Possible origin of the smaller-than-universal percolation-conductivity exponent in the continuum

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For quite a few systems in the continuum, such as carbon nanotube polymer composites and segregated composites, percolation electrical conductivity exponents that are much smaller than the universal value have been reported. This is unexpected in view of the classical lattice percolation theory. Here we provide a simple general phenomenological model that accounts for such observations within the framework of universality. We suggest that these small value exponents are due to the interplay between the connectivity and the structural variations that follow the increase of the fractional volume content of the conducting phase.

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I. INTRODUCTION

It is widely accepted that the electrical conductivity, σ, in many conductor-insulator two-phase continuum systems can be described by the relation [1–5]

$$\sigma = \sigma_0\left(x - x_c^0\right)^t, \tag{1}$$

where x is the fractional volume, or weight, content of the conducting phase in the system, while σ_0, x_c^0, and t are determined by the analysis of the $\sigma(x)$ data that is found experimentally or computationally. Equation (1) is borne out by the lattice theory of percolation as a phase transition and the possible mapping of the continuum on it [4] that leads to the same t values for the lattice and the continuum [6]. According to the lattice theory, that is briefly reviewed here in Appendix A, t is equal to its universal (only dimensionally dependent) value μ. In particular, $\mu(3D)\approx 2$ for three-dimensional (3D) systems and $\mu(2D)\approx 1.3$ for two-dimensional (2D) systems [1,3,7]. Indeed, in most percolation systems in the continuum $t = \mu$ but there are numerous reports on $t > \mu$ values [4,5,8]. These higher t values are well understood by now (both for lattices [9] and for the continuum [10,11]) to be a result of a diverging distribution of the local conductances, g, as $x \to x_c^0$, that yields to $g \to 0$ there [9–11]. For a brief review and background on this nonuniversal behavior, see Appendix B.

There are however, as detailed in Appendix C, quite a few experimental [8,12–17] and computational [18–20] reports on continuum systems for which t is smaller than (the relevant universal exponent [21]) μ and even smaller than 1. In particular, experimental values of $t = 1.2$ for carbon nanotube (CNT) composites [22], and as low as a $t = 0.4$ value for segregated composites, were reported [13,14]. Such low values are not consistent with the above mentioned universal values (even if one assumes [23] a 2D conducting subnetwork within the 3D system).

The $t < \mu$ observations are quite surprising since they appear, *a priori*, to contradict the sound and well-established classical percolation theory of the electrical conductivity as given by the simple links-nodes-blobs (LNB) model [7,24,25]. This model, described in Appendix A, is the only widely accepted topological description of an electrical (obeying Kirchhoff's laws) percolation network from which the μ values were derived.

The intriguing questions that arise then are whether the observed $t < \mu$ relations involve some other special universality class (as was suggested for other cases and different systems [26]), or if not, how can they be explained within the framework of the known percolation universality class [6,7]? Noting that this problem has not been adequately discussed, we try in this article to provide an explanation for those $t < \mu$ observations in accordance with the framework of that universality class. In particular, we use excluded volume considerations [27] to explain the observations for systems such as CNT-polymer composites [8], for which $t < \mu$ values were reported. While we limit our analysis here to these composites we also suggest (see below) that the values of $t < \mu$ found in other systems [12–17] result from the same basic reasons that we propose here for the CNT composites.

As the conductivity is associated with an electrical network, it is a bond percolation problem (as described by the LNB model) [7,24,25]. In lattices, the classical critical behavior of the conductivity is given by $\sigma \propto (p_b - p_{bc})^\mu$ where p_b is the bond (i.e., the local conductor) occupation probability and p_{bc} is its critical value. The average number of bonds per site in lattices is given by $B = p_b Z$ where Z is the lattice coordination number and thus $\sigma \propto (B - B_c)^\mu$ [1,7,24,25,28]. While in the continuum p_b and Z are not defined, the latter relation, as mentioned below, is still obeyed in view of the expected topological mapping of the continuum on the lattice problem [1,6]. Indeed in 2D systems of widthless sticks, where the only topological parameter that changes (and can be determined) is B, a universal behavior has been found [20,21]. Hence, in both the lattice and the continuum the conductivity can be described by $\sigma \propto (B - B_c)^\mu$. For permeable particles $B = nV_{ex}$ where n is the concentration of the particles and V_{ex} is the excluded volume, i.e., the volume around the center of a particle in which the center of another particle has to be for the two particles to have some overlap [27]. The existence of the overlap is defined as an occupied bond and is assumed to represent the electrical contact between the two particles, either by touching or by tunneling [4,5]. These models have been widely used for CNT composites [8,29].

