concentration range studied in this work (see the text).

the interactions may both lower or rise  $R_{th}$ : There is a compromise between the effect of the interactions which (i) promote the probability for the particles to cluster ( $R_{th}$  would be lower), but, (ii) render clusters more compact rising  $R_{th}$  (Fig. 2 of Ref. 30 is illustrative). The appearance of a minimum in  $R_{th}$  would be a consequence of a change in the balance of these two opposite effects. To investigate whether the percolation threshold exhibit a minimum at high concentrations we proceeded to simulate a 4 M solution. The results obtained for this point confirmed the existence of the minimum (see Fig. 8).

In the dilute region the situation is just the opposite. The natural reference system for comparison of the percolation trends at the lower concentrations is the ideal gas. This system has been widely used in percolation studies where it is usually referred to as randomly centered spheres (RCS) and, sometimes, as fully penetrable spheres (the radius of the penetrable spheres defines the connectivity condition).<sup>9,15</sup> The percolating properties of binary mixtures of randomly centered spheres with selective particle clustering—only links between particles carrying different labels are allowed which is the equivalent to our energetic criterion in noninteracting systems—are already known.<sup>28,31</sup> The absence of organizing forces brings about quite important departures between the percolation thresholds computed with and without the selective particle clustering. Accordingly, as Table II shows, the differences decrease with concentration.

The results also suggest a more striking feature, namely, the appearance of a maximum in  $R_{th}$  (at least when computed with the geometric criterion). It is difficult to assess the error of the percolation thresholds displayed in Table II. From the results in Fig. 7,  $\Delta R_{th} \approx 0.01$  is probably an upper estimate. This figure also manifest that finite size effects can be noticeably concentration dependent and thus the errors associated to the computed  $R_{th}$ 's. Anyway, despite the difficulties in establishing whether the difference between the percolation thresholds of the 0.25 M so-

lution and the RCS system are within the experimental uncertainties, the trends exhibited by the  $f(R_p)$  curves seem to indicate that a change in the behavior is to be expected at lower concentrations to eventually reach the infinite dilution limit. Besides, the existence of a maximum in  $R_{th}$  would be supported by experimental and theoretical instances. In particular, the Bjerrum theory of ionic association, which accounts for the deviation from the Debye-Hückel behavior at low concentrations, postulates the existence of neutral pairs. The formation of ionic pairs implies a decrease in the number of effective particles, and thus an increase of the percolation threshold (in much the same way as the equivalent conductivity decreases). The existence of neutral pairs is restricted to quite dilute solutions since higher aggregates can appear if the concentration is augmented. As commented in the discussion for the results in the high concentration range, the promotion of clustering leads to a rise in the percolation threshold. But, when the compaction of the aggregates becomes important  $R_{th}$  may reach a maximum and, thereafter, decreases when concentration increases. There are experimental evidences of changes due to the increase in cluster complexity. In particular, the appearance of a conductivity minimum has been associated to the existence of triplets.<sup>32</sup> We can summarize that, based on (i) arguments which proved to be true in other systems, (ii) experimental facts known to be closely related to ionic association, and (iii) the trends exhibited by our own results, a maximum in the percolation threshold must appear at low concentrations. Although the items (i) and (ii) could apply for both the geometric and the energetic clustering criteria, our results for the energetic connectivity do not show yet evidences of the appearance of a maximum. Its existence is then speculative.

Regarding 1:1 electrolytes, no new conclusions can be drawn since only one point has been simulated. Besides, the absence of relevant structural features in the pair connectedness functions does not compel to investigate other concentrations. As can be expected the percolation threshold obtained with the energetic condition is considerably higher than that of the 2:2 solution at the same concentration (Table II). Also consistent with results of previous sections is that the differences in  $R_{th}$  almost vanish in the case of purely geometric clustering.

