Connectedness Percolation of Elongated Hard Particles in an External Field

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A theory is presented of how orienting fields and steric interactions conspire against the formation of a percolating network of, in some sense, connected elongated colloidal particles in fluid dispersions. We find that the network that forms above a critical loading breaks up again at higher loadings due to interaction-induced enhancement of the particle alignment. Upon approach of the percolation threshold, the cluster dimensions diverge with the same critical exponent parallel and perpendicular to the field direction, implying that connectedness percolation is not in the universality class of directed percolation.

High-aspect-ratio nanofillers potentially enhance the physical properties of the material they are dispersed in. For instance, polymeric composites containing carbon nanotubes or graphene sheets acquire (some of) the remarkable thermal, mechanical, and electrical properties of these carbon allotropes even at loadings below one volume percent [1]. The minimum concentration required to observe significant changes in the material properties of the composite is dictated by the necessity for them to form a system-spanning network in it. For the composite to become, e.g., electrically conducting, the filler particles need not (and actually do not) make direct physical contact to be part of the conducting network [2]. The reason is that charge carriers are able to jump from one filler particle to the other over some distance.

The critical value beyond which clusters of, in some sense, connected particles are formed, linking regions of the material on macroscopic scales and beyond which the quantity of interest, e.g., the conductivity of the composite, exhibits a massive increase [1], is known as the (electrical) percolation threshold. A vast body of literature is devoted to the problem of percolation, both on a lattice and in continuous space [3]. Practically, the most fundamental insight for randomly dispersed, mutually penetrable particles is that the percolation threshold must scale inversely with the aspect ratio of the fillers [4]. For long enough carbon nanotubes, this scaling is confirmed experimentally, albeit that the scatter in the data is very large indeed, which may be due to the influence of polydispersity [5].

A source of variability in observed percolation thresholds that is often ignored is the processing that takes place in the fluid stages of the nanocomposite fabrication, e.g., compression molding, compounding, and extrusion [2,6]. If the fluid is not allowed to relax post processing, this may affect the network structure in the final solid product through alignment of filler particles. In fact, particle alignment has been induced deliberately by electric and magnetic fields to enhance and/or induce anisotropy in the conductivity of the material [4,7–10]. Naively, one expects the percolation threshold to go up if the particles become mutually aligned, as this increases the shortest distance separating them. This is confirmed by computer simulations for penetrable sticks in two [7] and three dimensions [11] and for impenetrable ones in three [9]. Contact-volume theories confirm this also: the mean volume swept out by the particles decreases with increasing alignment [4,7,12,13]. Unclarified, however, is how this competes with the transition to the nematic liquid-crystalline phase, which takes place in the absence and presence of orienting fields [14].

In order to shed light on this, we present an analytical theory showing how an externally applied alignment field and excluded-volume interactions conspire against the formation of a percolating network in fluid dispersions of elongated particles, although the formalism extends to other shapes, as well [5]. Our *anisotropic* continuum percolation theory self-consistently links (i) connectedness percolation theory for the cluster size and (ii) Onsager theory for the interplay between interactions and the field-induced particle alignment. Angular correlations between the particles, ignored in contact-volume theories, are explicitly taken into account [4,7,12,13].

We find that the system-spanning, self-assembled network that forms above some critical loading (that depends on the strength of the external quadrupole field) breaks up again at higher loadings; see Fig. 1. This kind of reentrance behavior is caused by the interaction-induced enhancement of the alignment of the particles and is not unlike the disentanglement of rodlike particles in elongational flow fields [15]. For weak fields, the densities at which this happens are preempted by the transition to the uniaxial nematic phase. For sufficiently strong fields, the low-density percolation threshold is suppressed completely.

