Continuum Percolation of Polydisperse Nanofillers

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We show that a generalized connectedness percolation theory can be made tractable for a large class of anisotropic particle mixtures that potentially contain an infinite number of components. By applying our methodology to carbon-nanotube composites, we explain the huge variations found in the onset of electrical conduction in terms of a percolation threshold that turns out to be sensitive to polydispersity in particle length and diameter. The theory also allows us to model the influence of the presence of nonconductive species in the mixture, such as is the case for single-walled nanotubes, showing that these raise the percolation threshold proportionally to their abundance.

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The exceptional thermal, mechanical, and electrical properties of carbon allotropes like nanotubes and graphene sheets, and the wide variety of potential applications of nanocomposites containing these allotropes, have generated a considerable interest in the buildup of networks by these highly anisometric particles [1,2]. Once formed in fluid precursor phases, such networks are capable of significantly improving the physical properties of the host material post solidification, but only if the networks are system spanning and if the nanofillers are connected in a sense that may be different for different physical properties of interest [3]. For instance, to significantly increase the electrical conductivity of the composite requires neighboring particles in the network to be within a short enough range of each other to enable charge-carrier transport between them. Connectedness can then be defined by some maximum surface-to-surface distance. Given this range, the quantity of interest is the (geometrical) percolation threshold (PT), which is the minimum filler packing fraction necessary to establish a network that spans the entire system [3].

Despite a large body of theoretical literature on the PT of highly anisometric filler particles, predicted to scale as the reciprocal of their aspect ratio [4,5] and found to approach values below 10^{-3} for carbon nanotubes (CNTs) [6] and graphene [2], little is known, let alone understood, about the influence of polydispersity in length and/or breadth, or the presence of a fraction of poorly conducting species [4]. Indeed, single-walled carbon nanotubes (SWNTs) consist of about one third metallic and two thirds semiconducting particles, while multiwalled carbon nanotubes (MWNTs) and graphene sheets are generally conductive. Both carbon allotropes can have quite a broad length and width distribution, and in fact it is quite a challenge to remove all bundles (stacks) even after significant processing [6]. Because of the connection between percolation phenomena and phase transitions, known to be influenced very strongly by polydispersity effects [7], we expect the PT to also be greatly affected by them. As we shall see, this expectation turns out to be justified theoretically, explaining the variation of several orders of magnitude observed in PTs of CNTs of approximately the same mean aspect ratio [8].

In this Letter, we make analytically tractable a generalized connectedness percolation theory of mixtures of sterically interacting particles. Specifically allowing for polydispersity in the linear dimensions of the particles and the way they are connected, we derive an expression for the mean cluster size from the pair-connectedness analog of the multicomponent Ornstein-Zernike equation of liquid-state theory [9], presuming the network builds up in the fluid stages of the production process of the nanocomposite. Provided the particles interact through a harshly repulsive potential and their size greatly exceeds the characteristic hopping or tunneling distance, the second-virial approximation represents an accurate closure for this equation. We apply the theory to CNTs and obtain an analytical expression for the PT at which the cluster size diverges. Although translation-rotation coupling gives rise to angular correlations between the CNTs, the PT that we obtain is a function only of higher-order moments of the full distribution of dimensions and connectivity ranges. This explains why the PT is so sensitive to the degree of size polydispersity. Likewise, there is a sensitivity of the PT to polydispersity in the extent of connectivity, which may be taken as a model for variations in nanofiller conductivities. In bidisperse mixtures of conductive and nonconductive CNTs, we find the PT to scale with the inverse fraction of the conductive species: the nonconductive ones act as dead mass.