Finally, we have computed the coordination numbers at the percolation threshold  $n_{th}$  given by the average number of neighbors within a distance equal to the percolation threshold. If the percolating cluster were a simple chain involving all the particles then  $n_{th}=2$ . However, only a fraction of the particles take part in the percolating cluster. For  $n_{th} < 2$  to be accomplished it is necessary that a path between the closest neighbors would span the whole system. It is the case of the more concentrated solutions (see Fig. 9). On the opposite, values higher than two indicate that the nearest links to the neighbors are unable to span the entire system so that farther ions are needed to connect the aggregates in a percolating cluster: Compact but disperse clusters would produce  $n_{th} > 2$ . This occurs in the more dilute of the 2:2 solutions studied. The results for  $n_{th}$

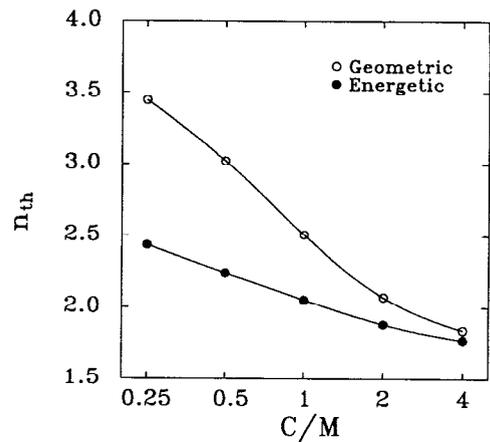


FIG. 9. Average coordination number for different systems at the percolation threshold.

give a further demonstration that in relatively dilute electrolytes the clustering is local and involves a few number of ions. Second neighbors act as a bridge to connect with other clusters. Note that, at such distances, the number of links between like-ions is already important as can be seen from the values obtained when the geometric criterion is used.

## V. SCALING LAWS

Percolation is a phase transition in the sense that a system exhibits a qualitative change at one sharply defined parameter value if that parameter is changed continuously.<sup>22</sup> Great attention has been paid to the question of the “universality” of the critical exponents. Stauffer<sup>22</sup> suggested a scaling assumption with two free exponents  $\tau$  and  $\sigma$ . These relate the number of clusters  $n_s$  with the cluster size  $s$ . At the percolation threshold

$$n_s(R_{th}) \propto s^{-\tau}, \quad (9)$$

whereas, for clustering distances close to the percolation threshold, a universal scaling function  $f(z)$  is assumed

$$n_s(R_{cl}) \propto s^{-\tau} f(z), \quad (10)$$

with  $z \equiv (R_{cl} - R_{th})s^\sigma$ . The cluster exponents  $\tau$  and  $\sigma$  are related to the other critical exponents. In particular,

$$\Omega = \left[ \sum_s n_s(R_{cl}) \right]_{\text{sing}} \propto |R_{cl} - R_{th}|^{2-\alpha}, \quad (11)$$

where the subscript sing denotes the leading nonanalytic part of the subscripted quantity. We must subtract off the analytic background. That part is dominated by the representative (largest) cluster in the vicinity of the percolation threshold, and thus<sup>21</sup>

$$\Omega = \sum_s R_{cl} [n_s(R_{cl}) - n_s(R_{th})] \propto |R_{cl} - R_{th}|^{2-\alpha}. \quad (12)$$

Another important exponent,  $\gamma$ , can also be easily evaluated from the second moment distribution  $\chi$

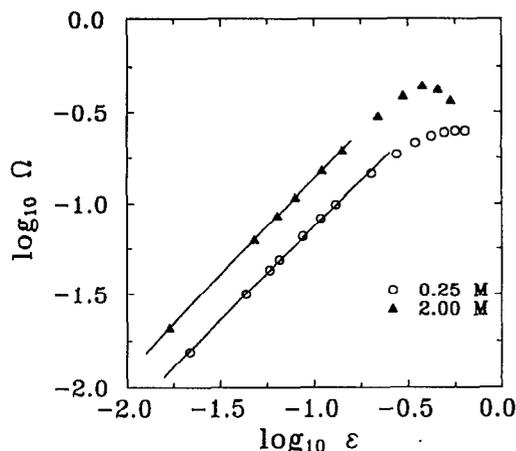


FIG. 10. Zeroth moment of  $n_s$  for 2:2 electrolyte solutions. Solid lines represent the regressions used to estimate the critical exponent  $\alpha$ .