Following that, in Sec. II we consider in some detail the above $\sigma \propto (B - B_c)^\mu$ relation, in Sec. III we show how the variation in the excluded volume can affect the $B(x)$ dependence, and in Sec. IV we show how the latter can yield $t < \mu$ values. Our conclusions are summarized in Sec. V.

II. CONNECTIVITY AND CONDUCTIVITY IN LATTICES AND THE CONTINUUM

As mentioned above, the excluded volume argument is conveniently applicable to permeable particles but the CNTs are *a priori* particles with a hard core. For the application of this to the CNT composites let us try now to bridge between the B's associated with permeable and nonpermeable objects. We start then with the well-known model of Scher and Zallen who suggested that for touching nonpermeable (rigid or "hard core") spheres of two types [1], the fractional volume of the conducting phase, x, is proportional to the lattice site occupation probability p_s. This led later to the general site-percolation assumption that, even for systems where the conducting particles are embedded in a continuum of an insulating matrix, one should expect that $\sigma \propto (p_s - p_{sc})^{\mu} \propto (n - n_c)^{\mu} \propto (x - x_c^0)^{\mu}$ [2,4]. Here p_{sc} is the site-percolation probability threshold value, n is the concentration of the conducting particles, and n_c is its threshold value. In the case of such hard core particles in the continuum $x = nV$, where V is the volume of the individual conducting particle (assumed to be independent of n). On the other hand, as mentioned above $B = p_b Z$ and $\sigma \propto (p_b - p_{bc})^{\mu} \propto (B - B_c)^{\mu}$ [7,24]. Comparison of the above $\sigma(x)$ and $\sigma(B)$ dependences led to the assumption that $B \propto x$. Hence, while not stated explicitly, this was the underlying assumption in numerous works associated with continuum systems. This of course overlooked the fact that $x = nV$ is a quantity that originated from the lattice site occupation probability, p_s, rather than from the bond percolation quantities p_b or B. The experimental and simulation observations of $t = \mu$ [3–5,8] in many continuum systems cannot be taken then as an *a priori* justification for the use of x for the conductivity problem. Here, in order to determine the proper exponent of the conductivity we consider the $B(x)$ dependence that we should substitute in the $\sigma \propto (B - B_c)^{\mu}$ relation in some systems of hard core particles. Our proposed model in this article is based on starting with the linear $B \propto x$ relation [1] and then noting that in the conspicuous system on which the $t < \mu$ values were reported, the CNT composites [8], there is enough experimental evidence to suggest that with the increase of x, some basic parameters of the systems change. In particular, we will show that these changes can result in a $B(x)$ dependence which can lead to the $t < \mu$ observation.

Returning to the concept of excluded volume we recall that in their seminal paper, Shante and Kirkpatrick [30] suggested that the total volume ϕ occupied by permeable particles or objects, each with a volume V, can be given by $\varphi = 1 - (1 - V)^n$, where n is the number of particles per unit volume ($n \gg 1$, $V \ll 1$ so that nV is finite). In the limit of large n (and thus satisfactory for the statistics) this yields that $(1 - V)^n = \exp(-nV)$. For permeable objects we also have that $B = nV_{ex}$ [24,27] and thus $\varphi = 1 - \exp(-nV) = 1 - \exp(-BV/V_{ex})$. Since topologically the B values involved are typically within the $1 < B < 10$ range throughout the relevant $nV \ll 1$ regime [4,27] we can write that $\varphi \approx nV = BV/V_{ex}$. On the other hand for nonpermeable particles $x \equiv \varphi = nV$, and thus, for dilute systems, we can use the latter relation to formally write that $x \approx BV/V_{ex}$. However, this is also justified physically; for a dilute system (i.e., $x \ll 1$) of hard core particles of volume V where the interaction is long range (i.e., $V_{ex}/V \gg 1$) the scenario from the connectivity point of view is the same as that of a system of permeable objects. Such is the case of the CNT composites where the typical studied x regime is from x_c^0 up to the order of 10^{-2} and where $V/V_{ex} \approx r/L$ is usually of this order [8]. Hence, for the present nonpermeable CNTs case the applicability of the permeable particles result as done below is justified only if $V/V_{ex} \ll 1$, i.e., only if $x \ll 1$. This condition is then a necessary condition for the applicability of our model.