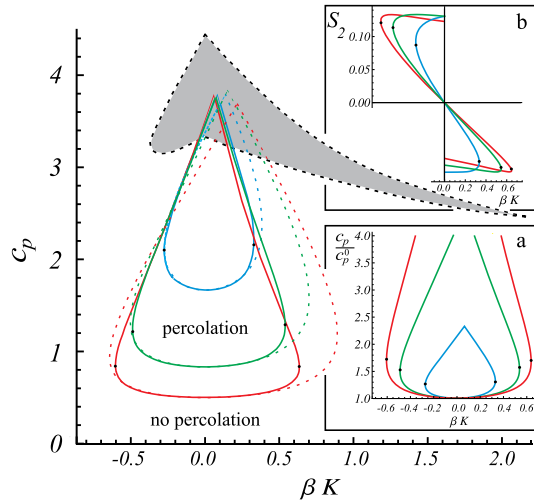According to our calculations, the dimensions of the clusters are different parallel and perpendicular to the field

FIG. 1 (color online). Scaled particle concentration $c_p = \pi D L^2 \rho_p / 4$ at the percolation threshold as a function of the dimensionless field strength βK. Solid lines: connectivity percolation; dashed curves: contact-volume approach for $\lambda/D = 0.3$ (top), 0.6 (middle), and 1 (bottom). Only in the enclosed areas does a percolating network exist. The shaded area is the region of coexisting isotropic (paranematic) and nematic phases [18]. Inset (a): calculated percolation thresholds scaled to the zero-field value c_p^0. Inset (b): order parameter S_2 with, from steepest to flattest, $\lambda/D = 0.3$, 0.6, and 1. The dots indicate the largest value of $|\beta K|$ that allows for a percolation threshold.

direction, albeit that both diverge with the same critical exponent. This field-induced cluster anisotropy might, in thin-film setups, be utilized to fabricate nanocomposites with strongly anisotropic electrical conductivities and very low particle loading [8,10].

In our model, we presume the network to be formed in the fluid stages of the composite processing and subsequently to be frozen in upon solidification. This allows us to invoke the connectedness analog of the Ornstein-Zernike equation of liquid-state theory and calculate the (weight) average cluster size of connected particles, N. Within connectedness percolation theory, we have [16]

$$N = 1 + \lim_{\mathbf{q} \to 0} \rho \langle \langle \hat{P}_\mathbf{q}(\mathbf{u}, \mathbf{u}') \rangle_\mathbf{u} \rangle_{\mathbf{u}'}, \quad (1)$$

in terms of the Fourier transform $\hat{P}_\mathbf{q}(\mathbf{u}, \mathbf{u}')$ of the pair connectedness function $P_{\mathbf{r}, \mathbf{r}'}(\mathbf{u}, \mathbf{u}')$ that describes the probability that two particles at positions $\mathbf{r}$ and $\mathbf{r}'$, and with orientations $\mathbf{u}$ and $\mathbf{u}'$, are in the same cluster. In Eq. (1), ρ is the overall number density of particles, presumed cylindrical with a main body-axis vector $\mathbf{u}$ that obeys an as yet unknown orientational probability distribution function $\psi(\mathbf{u})$. Here, $\langle ... \rangle_\mathbf{u} \equiv \int d\mathbf{u}(...) \psi(\mathbf{u})$ denotes an orientational average, and $(\hat{.})_\mathbf{q} = \int d\mathbf{r}(...) \exp(i\mathbf{q} \cdot \mathbf{r})$ a Fourier transform with $\mathbf{q}$ the wave vector [5,16].

This connectedness function can be calculated from the connectedness Ornstein-Zernike (OZ) equation [16], which in Fourier space reads

$$\hat{P}_\mathbf{q}(\mathbf{u}, \mathbf{u}') = \hat{f}_\mathbf{q}^+(\mathbf{u}, \mathbf{u}') + \rho \langle \hat{f}_\mathbf{q}^+(\mathbf{u}, \mathbf{u}'') \hat{P}_\mathbf{q}(\mathbf{u}'', \mathbf{u}') \rangle_{\mathbf{u}''}, \quad (2)$$

if we invoke the second-virial approximation. This is accurate, provided the rod length is much larger than its width, which we presume to be of the order of the typical distance over which charge transport can take place [5]. Charge transport enters effectively in Eq. (2) via the connectedness Mayer function $f_{\mathbf{r}, \mathbf{r}'}^+ = \exp(-\beta u^+)$, with $\beta = 1/k_B T$, where k_B is Boltzmann's constant and T the absolute temperature. u^+ is the connectedness potential that we choose such as to mimic an exponentially decaying conductivity between two rods, presumed impenetrable. This we do below.