$$\chi = \sum'_s s^2 n_s(R_{cl}) \propto |R_{cl} - R_{th}|^{-\gamma}. \quad (13)$$

The prime denotes the omission of the largest cluster in each sample configuration. These expressions apply strictly only in the vicinity of the percolation threshold  $R_{th}$ , and describe the behavior both above and below that point.<sup>29</sup> In a critical review, Stauffer<sup>22</sup> concluded that the scaling laws for the exponents are accomplished rather well (within statistical uncertainties) in lattice systems. It is worthwhile to investigate if the same is fulfilled by nonlattice systems. Some attempts in this way have been done by several authors,<sup>21,33,34</sup> who reported several exponents calculations for a Lennard-Jones fluid. In this section we report values for the critical exponents of the ionic systems described above. Note that a rigorous study would require the elimination of finite size effects. As this is out of the scope of the present paper, the results presented here must be taken as rough estimations of the critical exponents for the percolation transition in electrolytes.

In estimating  $\alpha$  and  $\gamma$  we have applied the scaling law only in the region  $R_{cl} < R_{th}$ . In Fig. 10 the zeroth moment of  $n_s$ ,  $\Omega$ , is represented as a function of the separation from the percolation threshold  $\epsilon = |R_{cl} - R_{th}|/R_{th}$  for two 2:2 electrolyte solutions. Only the computations using the energetic criterion are depicted (those with the geometric one exhibit similar behavior). The line represents the regression giving  $\alpha$  (numerical values are reported in Table III).

TABLE III. Critical exponents. Subscripts  $g$  and  $e$  refer to computations using the geometric and energetic clustering criteria.

System	$\alpha_g$	$\alpha_e$	$\gamma_g$	$\gamma_e$	$\tau_g$	$\tau_e$
RCS	1.02	1.08	1.48	1.51	2.03	2.00
1:1 1.0 M	0.99	0.96	1.53	1.54	1.98	1.99
2:2 0.25 M	0.98	0.96	1.63	1.56	1.95	1.96
2:2 0.5 M	0.96	0.96	1.72	1.68	2.00	1.98
2:2 1.0 M	0.96	0.95	1.79	1.81	2.02	2.03
2:2 2.0 M	0.94	0.94	1.61	1.66	2.09	2.04
2:2 4.0 M	1.00	0.98	1.45	1.49	2.06	2.11

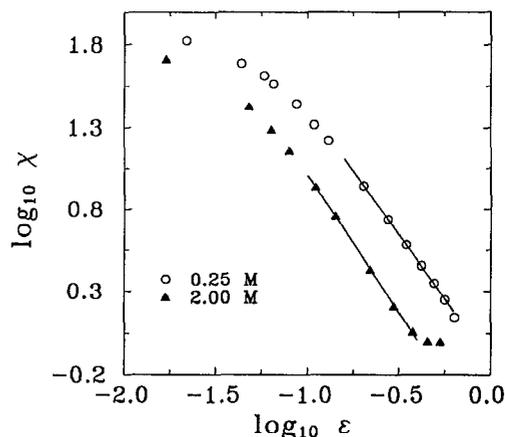


FIG. 11. Susceptibility  $\chi$  (2:2 electrolyte solutions). Solid lines represent the regressions used to estimate the critical exponent  $\gamma$ .