III. APPLICATION OF THE EXCLUDED VOLUME TO CNT-POLYMER COMPOSITES

Turning to our $t < \mu$ problem let us utilize now the concept of the excluded volume [8,27,30] as manifested in CNT composites [31]. As we mentioned above, in order to use the $B = nV_{ex}$ relation for the conductivity one needs first that the actual (hard core or soft core) volume V of the particle is very small in comparison with its "interaction" volume (i.e., V_{ex}). Now let us suppose that V_{ex}/V is x dependent. We suggest that such dependence can result from the well-known processes that may take place during the fabrication of the CNT composites and can be intensified with the increase of x. These are the flocculation [32–35] and/or bundling [36–38] (or other aggregations [39]) of the CNTs as well as the increase of the CNTs' alignment during molding [40–43]. We point out here that while in the literature there are statements that the preparation conditions can affect the measured t exponent [41,44,45], in these articles there are no suggestions as how this will take place. In fact, there is not even a speculation, as what will be the tendency of the change in the value of t. In this article we go much further than that, by connecting between the molding procedure, the CNT-composites' parameters, the variation of t with x, and the $t < \mu$ observations. In passing, we remark that for the segregated composites the increase of x can result in a widening of the conduction channels [13], an effect that is reminiscent of the bundling effect in the CNT composites.

We recall now (see above) that in a system of permeable objects $B = nV_{ex}$ [24,27]. Hence, following the bond percolation picture we find that

$$\sigma \propto (\mathrm{B} - \mathrm{B}_c)^{\mu} \propto [(n - n_c)V_{ex}]^{\mu}, \tag{2}$$

where B_c and n_c are the corresponding thresholds of the percolation network. The important physical point that we note here is that V_{ex} actually transfers the site-percolation quantity n to the bond percolation quantity $B = nV_{ex}$ [46–48] that is needed for the conductivity. As we saw above, when $V \ll V_{ex}$ we can use the relation $B = nV_{ex}$ also for nonpermeable objects and thus, in systems with $x \ll 1$ values, such as CNT [8,40,49] or graphene [15–17] composites, we can use the results obtained for permeable particles, yielding that in Eq. (2) we can write $B \approx xV_{ex}/V$. We know that for long cylinders of length L and radius r (representing CNTs [31]) $V = \pi r^2 L$ and (for $L \gg r$) $V_{ex} = 4rL^2\langle \sin\theta \rangle$ [27], where θ is the angle between two (partially overlapping) connected cylinders and $\langle \sin\theta \rangle$ is an average over the ensemble of CNT pairs [27,46]. Substituting these expressions for V and V_{ex} in B we get

$$B = (4/\pi)(xL/r)\langle \sin\theta \rangle. \tag{3}$$

From this it follows that the very large $V_{ex}/V = (4/\pi)(L/r)\langle \sin\theta\rangle$ values yield very small x values (and thus also the small typical x_c^0 ($\ll 1$) values in CNT-polymer composites [31].

Let us examine now the possible effects of the variations of the systems' parameters L, r, and $\langle \sin\theta\rangle$ on B in Eq. (3) with the increase of x during the fabrication of the material (e.g., due to the increase of direct or indirect "friction" between the particles [8,32]). In flocculation, the "breaking" of the particles causes L to decrease with x while in bundling the effective r increases with x, and in some molding processes the function $\langle \sin\theta\rangle$ of x $[\langle \sin\theta\rangle(x)]$ may be a decreasing function of x [40]. Hence, considering these dependences we have that B in Eq. (2) is given by the resulting function $B(x) \propto x\{L(x)[\langle \sin\theta\rangle(x)]\}/r(x)$. Correspondingly we denote now the value of x that is associated with $B_c = n_c V_{ex}$ in Eq. (2) by x_c. [Note that this is different than x_c^0 that is derived from the experimental or computational analysis according to Eq. (1)]. We expect then that for any reasonable (in the above context of CNT composites) x-decreasing $B(x)/x \propto L(x)[\langle \sin\theta\rangle(x)]/r(x)$ function, the conductivity exponent will vary with x. To see if and how such dependences can lead to a $t < \mu$ behavior we will present here a couple of such $B(x)$ dependences (more presentation and analyses will be presented elsewhere). We remark here that in general the molding processes do not necessarily yield the above effects.

In passing we note that the alignment (unlike the results of flocculation and bundling) does not affect the size of the individual particles but changes a global property of the system. This increasing alignment of the particles is also evident from the observed increase of the percolation threshold that is well known to be associated with that increase [40,49].