Solving Eq. (2) for $\hat{P}$, averaging this function over the orientation distribution $\psi(\mathbf{u})$, and inserting this into Eq. (1) gives the cluster size N. The critical density ρ_p for which this quantity diverges we identify as the percolation threshold. The distribution of the particles in the absence of an external field is isotropic, $\psi = 1/4\pi$, at least for densities below which the fluid undergoes a spontaneous transition to the uniaxial nematic liquid-crystalline state. In the presence of an orienting field, the distribution function becomes a function of the strength of this field and the density of the particles.

The orientation distribution function we calculate from Onsager's density functional theory for impenetrable rods in an alignment field [17]. The degree of alignment of the rods depends self-consistently on the sum of the external and molecular field strengths, because the latter is a function of excluded-volume interactions that themselves are a function of the degree of alignment. This makes $\psi(\mathbf{u})$ depend on both the field strength and the density. According to Onsager's second-virial theory [17], it obeys the nonlinear self-consistent field equation [18,19]

$$\log \psi(\mathbf{u}) = \mu + \rho \langle \hat{f}_0(\mathbf{u}, \mathbf{u}') \rangle_{\mathbf{u}'} - U(\mathbf{u}), \quad (3)$$

where $\hat{f}_0$ is the zero-wave-vector Fourier transform of the Mayer function $f_{\mathbf{r}, \mathbf{r}'} = \exp(-\beta u) - 1$ for the interparticle interaction potential u, μ serves as a Lagrange multiplier, and U is the dimensionless external potential.

We presume U to be of the quadrupole type, so $U = \beta K \cos^2 \vartheta$, where K is the field strength and ϑ the polar angle between the field direction and the main body-axis vector. For negative values of K, the rods align along the field direction (orienting field), while, for positive ones, they align perpendicular to it (disorienting). The field in our model is generic, and its strength depends on the type of field. If we align the particles in an electric field of strength E and they do not have a permanent dipole moment, we have $K = -\Delta \alpha E^2 / 2$, with $\Delta \alpha$ their electric polarizability anisotropy. For a magnetic field, $K = -\Delta \chi H^2 / 2$, with H the magnetic field strength and $\Delta \chi$ the susceptibility anisotropy of the rods. If they are coupled to an extensional flow field, $K = -3\dot{\epsilon}/4D_r$, with $\dot{\epsilon}$ the strain rate and D_r the rotational diffusivity [19].

Equations (1)–(3) form the basis of our model and connect the cluster size N, the external field strength K, the orientation distribution function ψ, and the particle density ρ. Evidently, the calculation of the particle density at which the mean cluster size diverges (the percolation threshold) requires a self-consistent treatment of this set of three equations. The complicating term here is the interaction term in Eq. (3) that makes solving them a nontrivial exercise. To actually perform the calculation, we need to specify the connectedness potential u^+ and the interaction potential u. Again, we presume the rods to behave as mutually impenetrable, rigid cylinders of length L and diameter D. This implies that $u \to \infty$ and $u^+ \to \infty$ for all centerline-to-centerline distances $r < D$ between two rods. Furthermore, $u = 0$ for $r > D$.