To calculate from connectedness percolation theory [9] the PT of anisometric filler particles, i.e., the volume fraction for which the average cluster size of connected particles diverges, let $x_{i\alpha\dagger}$ denote the number fraction of particles that can be described by an arbitrary length L_i, width D_α, and height $H_\dagger$. Here, and in the following, we use indices with Roman symbols to denote length polydispersity, Greek ones to denote variations in width, and the symbols †, ‡, and § to indicate different heights. The weight-average number of particles in a cluster S is the sum of the weight-average "partial cluster sizes" $S_p \equiv S_{ij\alpha\beta\dagger\ddagger}$ that obey

$$S_p = x_{i\alpha\dagger}\delta_{ij}\delta_{\alpha\beta}\delta_{\dagger\ddagger} + \lim_{\mathbf{q}\to 0}\rho x_{i\alpha\dagger}x_{j\beta\ddagger}\langle \hat{P}_{ij\alpha\beta\dagger\ddagger}\rangle_{\mathbf{u},\mathbf{u}'} \quad (1)$$

and can be computed from the so-called pair-connectedness function, $P_{ij\alpha\beta\dagger\ddagger}$. Here, δ_{ij} is the Kronecker delta, ρ the number density of the particles in the system, $\mathbf{u} \equiv (\mathbf{u}_1, \mathbf{u}_2)$ with $\mathbf{u}_1$ and $\mathbf{u}_2$ the unit vectors in the direction of the main axes of a particle, and $\langle\ldots\rangle_{\mathbf{u}_n} \equiv (4\pi)^{-1}\int d\mathbf{u}_n(\ldots)$, $n = 1, 2$ an orientational average. (A similar prescription holds for the primed variables.) The hat $(\hat{\ldots}) \equiv \int d\mathbf{r}(\ldots)\exp(i\mathbf{q}\cdot\mathbf{r})$ indicates a spatial Fourier transform with $\mathbf{q}$ the wave vector, so $\hat{P}_{ij\alpha\beta\dagger\ddagger} = \hat{P}_{ij\alpha\beta\dagger\ddagger}(\mathbf{q}, \mathbf{u}, \mathbf{u}')$ is the Fourier transform of $P_{ij\alpha\beta\dagger\ddagger}(\mathbf{r}, \mathbf{r}', \mathbf{u}, \mathbf{u}')$. This pair-connectedness function is defined such that $\rho^2 P(\mathbf{r}, \mathbf{r}', \mathbf{u}, \mathbf{u}')d\mathbf{r}d\mathbf{r}'/(4\pi)^2$ equals the probability of simultaneously finding a rod in a volume element $d\mathbf{r}$ at position $\mathbf{r}$ and a second rod in $d\mathbf{r}'$ at $\mathbf{r}'$, given that the particles are part of the same cluster [9].

$\hat{P}_{ij\alpha\beta\dagger\ddagger}$ obeys the pair-connectedness analog of the multicomponent Ornstein-Zernike equation [9],

$$\hat{P}_{ij\alpha\beta\dagger\ddagger}(\mathbf{q}, \mathbf{u}, \mathbf{u}') = \hat{C}^{+}_{ij\alpha\beta\dagger\ddagger}(\mathbf{q}, \mathbf{u}, \mathbf{u}') + \frac{\rho}{(4\pi)^2}\sum_{k,\gamma,\S} x_{k\gamma\S}\int d\mathbf{u}''\hat{C}^{+}_{ik\alpha\gamma\dagger\S}(\mathbf{q}, \mathbf{u}, \mathbf{u}'')\hat{P}_{kj\gamma\beta\S\ddagger}(\mathbf{q}, \mathbf{u}'', \mathbf{u}'), \quad (2)$$

with C^+ the direct pair-connectedness function that probes short-range correlations, to be determined later on. Because the cluster size obeys $S \equiv \sum_p S_p$ with $p \equiv \{i, j, \alpha, \beta, \dagger, \ddagger\}$, we conclude from Eq. (1) that we require information only on the average of $\hat{P}$ over its four orientations and six indices. Therefore, we need not find the individual components of $\hat{P}_{ij\alpha\beta\dagger\ddagger}$, and the key to solving Eq. (2) is to take averages over j, β, ‡, and $\mathbf{u}'$. We thus obtain an equation that gives this average of $\hat{P}$ in terms of an operator that works on the same average of $\hat{C}^+$. We substitute this in Eq. (1), which then gives an expression for the average cluster size $S = \langle T_{k\gamma\S}(\mathbf{u})\rangle_{k\gamma\S,\mathbf{u}}$ in terms of the function $T_{k\gamma\S}(\mathbf{u})$ that depends on the indices and orientation of a single particle rather than two. It obeys the reduced integral equation