We should also add here that while in the computer simulation studies [18,19] the results of the molding have not been explicitly considered, they were included implicitly by the interaction between the CNT fibers that induced possible variations of the spatial and orientational distributions. Correspondingly, we tentatively attribute the observed low values of t there (0.4 and 0.87 respectively) to these changes. The fact that in both simulation studies the observed t values are smaller than 1 cannot be explained by the simple tendency of the crossover between percolation and effective medium behavior [2] which yields that $t = 1$. This is of course at variance with the simulation results [21] in which there are no interactions between the widthless sticks in 2D, and the increase of their concentration just represents the transition between the percolation μ(2D) and the value of 1 as derived from the effective medium approximation.

IV. THE EXPECTED MANIFESTATION OF THE $t < \mu$ EFFECT IN COMPOSITES

For a transparent and simple illustration of the $t < \mu$ problem and its solution let us assume that in the x region of interest (i.e., $x > x_c$,) the effect of x on L due to flocculation can be described (phenomenologically) by $L = L_0(x/x_c)^{-\beta_1}$ where L_0 is the value of L at the percolation threshold x_c. Similarly we can use $r \propto (x/x_c)^{\beta_2}$ and $\langle \sin\theta\rangle \propto (x/x_c)^{-\beta_3}$ where for each of the above mentioned different effects (that result during the composite fabrication) a different value of $\beta_i > 0$ may apply. We get, then, that for this simple model the combination of these effects can yield that $B(x) \propto xL\langle \sin\theta\rangle/r \propto x^\gamma$ where $\gamma = 1–(\beta_1 + \beta_2 + \beta_3)$. One notes of course that since the functional dependence of the system parameters on x due to the fabrication processes is not available explicitly at present (experimentally or theoretically), our above model is just a possible illustrative description of how the x-decreasing $B(x)/x$ dependence can yield to the $t < \mu$ observation. Considering our interest in the conductivity we start by substituting the x^γ dependence for B in Eq. (2) which yields that

$$\sigma = A\left(x^\gamma - x_c^\gamma\right)^\mu, \tag{4}$$

where A is a constant. Since σ is found always (experimentally or computationally) to increase with x, one concludes from Eq. (4) that $\gamma > 0$. Using Eq. (2) or Eq. (4) for the extreme case where B deviates enough from B_c the conductivity exponent t approaches $\gamma\mu$. The request that $B(x)/x$ will be a decreasing function of x simply yields in this model that $\gamma < 1$.

Let us turn now to the consequences of the above $B \propto x^\gamma$ dependence when the observed $\sigma(x)$ dependence is analyzed according to Eq. (1). Assuming that Eq. (4) describes the actual behavior of the system, we suggest that in the many experimental [8,22,23] and computational [18,19] works (see Appendix C) that showed the $t < \mu$ effect, researchers essentially tried to analyze an Eq. (4)-like behavior by fitting the data to Eq. (1). We also see that when the analyzed x range is close to x_c^0 ($x \to x_c^0$), the universal exponent ($t = \mu$) is achieved. In the power-law example that we use, the fits of such data to Eq. (1) can be distinguished analytically in the two extreme cases. In the first case we consider the fitting to Eq. (1) in an x interval for which $x^\gamma \gg x_c^\gamma$ and $x \gg x_c^0$. In this case one actually fits the data to a $\sigma \propto x^t$ dependence. However, according to Eq. (4) $\sigma \propto x^{\gamma\mu}$ and this yields that $t = \gamma\mu$, and then, since $\gamma < 1$, a $t < \mu$ value will be found. The second case is the other extreme where the examined x range is close to x_c^0. Equating Eqs. (1) and (4) we get, then, that $x^\gamma - x_c^\gamma = (\sigma_0/A)^{1/\mu}(x - x_c^0)^{t/\mu}$. The derivatives of both sides of the equation have to be the same and this yields that $\gamma x^{\gamma-1} = (\sigma_0/A)^{1/\mu}(t/\mu)(x - x_c^0)^{(t/\mu)-1}$. In particular, for $x \to x_c^0$ the derivative on the left side has a finite (>0) value, while (since $x - x_c^0 \to 0$) the derivative on the right side has a finite value only for $t = \mu$. Therefore, the value of t will vary from $\gamma\mu$, when $x \gg x_c^0$, to μ as the studied x range approaches x_c^0. We note of course that for any reasonably smooth $B(x)$, $t \to \mu$ for $x \to x_c^0$. The physics of the above described behavior is quite simple; while the exponent μ represents the changes in the (phase-transition-like) connectivity that determines the universal critical behavior, the exponent γ accounts for the x-dependent changes in the basic parameters of the system (here, L, r, and $\langle \sin\theta\rangle$). In particular, if x is very close to x_c^0 the character of the system (e.g., due to flocculation) has not been changed significantly compared to that at x_c^0. In contrast, when x and x_c^0 are far apart, the system's character (e.g., the decrease of L and the corresponding increase of n with the increase of x) could have varied considerably. Hence, universality will always dominate when $x \to x_c^0$, but as x departs from x_c^0 a $t < \mu$ value may be reflected by the measured exponent. As preliminary recent experimental evidence for this behavior, we can consider the results of Grunlan *et al.* [50] and of