We effectively incorporate an exponentially decaying probability of charge transport between two rods for distances $r > D$ in our description by taking $\beta u^+ = (r - D)/\lambda$, with λ the typical hopping distance. This produces an exponentially decaying connectedness Mayer function that in our model describes short-range correlations between connected particles. With these ingredients and using Straley's oblique coordinate system, we find $\hat{f}_{\mathbf{q}}^+ = 2L^2 \lambda j_0(\mathbf{q} \cdot \mathbf{u}L/2) j_0(\mathbf{q} \cdot \mathbf{u}'L/2)|\sin\gamma|$ and $\hat{f}_{\mathbf{q}} = -\hat{f}_{\mathbf{q}}^+ D/\lambda$, at least in the slender-rod limit $L \gg \lambda, D$ and $|\mathbf{q}|D \ll 1$ [5]. Here, $\gamma = \gamma(\mathbf{u}, \mathbf{u}')$ is the angle between two rods $\mathbf{u}$ and $\mathbf{u}'$, and $j_0(x) \equiv \sin x/x$.

It turns out not to be necessary to know the full angular and wave-vector dependence of the pair connectedness function $\hat{P}_{\mathbf{q}}(\mathbf{u}, \mathbf{u}')$ to calculate the percolation threshold. The reason is that the cluster size can be written as $N = 1 + \rho\langle g(\mathbf{u})\rangle_{\mathbf{u}}$, with $g(\mathbf{u}) \equiv \langle\hat{P}_0(\mathbf{u}, \mathbf{u}')\rangle_{\mathbf{u}'}$. The latter function we obtain from Eq. (2), which, for $\mathbf{q} \to 0$, reduces to $g(\mathbf{u}) = \langle\hat{f}_0^+(\mathbf{u}, \mathbf{u}')\rangle_{\mathbf{u}'} + \rho\langle\hat{f}_0^+(\mathbf{u}, \mathbf{u}')g(\mathbf{u}')\rangle_{\mathbf{u}'}$, which can be viewed as a "reduced" OZ equation. Because of cylindrical symmetry, the angular distribution function $\psi(\mathbf{u}) = \psi(\vartheta)$ depends only on the polar angle ϑ, implying that the integration over the azimuthal angle φ involves only the $|\sin\gamma|$ in the connectedness Mayer function that enters the reduced OZ equation.

Another simplification follows from expressing this integral in terms of a sum of the Legendre polynomials $P_{2n}(\cos\vartheta)$ by invoking the addition theorem [15]. Because of cylindrical symmetry, we write $\psi(\vartheta) = (2\pi)^{-1}[a_0 + a_2 P_2(\cos\vartheta) + a_4 P_4(\cos\vartheta)]$ [20], where $a_0 = 1/2$ because ψ is normalized. For this expansion to be meaningful, we insist that $|a_4| \ll |a_2|$. Because (i) we are only interested in an orientational average of $g(\vartheta)$ and (ii) we truncate the expansion of the distribution function ψ after the third term [21], we find that we only need to account for three "moments" of the type $\int_0^\pi d\vartheta \sin\vartheta P_{2n}(\cos\vartheta)g(\vartheta)$, i.e., those for $n = 0, 1, 2$. Solving $N^{-1} = 0$ for the density ρ now gives a third-order polynomial in ρ in terms of the coefficients a_2 and a_4, the root of which is the percolation threshold, ρ_p. It is important to note that the coefficients themselves also

depend on the density ρ, as well as on the field strength K, because they obey Onsager's equation (3). To determine their functional dependence on ρ and K, we again apply the addition theorem in Eq. (3) and expand the logarithm for small values of a_2/a_0 and a_4/a_0. This gives two equations for a_2 and a_4 as a function of ρ and K.

The polynomial equation for the percolation threshold ρ_p that we obtain needs to be combined with the set of equations for a_2 and a_4 derived above. This gives three equations for the three unknowns a_2, a_4, and ρ_p in terms of the field strength K and the ratio λ/D describing how easily charge transport between two rods takes place. The percolation threshold we calculate is plotted in Fig. 1 for sensible values of λ/D for single- and multi-walled carbon nanotubes [5]. We see that the percolation threshold strongly increases with increasing field strength, irrespective of whether the field is orienting or disorienting. For strong enough fields, $|\beta K| \gtrsim 0.5$, which depends on the precise value of λ/D, a percolating network does not form in the regime where c_p is of the order unity and the volume fraction of the order $\phi_p = \mathcal{O}(D/L) \ll 1$.