$$T_{k\gamma\S}(\mathbf{u}) - \rho\langle \hat{C}^{+}_{km\gamma\delta\S\dagger}(0, \mathbf{u}, \mathbf{u}')T_{m\delta\dagger}(\mathbf{u}')\rangle_{m\delta\dagger,\mathbf{u}'} = 1, \quad (3)$$

where $\langle\ldots\rangle_{m\delta\dagger} \equiv \sum_{m,\delta,\dagger} x_{m\delta\dagger}(\ldots)$. Again, we need not solve T explicitly but only averages of T over its indices and argument, simplifying the calculation considerably. Obviously, this can only be done with an appropriate closure as C^+ is not known *a priori*.

However, as to be argued below, the second-virial approximation, in which C^+ is replaced by the connectedness Mayer function [9], should be an accurate closure for harshly repulsive particles if the hopping range is sufficiently small on the scale of the largest particle dimension. In practice, this is probably always the case, i.e., it holds for CNT rods and graphene sheets alike.

We now focus on the application of our theory to CNTs, for which the mean length is typically 3 to 4 orders of magnitude larger than any reasonable estimate for the hopping distance, which at most is in the nanometer range. We assume cylindrical symmetry of the particles so they can be described by a length, a diameter, and a single orientation vector denoted $\mathbf{u}$ or $\mathbf{u}'$ henceforth. Within the second-virial approximation, $\hat{C}^{+}_{ij\alpha\beta}(0, \mathbf{u}, \mathbf{u}') \approx \hat{f}^{+}_{ij\alpha\beta}(0, \mathbf{u}, \mathbf{u}') \equiv \int d\mathbf{r} f^{+}_{ij\alpha\beta}(\mathbf{r}, \mathbf{u}, \mathbf{u}')$ [4,9], with $f^{+}_{ij\alpha\beta} \equiv \exp(-\beta u^{+}_{ij\alpha\beta})$ the connectedness Mayer function of particles that belong to the same cluster and interact via the connectedness potential $u^{+}_{ij\alpha\beta}(\mathbf{r}, \mathbf{u}, \mathbf{u}')$; $\beta^{-1} = k_B T$, with k_B the Boltzmann's constant and T the absolute temperature.

We now specify the connectedness potential u^+ that by definition is infinite for all configurations in which the rods are not connected. Although our aim is to model particles that interact via a harshly repulsive excluded-volume interaction, we use a form that interpolates between these and ideal ones that can freely interpenetrate (see Fig. 1). In this description, $u^+ = \varepsilon$ for distances $r \le D_{\alpha\beta}$, with $\varepsilon \to \infty$ for impenetrable rods and $\varepsilon = 0$ for ideal ones and where $D_{\alpha\beta} \equiv \frac{1}{2}(D_\alpha + D_\beta)$ is their average diameter. Furthermore, $u^+ = 0$ for $D_{\alpha\beta} \le r \le \Delta_{\alpha\beta}$ in the overlap or connectedness zone and $u^+ \to \infty$ for $r \ge \Delta_{\alpha\beta}$ outside of it. The length $\Delta_{\alpha\beta}$ is the range beyond which charge transport is negligible and is a for our purposes adjustable

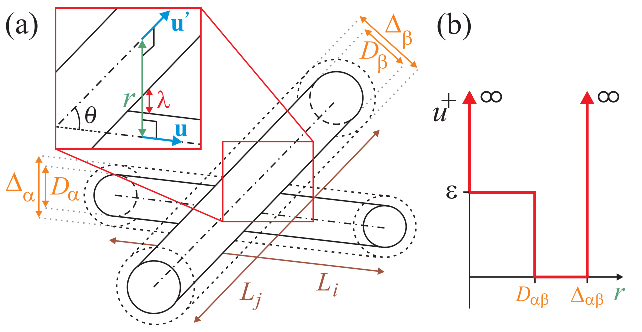

FIG. 1 (color online). (a) Two nanotubes with orientations $\mathbf{u}$ and $\mathbf{u}'$, lengths L_i and L_j, and diameters D_α and D_β separated by a distance r between their center lines and skewed at an angle θ. Charge transport between the rods requires r to be smaller than $D + \lambda = \Delta$: the dashed cylinders of diameter Δ enclosing the rods must overlap. (b) The connectedness potential u^+ between two particles in the same cluster versus their distance r for ideal ($\varepsilon = 0$) and hard particles ($\varepsilon \to \infty$).