Irrespective of the concentration considered, this critical exponent exhibit a manifest disagreement with respect to the value accepted for three dimensional lattice systems,  $\alpha \approx -0.6$ .<sup>29</sup> However, they show a good agreement with those reported by Heyes and Melrose<sup>21</sup> for a Lennard-Jones system. Similar calculations for the susceptibility  $\chi$  are presented in Fig. 11, the results for the exponents being collected in Table III. Notice that the scaling law is fulfilled only at large values of  $\epsilon$ . The discrepancy at low  $\epsilon$  is likely related to finite size effects because the existence of big clusters is clearly restricted (there is an upper bound for the maximum size of a cluster  $s < N$ ). Nevertheless, the results agree with those accepted for three dimensional lattices ( $\gamma = 1.8$ ) and also with the reported ones for continuum systems.<sup>21</sup> As for  $\tau$ , finite size effects occur in the large clusters limit and the small clustering region as well (Fig. 12). Therefore, the scaling law has to be applied in the intermediate cluster size range. The values for  $\tau$  shown in Table III are in good agreement with the lattice value 2.2 and with other estimations in continuum systems (2.1

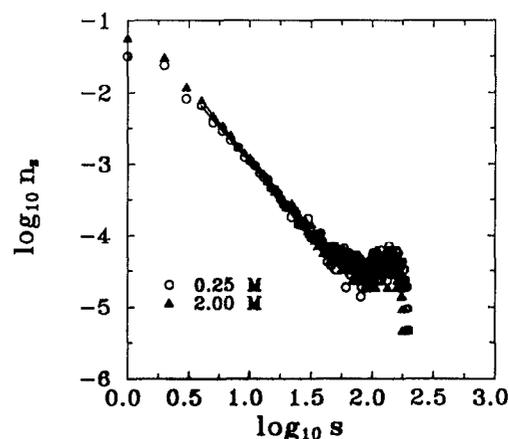


FIG. 12. Cluster number distribution for 2:2 system at the percolation threshold  $R_{th}$ . The slope of the straight lines gives the critical cluster exponent  $\tau$ .

$\pm 0.1$ ,<sup>21</sup> 1.98-2.15<sup>18</sup>). Finally, notice that the dependence on concentration of the critical exponents seems to follow similar trends to that of the percolation thresholds (maxima or minima appear in the vicinity of the concentration at which the minimum in the percolation threshold occurs). Our study does not enable one to ascertain whether this would be true in the thermodynamic limit or it could be due to indirect effects of the finite size which might be dependent on the percolation threshold value.

## VI. CONCLUSIONS

In this work we have studied the structure (with the emphasis put in ionic association) of highly charged electrolytes as a function of concentration and ionic strength. The features exhibited by the unlike and like pair connect- edness functions reveal a distinct underlying structure in these systems. The use of both geometric and energetic clustering criteria helps to clarify the extent of ionic association. Moreover, the calculation of the percolation thresholds has served to unambiguously assess the physical significance of the percolating clusters. It is concluded that the ions in concentrated 2:2 (model) electrolytes form a unique cluster made of bonds between unlike-charged particles whereas the clustering in the 0.25 M solution are rather local. The concentration dependence of the percolation threshold shows a nonmonotonic behavior leading to a minimum which can be explained in terms of structural changes related with the size of the ionic aggregates (nevertheless, the dilute regime seems to demand a more rigorous study to verify the existence of a maximum in the percolation threshold). Interestingly, similar arguments have been used to justify changes in the electrical conductivity of highly charged electrolytes. The speculation about a common origin of these structural and dynamical properties is tempting.

Although we have not attempted a rigorous study of the critical exponents (especially, the influence of finite size effects is not investigated) our results are similar to those obtained elsewhere. It is striking that  $\alpha$  is of opposite sign to the accepted value for lattice systems. A value of the same order was obtained by Heyes and Melrose. They claim this to be a finite size effect related with the restrictions in the number of particles. Actually, their sample size was of the same order than that used in this report. Thus the question of the universality of  $\alpha$  in 3D remains open.

Other exponents  $\gamma$  and  $\tau$  are however in good agreement with values obtained both for 3D lattice and continuum systems.

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