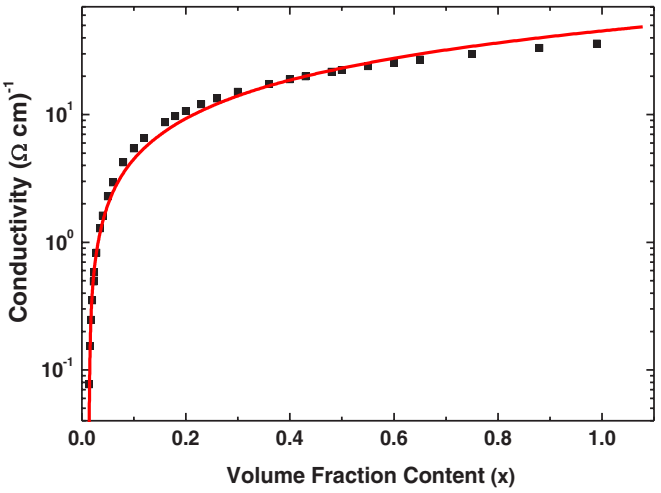

FIG. 1. The best fit of Eq. (1) to data produced by the use of Eq. (4) with $A = 100\,(\Omega\,\mathrm{cm})^{-1}$, $\gamma = 0.2$, $x_c = 0.01$, and $\mu = 2$.

Mukherjee *et al.* [14] on segregated composites for which they found that with the departure of the x intervals from x_c^0, the t values decreased from 1.87 to 0.90 and from 0.8 to 0.4, respectively. Note that these values were derived from experimental results on macroscopic systems and thus there are no finite size effects, or deviations from percolation criticality, that could have yielded a conductivity exponent below $t = 1$.

As a numerical illustration for our above conclusion and for appreciating how this t value transition from μ to $\gamma\mu$ takes place we started by generating data points by using Eq. (4) with $A = 100\,(\Omega\,\mathrm{cm})^{-1}$, $\gamma = 0.2$, $x_c = 0.01$, and the 3D value of $\mu = 2$. The data, shown in Fig. 1, include 31 values of σ in the interval $0.014 \leqslant x \leqslant 0.99$. The best fit of Eq. (1) for this wide x interval yielded the values of $\sigma_0 = 46\,(\Omega\,\mathrm{cm})^{-1}$, $x_c^0 = 0.013$, and $t = 0.95$. As seen in Fig. 1, the quality of the fit to this entire x regime varies along different x intervals. To follow the variation of the t and x_c^0 values with the proximity of the x interval to x_c^0, we have fitted the data points to Eq. (1) for a few types of x-interval selections. In all those selections we saw a

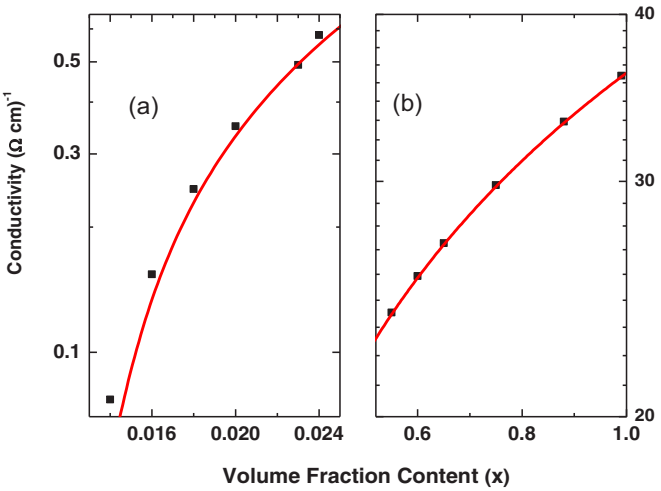

FIG. 2. The best fit of Eq. (1) to data produced for the six lowest x values (a) and for the six highest x values (b) used in Fig. 1.