parameter [10]. In practice, the nanotubes in conducting networks do not actually touch each other, confirming the connectedness criterion to be a valid concept [6]; our model extends the so-called "cherry-pit" model from spherical to rodlike particles [11]. To compute $\hat{f}^+$, it is convenient to make use of Straley's oblique coordinate system [12] and tentatively presume additivity of charge-carrier hopping distances, so $\Delta_{\alpha\beta} = (\Delta_\alpha + \Delta_\beta)/2$. (We explicitly study nonadditivity effects below.) This gives to leading order for slender rods [13]

$$\hat{f}^{\,+}_{ij\alpha\beta}(0, \mathbf{u}, \mathbf{u}') = 2L_iL_j(\Delta_{\alpha\beta} - D^{\rm eff}_{\alpha\beta})|\sin\theta|, \qquad (4)$$

with $\theta(\mathbf{u}, \mathbf{u}')$ the angle between two rods with orientations $\mathbf{u}$ and $\mathbf{u}'$ and with $D^{\rm eff}_{\alpha\beta} \equiv D_{\alpha\beta}[1 - \exp(-\beta\varepsilon)]$ an effective diameter, so that $D^{\rm eff}_{\alpha\beta} = D_{\alpha\beta}$ for hard and $D^{\rm eff}_{\alpha\beta} = 0$ for ideal rods (see also Fig. 1).

Returning to Eq. (3) for the cluster size S, we insert Eq. (4) for $\hat{C}^+$, average over $\mathbf{u}$, and use that $\langle|\sin\theta|\rangle_{\mathbf{u}} = \pi/4$ for an isotropic distribution of the orientations [13]. Averaging the resulting integral equation over the variables k and γ produces an expression for S and two of its higher moments. To solve for S, we take the average also after multiplying the integral equation with L_k and $(\Delta_\gamma - D^{\rm eff}_\gamma)L_k$, respectively. The solution of the set of equations gives an expression for S that diverges at the PT if the rod volume fraction $\phi_p = \frac{\pi}{4}\rho\langle L_kD^2_\gamma\rangle_{k\gamma}$ obeys

$$\phi_p = \frac{\langle L_kD^2_\gamma\rangle_{k\gamma}}{\langle L^2_k\lambda^{\rm eff}_\gamma\rangle_{k\gamma} + \sqrt{\langle L^2_k\rangle_k\langle L^2_k(\lambda^{\rm eff}_\gamma)^2\rangle_{k\gamma}}}, \qquad (5)$$

with $\lambda^{\rm eff}_\gamma \equiv \Delta_\gamma - D^{\rm eff}_\gamma$. This is our central result for rod dispersions. It can be rationalized, in part, by presuming that percolation takes place if there is about one rod per average contact volume [14], here equal to $\langle L^2_k\lambda^{\rm eff}_\gamma\rangle_{k\gamma}\pi/2$. This reproduces Eq. (5) apart from the second term in the denominator which, according to our simple argument, becomes $\langle L^2_k\lambda^{\rm eff}_\gamma\rangle_{k\gamma}$ due to the neglect of translation-rotation coupling between the rods.