Another remarkable finding that we read off from Fig. 1 is that, for values of βK where a percolating network does form at some low particle concentration, the network dissolves again at higher particle loadings, i.e., exhibits reentrance behavior. Interestingly, a similar kind of reentrance with increasing imposed alignment was observed in computer simulations of the electrical conductivity of systems of penetrable rodlike particles [11]. According to our calculations, this is caused by the enhancement of the field-induced alignment due to the anisotropic excluded-volume interactions.

For weak fields, the reentrant transition penetrates the region where the transition to a nematic phase occurs [22]. The shape and size of the percolating domain depend sensitively on the ratio λ/D. Figure 1 shows that the lower percolation threshold decreases with increasing λ/D, whereas the reentrance threshold depends weakly on λ/D. If we amend the contact-volume approach that predicts $\rho_p = \langle\langle\hat{f}_0^+\rangle_{\mathbf{u}}\rangle_{\mathbf{u}'}^{-1}$ [4,7,12,13] with the Onsager theory for the alignment of hard rods and compare it to our theory, we conclude that it significantly underestimates the impact of the external field on the percolation threshold. At reentrance for high loadings, the error can be up to a few hundred %. It appears that ignoring couplings between angular correlations of particles is at the root of this discrepancy [5].

It is instructive to evaluate the relevant order parameters along the stability boundary of our model of electrical percolation in rod dispersions. These are the familiar nematic order parameters $S_2 \equiv \langle P_2(\cos\vartheta)\rangle_{\mathbf{u}} = 2a_2/5$ (shown in Fig. 1) and $S_4 \equiv \langle P_4(\cos\vartheta)\rangle_{\mathbf{u}} = 2a_4/9$ (not shown). First, we find S_4 to be always positive and much smaller than the corresponding value of S_2, justifying our earlier assumption. Second, S_2 increases along the curves where the percolation threshold increases, even beyond the
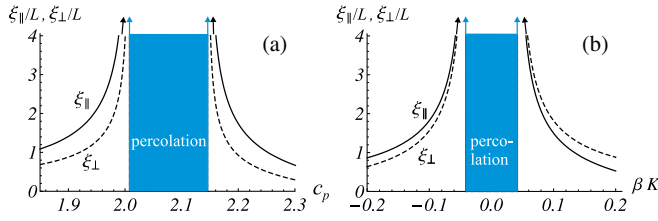
FIG. 2 (color online). The parallel (solid) and perpendicular (dashed) correlation lengths $\xi_\parallel$ and $\xi_\perp$ near the percolation threshold for $\lambda/D = 0.3$. (a) $\beta K = -0.27$ and (b) $c_p = 1.67$. Away from the percolation threshold, the correlation lengths decay to the radius of gyration $L/\sqrt{12}$ of a rod.

inflection point where $|S_2| \approx 0.1$. This confirms that, for a given field strength, the degree of order increases with increasing density. The largest value of S_2 for which percolation occurs is below that of the nematic phase [18], so there percolation is lost completely.