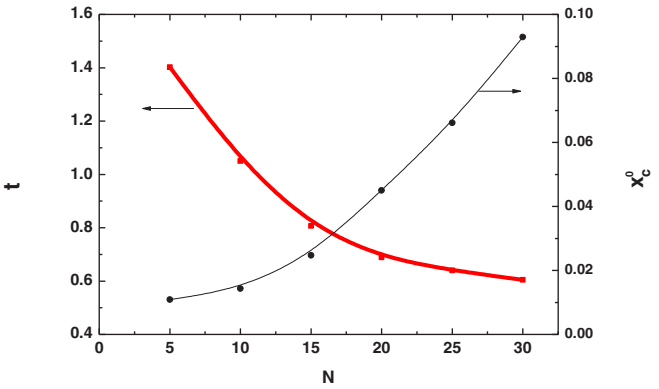

FIG. 3. A summary of the t (bold curve) and the x_c^0 values obtained from fits such as in Fig. 2, where N is the number of the last point in the interval considered in each fit.

systematic decrease of t and a systematic increase of x_c^0 with the departure of the intervals from x_c^0. The type we selected to show here was chosen in order to mimic the typical available data sets that usually contain fewer than ten experimental [8,12–14,45,49,51] or computational [18,44] points. We have considered, then, six intervals, of six points each, from the data of Fig. 1, i.e., from points 0–5 to points 25–30, denoting the last point of each interval by N. The fits in the extreme cases, $N = 5$ and $N = 30$, are shown in Fig. 2. The results for the first (lowest σ values) six data points yielded [Fig. 2(a)] $t = 1.40$ and $x_c^0 = 0.011$ while for the last (highest σ values) six data points [Fig. 2(b)] we got $t = 0.60$ and $x_c^0 = 0.093$. All the t and x_c^0 values obtained by such fittings are shown in Fig. 3 as a function of N. The t dependence confirms the analytical result that we described above and also exhibits the general effect of the x interval used on the t ($< \mu$) values observed when the system's parameters are x dependent.

For completeness, and to show that our choice of the above x^β dependence is not a necessary condition or a unique example for obtaining the $t < \mu$ behavior, we have also substituted the phenomenological $B(x) \propto xL(x) \propto x/(1 + x^2)$ dependence (with $\mu = 2$ and $x_c = 0.1$) in Eq. (2). This yielded, as in Fig. 3, to a decrease of the value of t (from $t = 2$), as x increases above x_c. For example, considering the data from $x = 0.2$ to $x = 0.7$ yielded that $t = 0.88$. Other examples and their analysis will be reported elsewhere.

V. CONCLUSIONS

In lattice percolation theory the conductivity depends in a critical manner on the number of occupied bonds per site, B, yielding that the observed conductivity critical exponent, t, cannot be smaller than its universal value μ. We suggest that in the continuum, however, there are systems where B can have a sublinear dependence on the particle concentration that brings about the observation of measured or simulated $t < \mu$ values. Our results show that this behavior of B can be associated with the variation of the character of the system with the change of x. We have shown, however, that the observed value of t will always reach the value of μ as the percolation threshold is approached. This is because the phase transition effect will overcome there the effect of the material variation with x.

APPENDIX A: THE LINKS-NODES-BLOBS (LNB) MODEL

Being concerned in this article with the $t < \mu$ problem, we discuss here why the clear and unequivocal prediction of the classical lattice percolation theory cannot yield a $t < \mu$ value.

In percolation theory, the only characteristic scale is the correlation length ξ that determines the structure of the electrically conducting network in the system (known as the backbone) [7,24]. The electrical properties of a system of size $\Gamma \gg \xi$ can be described by a structure that is topologically consistent with cubic units of volume ξ^D where D is the Euclidian dimension of the system. Each of these cubes consists of electrically conducting links of length ξ. Hence, the global conducting network has the resistance $R = R_\xi(\Gamma/\xi)^{(2-D)}$ where R_ξ is the resistance of a link [4,7,24,25]. The links intersect at nodes (the corners of the cubes) and consist of singly connected bonds in series with blobs (bunches of resistors, i.e., of bonds, that provide more than a single path between the two ends of the bunch).

The correlation length depends on the bond occupation probability, p_b, as $\xi \propto (p_b - p_{bc})^{-\upsilon}$, where υ is the corresponding critical correlation length exponent (0.85 in 3D) [7]. The only question that remains then, for the evaluation of R, is the dependence of R_ξ on $p_b - p_{bc}$. While the exact dependence is determined by the structure of the link, it is well established [24,25] that $R_\xi \propto (p_b - p_{bc})^{-\zeta}$ where the value of ζ (in 3D) can be only between 1 and ~ 1.13 [25] or 1.3 [3], and thus $\mu \equiv \upsilon + \zeta$ can only be within the small interval between the two values, 1.85 and 2.15 [1,7], for any internal structure of the link. We have, then, that $\sigma \propto (p_b - p_{bc})^\mu$ [2,25].