Equation (5) holds for arbitrary length and diameter distributions that may or may not factorize. If we presume the distributions to be independent for lack of experimental evidence otherwise, then ϕ_p is inversely proportional to $\langle L^2_k\rangle_k/\langle L_k\rangle_k = \langle L\rangle_w$, i.e., the *weight* average of the distribution of rod lengths. This implies that increasing the length polydispersity lowers the PT for a fixed average length, because longer rods contribute more to the expanding network than shorter ones do and more strongly for a larger length difference. This is a very considerable effect as is illustrated in Fig. 2. A reciprocal weight-average length dependence of the PT was also found for systems of interpenetrable sticks [14]. For hard rods with $D^{\rm eff}_\gamma = D_\gamma$, we obtain for the case of monodisperse rod widths, i.e., $D_\gamma = D$ and $\Delta_\gamma = \Delta$, $\phi_p = D^2/2\langle L\rangle_w(\Delta - D)$, in agreement with earlier work based on a formal mapping of the cluster size to the osmotic compressibility of the rod fluid [10]. For ideal particles with $D^{\rm eff}_\gamma = 0$, the PT in the monodisperse limit reduces to $\phi_p = D^2/2\Delta L = D/2L$, where by convention we put $\Delta = D$ [10]. This is also consistent with earlier findings based on geometric arguments [4,15] and with computer simulations [16].

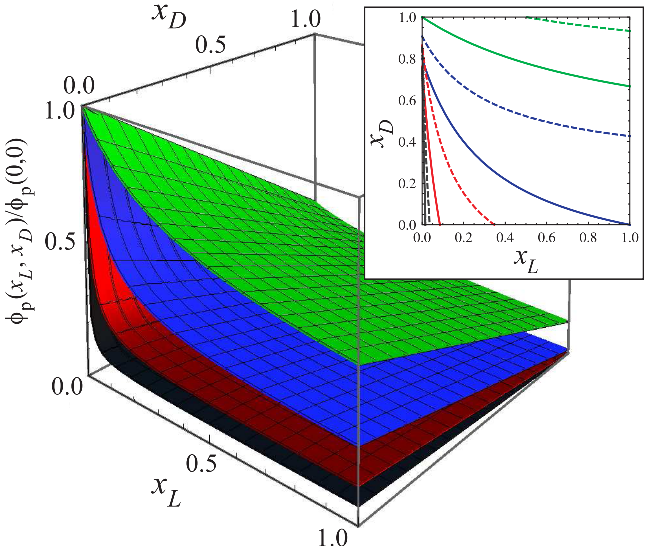

FIG. 2 (color online). The percolation threshold ϕ_p as a function of the number fractions x_L of long rods and x_D of thin rods in a tetradisperse mixture of long, short ($L_{\rm long}$ and $L_{\rm short}$), thick, and thin rods ($D_{\rm thick}$ and $D_{\rm thin}$) for various values of $n \equiv L_{\rm long}/L_{\rm short}$, which we take equal to $D_{\rm thick}/D_{\rm thin}$. A constant tunneling length λ is assumed. Top to bottom: $n = 2$, 4, 8, and 16. Inset: cross section for constant $\phi_p(x_L, x_D)/\phi_p(0, 0) = 0.25$ (0.15) for the solid (dashed) lines showing the nonlinear behavior of ϕ_p. Pairs of lines from top right to bottom left: $n = 2$, 4, 8, and 16.

Before discussing the impact of a distribution of widths, we note that the ansatz $\beta u^+ = (r - D)/\lambda$ for distances $r > D$ more accurately mimics an electron-tunneling probability that decays exponentially with a decay length λ. However, this leaves $\hat{f}^+$ invariant, implying that our model takes this effect into account with $\lambda = \Delta_\gamma - D_\gamma$ acting as the characteristic tunneling distance. It seems reasonable to presume that λ depends only weakly on the dimensions of the CNTs. If true, we deduce from Eq. (5) that $\phi_p \approx \langle D^2_\gamma\rangle_\gamma/2\lambda\langle L\rangle_w$: the presence of wider rods raises the PT (see also Fig. 2). A similar conclusion can be drawn from the monodisperse result $\phi_p = D^2/2L\lambda$ if we would set $D = \langle D_\gamma\rangle_\gamma$ [14], except that the effect is stronger because $\phi_p \propto \langle D^2_\gamma\rangle_\gamma = \langle D_\gamma\rangle^2_\gamma + {\rm Var}(D_\gamma)$. This makes the PT proportional to an additional term $1 + {\rm Var}(D_\gamma)/\langle D_\gamma\rangle^2_\gamma$ that in practice remains close to unity, however; for both SWNTs and MWNTs, we estimate it to be in the range from 1.0 to 1.2 [17]. As shown in Fig. 2, the combined effect of length and width polydispersity gives rise to a highly nontrivial dependence of the PT on the prevalence of the various species.