In order to investigate the structure of our clusters upon approach of the percolation threshold, we probe the wavevector dependence of the connectedness function $\langle\langle \hat{P}_\mathbf{q}\rangle_\mathbf{u}\rangle_{\mathbf{u}'} = \langle\langle \hat{P}_0\rangle_\mathbf{u}\rangle_{\mathbf{u}'} + \langle\langle \mathbf{M}(\mathbf{u},\mathbf{u}')\rangle_\mathbf{u}\rangle_{\mathbf{u}'}{:}\mathbf{q}\mathbf{q}/2 + \dots$, with $\mathbf{M}(\mathbf{u},\mathbf{u}') \equiv \partial^2 \hat{P}_\mathbf{q}/\partial \mathbf{q}^2|_{\mathbf{q}=0}$ [16]. The linear term in $\mathbf{q}$ drops out for symmetry reasons. From Eq. (2), we obtain a self-consistent equation for $\langle \mathbf{M}(\mathbf{u},\mathbf{u}')\rangle_{\mathbf{u}'} = 2\lambda L^2\rho\langle|\sin\gamma(\mathbf{u},\mathbf{u}')|\langle\mathbf{M}(\mathbf{u}',\mathbf{u}'')\rangle_{\mathbf{u}''}\rangle_{\mathbf{u}'} - \lambda L^4\langle|\sin\gamma(\mathbf{u},\mathbf{u}')|$ $(\mathbf{u}\mathbf{u} + \mathbf{u}'\mathbf{u}')[1 + \rho g(\mathbf{u}')]\rangle_{\mathbf{u}'}/6$. Because of azimuthal symmetry, the matrix $\langle\langle \mathbf{M}(\mathbf{u},\mathbf{u}')\rangle_\mathbf{u}\rangle_{\mathbf{u}'}$ has nonzero elements on its diagonal only, one associated with cluster growth parallel to the field direction and the others with that perpendicular to it. The wave vector $\mathbf{q}$ separates into components $q_\parallel$ parallel and $q_\perp$ perpendicular to the field. We compute $\langle\langle \mathbf{M}(\mathbf{u})\rangle_\mathbf{u}\rangle_{\mathbf{u}'}$ in a manner similar to that of the cluster size N. Our final result can be expressed as $\langle\langle \hat{P}_\mathbf{q}\rangle_\mathbf{u}\rangle_{\mathbf{u}'}/\langle\langle \hat{P}_0\rangle_\mathbf{u}\rangle_{\mathbf{u}'} = 1 - \xi_\parallel^2 q_\parallel^2 - \xi_\perp^2 q_\perp^2$, with correlation lengths $\xi_\parallel$ and $\xi_\perp$. Values of $\xi_\parallel$ and $\xi_\perp$ for vertical and horizontal cuts through the phase diagram of Fig. 1 are shown in Fig. 2.

Both correlation lengths $\xi_\parallel$ and $\xi_\perp$ diverge as $1/|\rho_p - \rho|^{1/2}$ for constant K and as $1/|\beta K_p - \beta K|^{1/2}$ for constant ρ, with K_p the critical field strength for a given density. The mean-field exponents $\nu_\parallel = \nu_\perp = 1/2$ that we find are exact for hard rods in the limit of the infinite aspect ratio [5]. However, the prefactors are not equal and depend on the density, the sign, and the strength of the external field. For a disorienting field, $\beta K > 0$, the clusters are flat because $\xi_\perp > \xi_\parallel$, while, for an orienting field, $\beta K < 0$, they are elongated: $\xi_\perp < \xi_\parallel$. Although percolation in systems of aligned rods seems superficially related to that of directed percolation, the critical exponents for the latter have been found to be $\nu_\parallel = 1$ and $\nu_\perp = 1/2$ in three dimensions in mean-field theory [23]. Hence, anisotropic continuum connectedness percolation of elongated particles is not in the universality class of directed percolation.

In conclusion, an externally applied field enhanced by excluded-volume interactions significantly destabilizes percolating clusters of hard, rodlike particles, limiting them to an island of stability in the phase diagram, bounded from above by the isotropic-nematic phase transition. Upon approach of the percolation threshold, the size of clusters of connected particles diverges with the same scaling exponent parallel and perpendicular to the field direction. Hence, directed percolation and anisotropic continuum percolation of elongated particles do not belong to the same universality class. Still, due to nonuniversal prefactors, the clusters are anisotropic, elongated for orienting and flat for disorienting fields.

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