The important points to note here are that υ is universal since it is determined by the universal structure of the percolation network, while the above two extreme μ(3D) values are due to the extreme estimates for ζ. The first estimate considers the minimal possible resistance of the link (by assuming the blobs to be electrical shorts) yielding that $\zeta = 1$ [24]. The other extreme estimate evaluates the maximal resistance of the link by considering the shortest path through it (i.e., a path that includes the blob resistors that belong to that path while neglecting the other parallel resistors' configurations to it in the blob) yielding that $\zeta \sim 1.13$ [25]. Hence, there is no 3D structure of the electrically conducting backbone that can yield μ(3D) values outside the above (rather narrow) range. Within the context of our article the important consequence is that there is no percolation backbone structure for which the exponent t can be smaller than 1.85 $(= \upsilon + \zeta)$. Correspondingly the explanation given by Shao *et al.* [12] for their experimental $t = 0.87 < \mu$ observation by a particular backbone structure is not valid.

APPENDIX B: THE NONUNIVERSAL $t > \mu$ BEHAVIOR

In Eqs. (1) and (2) one implicitly assumes that all the local conductances in the system have the same value g, or that their average value $\langle g \rangle$ is independent of $p_b - p_{bc}$, $B - B_c$, or $x - x_c$. However, there are distributions of g values such that $\langle g \rangle \propto (p_b - p_{bc})^u$ or $\langle g \rangle \propto (x - x_c)^u$ where the exponent u (> 0) is determined by the properties of the system. The most known example for such behavior follows the divergent, but normalizable, distribution of the values of the local conductances as $g \to 0$. As suggested originally by Kogut and Straley [9] such a distribution is

$$f(g) = (1 - \alpha) g^{-\alpha}, \tag{B1}$$

where $0 < \alpha < 1$. Considering that the global conductivity σ of the conducting network is dominated by the higher value conductances and using a normalized g value of 1 for the highest value in the system, it is apparent that the lowest g value that must be used in order to provide percolation (i.e., that $\sigma > 0$), g_c, is given in the lattice model by

$$\int_{g_c}^{1} f(g) dg = p_{bc}/p_b. \tag{B2}$$

Using Eq. (B1) this yields that

$$g_c = [(p_b - p_{bc})/p_b]^{1/(1-\alpha)}, \tag{B3}$$

and that the average local *resistance* in the system is

$$\langle g^{-1} \rangle = \int_{g_c}^{1} f(g)(1/g) dg = [(1 - \alpha)/\alpha](g_c{}^{-\alpha} - 1). \tag{B4}$$

Hence, from Eq. (B4) one can appreciate the behavior of $\langle g^{-1} \rangle$ for various values of α. For $\alpha \to 0$, $\langle g^{-1} \rangle$ has the logarithmic dependence $[-\ln(g_c)]$ that becomes divergent as $g_c \to 0$. If $\alpha < 0$ and $g_c \ll 1$, $\langle g^{-1} \rangle$ is the constant $(1-\alpha)/(-\alpha)$; i.e., the system in the $p_b \to p_{bc}$ limit behaves as if it is made of local resistors all of which have this average constant value. If $0 < \alpha < 1$ one gets from Eqs. (B3) and (B4) that, as $p_b \to p_{bc}$,

$$\langle g^{-1} \rangle \approx [(1 - \alpha)/\alpha] g_c{}^{-\alpha} \propto [(p_b - p_{bc})]^{-\alpha/(1-\alpha)}, \tag{B5}$$

and thus $\langle g \rangle$, defined as $\langle g^{-1} \rangle^{-1}$ [9], yields that

$$\sigma \propto \langle g \rangle [(p_b - p_{bc})]^\mu \propto [(p_b - p_{bc})]^t, \tag{B6}$$

where here

$$t = \mu + \alpha/(1 - \alpha). \tag{B7}$$

This $t > \mu$ behavior is commonly referred to as the nonuniversal behavior [3,4,7,10].

Following the above discussion we consider now the attempt of Shao *et al.* [12] to account for their $t < \mu$ observation in segregated composite by two arguments. One argument, considering the basic backbone structure, was already negated in Appendix A. Their other argument for $t < \mu$ was that $\alpha/(1-\alpha) < 0$. However, this can happen only if $\alpha < 0$ or $\alpha > 1$. For the $\alpha < 0$ possibility, we have just shown that $\langle g \rangle = \langle g^{-1} \rangle^{-1}$ is a constant independent of $p_b - p_{bc}$, and thus $t = \mu$. For the $\alpha > 1$ possibility, the distribution function [Eq. (B1)] cannot be normalized. Hence, this $t < \mu$ argument of Shao *et al.* is also not valid.