In Eq. (5), we presume that all CNTs are conductive, i.e., can contribute to the percolating network and that connectivity is an additive property, implying $\Delta_{\alpha\beta} = (\Delta_\alpha + \Delta_\beta)/2$. If the nanocomposite also contains nonconductive particles, then the additivity assumption breaks down because charge carriers only move between pairs of conductive particles and transport is blocked if one or both are nonconductive. It turns out that we can quite easily amend Eq. (5) to model the idealized case of a mixture of conductive and nonconductive rods of equal breadth by insisting that $\Delta_{\alpha\beta} = D + \lambda$ for a pair of conductive rods and $\Delta_{\alpha\beta} = D$ for any other pair. If $\Delta_{\alpha\beta} = D$, the rods need to touch for charge transport to take place, which statistically happens with zero probability. Of course, CNTs are not perfect insulators and in fact exhibit semiconducting behavior [1], but for our purposes this idealized model will do.

For a binary mixture of conductive and nonconductive rods of respective number fractions x and $1 - x$, we find that the size of a cluster of conductive particles diverges at a packing fraction $\phi_p \approx D^2/2x\lambda\langle L\rangle_w \sim 1/x$. Hence, if, say, one third of the CNTs is conductive, then the PT is 3 times higher than would have been if all of them had been conductive. It does indeed seem sensible, then, to select for high fractions of conductive CNTs if as low as possible a PT is required for the envisaged nanocomposite application [6]. Our prediction that the percolation threshold is governed solely by the concentration of conductive nanotubes, i.e., $x\phi$, might appear counterintuitive because one would expect that if only contacts between conductive rods contribute to the network, the presence of small numbers of insulating ones should raise the PT disproportionately. The reasoning is that the presence of a single insulating nanotube in it potentially takes out at least one complete conductive path in a system-spanning network. On the other hand, if this nanotube sits in a dead branch its impact is zero, and it is likely this effect that provides the compensation.

In fact, our prediction can be understood at a more quantitative level by considering the simplified case of percolation on a Bethe lattice. This connected cycle-free tree, sprouting z branches per lattice site, can straightforwardly be shown to have a conductivity threshold, defined here in terms of the fraction of sites occupied, of $\phi_p^c = 1/x(z - 1)$, if a fraction x of these particles contributes to the charge transport [3]. We conclude that the absence of loop correlations between particles on a Bethe lattice and ones in free space within the second-virial approximation causes the PT to scale as $1/x$.

We now turn to the important issue of the validity of this second-virial approximation. For hard monodisperse rods with connectedness range λ, three-body cluster integrals [4] can only raise the PT by a relative amount of the order of the ratio of the third and the square of the second connectedness coefficients. This ratio is proportional to λ/L, so, as long as the rod length L is large on the scale of the hopping distance λ, we can ignore three-body corrections. In fact, all higher nth order terms drop out, too, because their contribution scales as $(\lambda/L)^{n-2}$. In practice, $L/\lambda \gg 1$ is true for almost all rods in the distribution, where we note that the PT is anyway dominated by the longest ones in the distribution. Similar arguments should also hold for spherical and platelike particles, such as graphene, where L now denotes the largest linear dimension.

In summary, we reduced an unwieldy multicomponent continuum percolation theory to a compact, tractable form for a large class of particles with variable dimensions and degrees of connectivity. The analytical expression that we derive for the percolation threshold of rodlike particles is a nontrivial function of the composition of lengths, widths, and connectivities, yet it depends only on a few higher moments of the full distribution. This generalizes earlier findings for the geometrically much simpler spherical particles [18] and explains the large variations observed in the PT of carbon nanotubes. Finally, our calculations confirm that enriching the fraction of conductive single-walled carbon nanotubes in the nanocomposite is sensible because the PT depends quite sensitively on that fraction.

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