APPENDIX C: THE $t < \mu$ OBSERVATIONS IN VARIOUS COMPOSITES

There were quite a few experimental and simulation reports with $t < \mu$ results [12–20]. The conspicuous system for which those results were found is that of the CNT-polymer composites. To show the validity of the $t < \mu$ problem, we mention here the findings on this and some other systems and discuss how all those findings can be attributed to the

same reasons. These reasons are that the volume of the particles is negligible compared with their excluded volume and that changes in the particles (e.g., L and/or r) or in their ensemble (e.g., $\langle \sin\theta \rangle$) take place with the increase of the conducting-phase volume, x.

An important class of composites in which particularly small t [$< \mu(2D)$] values were observed is that of segregated composites [12–14] where small conducting particles are confined to channels or slit-like structures (or cracks). For these, even a suggested [33] 2D conducting subsystem cannot account for the $t < \mu(2D)$ observations. In those composites, t values as small as 0.4 [13,14], and very small percolation thresholds, as small as $x_c^0 = 0.001$, were found (showing that $V \ll V_{ex}$). We suggest that the small t values may be due to the fact [13] that with the increase of x "the conducting channels become much thicker." This is similar to the increase of r with x in our model for the CNT composites as given by Eq. (3). The low percolation threshold is also consistent with the very low percolation thresholds that we have shown previously [27] to exist in similar systems of channels and cracks where the conducting phase consists of a liquid. Hence, the two necessary conditions for the observation of $t < \mu$ that we suggest are fulfilled also for the segregated composites. Moreover, the x range for the determination of t in Ref. (13) was $(x - x_c^0)/x_c^0 \approx 10$. This is consistent in particular with our prediction for small $t \approx \gamma\mu$ values (and even $t < 1$ values) when $(x - x_c^0) \gg x_c^0$.

For the very many experimental studies reported on CNT-polymer composites the value of t was found "in the range from 1.3 to 4 peaked around $t = 2''$ [8]. The broad range of values found by experiments was described as a nonuniversal behavior [37] and it was suggested [8,44,45] that the values of the exponent t depend on the preparation conditions. However, no specific connection between the observed values of the exponent and those conditions was proposed. In particular, quite a few t values in those 3D CNT composites were found to be between $\mu(2D) \approx 1.3$ and $\mu(3D) \approx 2$. Some of these observed values were explained [23] as due to a possible conducting 2D subnetwork within the 3D conducting network, but no structural experimental or computational evidence was presented for that. In addition, simulation works on elongated 3D constant size cylinders that represent CNTs in the composites do not support this 2D explanation since $t < \mu(2D)$ and even $t < 1$ values (as small as 0.4) have been reported [18,19]. In these simulations, interactions that may change the system parameters with increasing x have been introduced. On the other hand, simulations on 2D systems of widthless sticks [20,21], where no interactions that can cause parameters changes have been introduced, showed t values varying from $\mu(2D)$ to $t = 1$ (with departure from the threshold). Accordingly, with no system parameter change t cannot be smaller than $\mu(2D)$ (or 1) and obviously cannot account for experiment [13,14] or simulation [18,19] with t values as small as 0.4. This is important since it shows that at least the $t < 1$ result should be attributed to another effect such as the one that we propose in the present article.

The findings of $t < \mu$ for other carbon allotrope composites were reported also for 3D polymer composites of graphene and graphite nanosheets. For example, for these systems, for which $V_{ex} \gg V$ (as shown for a system of disks [27]), values of t of 1.26 [15], 1.67 [16], and 1.54 [17] were found. It is important to note here that all the results that we cite were measured (or simulated) on composites after their molding and curing processes were completed and no further changes in the samples' structure took place. In other words, the $\sigma(x)$ dependence does not represent any kinetic effect [8,44] and the values of x represent a series of independently prepared samples.

We remark here that in all the above mentioned composites (where $V \ll V_{ex}$), x_c^0 can be of the order of 0.01 and thus typical studies consider x ranges with $(x - x_c^0)/x_c^0$ values of the order of 10 [8]. The fact that in the overwhelming majority of observations, values of $t = \mu$ [8,45] have been found, shows that this range is still within the critical regime of classical percolation [7]. A similar conclusion appears to apply also for simulations, as follows from recent detailed studies [52] that have shown that universal values for t can be obtained even for $(x - x_c^0)/x_c^0$ between 10 and 100.

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