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Dispersions of multi-walled carbon nanotubes in liquid crystals: A physical picture of aggregation

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ABSTRACT

Aggregation of carbon nanotubes dispersed in nematic liquid crystalline medium is discussed. A model assuming that the aggregates consist of a “skeleton” formed by stochastically arranged nanotubes and a “shell” (“coat”) of incorporated and adjacent nematic molecules is proposed. The aggregates of this type can be considered as large quasi-macroscopic particles in the nematic matrix. The resulting composite system is a representative of a new type of complex molecular liquids with self-organization of particles in anisotropic medium. Many essential features and implications of the theoretical model (e.g., effect of concentration, aspect ratio and orientational order parameter of the nanotubes on the size and fractal dimensionality of the aggregates formed, as well as on the rate of aggregation) are in good agreement with experimental data obtained by various physical methods.

1. Introduction

Recently, great attention has been attracted by the anisotropic soft matter systems including systems of particles with different size, shape and aspect ratio. Among the most interesting are multi-walled carbon nanotubes (NT) dispersed in a liquid crystalline (LC) medium [1–3]. These composites display many interesting and unexpected features and are very interesting in both practical point of view and challenges to molecular theories of anisotropic liquids.

For theoretical purposes, two different types of LC + NT dispersions can be discerned. At low NT concentrations, each NT aligns several molecular layers of nematic molecules on a short-range scale [4,5]. On a long-range scale, nematic orients the NTs that can be formally considered as non-mesogenic dopants of anisotropic fluid [6–8]. At higher NT concentrations (above the certain “percolation threshold” [9]), NTs show a strong tendency to aggregation in a LC medium with formation of a random network of contacting aggregates. In most cases, LC + NT dispersions, obtained by conventional ultrasonication procedures, contain a number of NT “bundles”, i.e., more or less large agglomerations of nanotubes that are strongly anchored to each other in the lateral direction. These bundles are often clearly visible in an optical microscope, and in principle they can be mechanically removed from dispersion, which makes it more homogeneous. Such “quasi-homogeneous” dispersions with minimized quantity and size of bundles can also be obtained by careful sonication under certain optimized conditions. However, spontaneous processes of NT aggregation begin immediately after such sonication. The spanning networks of nanotubes arise and grow with time due to incorporation of individual NTs from the quasi-homogeneous dispersion. Such process of aggregation manifests itself in changes of the certain macroscopic properties of LC + NT dispersions (e.g., optical transmission, electrical conductivity, singular and polarization structure of transmitted laser beam, etc.), which can be measured on the time scale of several hours [9]. An important point is that such “secondary” aggregates formed in LC + NT dispersions are substantially different from the initial NT bundles occurring in imperfectly sonicated samples. These aggregates are rather “loose” and are obviously of fractal nature. The preliminary study of such aggregates was reported in our recent paper [10]. It was shown that the ramified aggregates of nanotubes capture (incorporate) surrounding LC molecules, and their volume becomes 2–2.5 orders greater than the total volume of the NTs involved. Such aggregates can be considered as large quasi-macroscopic particles in the nematic LC matrix. The supramolecular formations of this type were named as “S-aggregates” [10]. It was shown by methods of singular optics that anisotropic micro-sized LC cladding of these ramified aggregates initiates strong speckled scattering with induced optical singularities [11].

The theoretical studies of LC + NT dispersions are scarce [12–14], and are devoted, in fact, only to the “idealized” dispersions, with no account for the aggregation processes. This work considering the above-mentioned LC + NT dispersions with S-aggregates as a new

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type of complex liquids, is aimed at development of a preliminary theoretical approach to description of such anisotropic systems.

2. Theory

2.1. Formation of fractal aggregates in dispersions of carbon nanotubes in a liquid crystalline medium

The starting point of our theoretical consideration is a tentative picture of the fractal clusters of rods formed in colloidal rod suspension as presented by Solomon and Spicer [15] (Fig. 3b of their paper). Fig. 1 presents a simplified picture of such structure adjusted for the specific case of nanotubes forming loose fractal aggregates in the anisotropic liquid crystal medium.

Let us consider the S-aggregate comprising nanotubes (NT) as linear elements forming a compact skeleton that bounds a confined space. The NTs are presented by cylindrical particles with huge aspect ratio $r = l/d (r \gg 1)$, where l and d are the nanotube length and diameter, respectively. We determine the volume encompassed by such skeleton using only one characteristic spatial dimension of NT: its linear length l. It is fully justified if the aspect ratio $r \gg 1$.

Under considerations of geometrical similarity, the volume of a cluster with all its links having the same characteristic linear dimension l can be presented as $V_{cl} = V_{cl}(l) = A_{cl} l^3$, where A_{cl} is a constant depending on the cluster geometry (e.g., $A_{cl} = 1$ for cubic structure, $A_{cl} = \sqrt{2}/12$ for spatial structure formed by tetrahedrons, etc.). Similarly, the total volume of the nanotubes forming the skeleton is $V_{nt}(l) = B_{nt} l g(d)$, where B_{nt} is a new constant. The value of B_{nt} depends upon cluster geometry. Function $g(\ldots)$ determines the volume of a single nanotube in the cluster as function of its characteristic cross-section area. The form of $g(\ldots)$ in the case of a regular skeleton structure depends on geometry of isolated nanotubes, accounting for the bends, fractures, non-cylindrical shape, scatter of lateral dimensions, etc. In the case of fractal geometry of the cluster, $g(\ldots)$ should "feel" how the nanotubes are connected. Then, instead of $g(x) \sim x^2$ one can choose a characteristic self-similar dependence of a typical area of the irregular surface, $g_f(x) \sim x^{d_f}$, where d_f is the fractal dimension of the cluster surface. For regular geometry, $d_f = 2$; for fractal geometry, the value of d_f is fractional.

If skeleton geometry is regular, the total volume of the constituent nanotubes is $V_{nt}(l) = B_{nt} l g(d)$. Taking into account that $g(d) = (\pi/4) d^2$ for cylindrical nanotubes, $V_{nt}(l) = B_{nt}(\pi/4)\ l^3 r^{-2}$. The coefficient B_{nt} depends on the type of the regular skeleton: e.g., $B_{nt} = 3\pi/2$ for tetrahedral skeleton, $B_{nt} = 3\pi$ for cubic cells, etc.

Thus, the volume ratio of the cluster and the regular skeleton (i.e., the ratio of the volume encompassed by the skeleton of nanotubes and the total volume of nanotubes involved) is $W_{aggr} = V_{cl}/V_{nt} = (A_{cl}/B_{nt}) r^2 = Ar^2$. With increase of the aspect ratio (i.e., when we pass from shorter to longer or from thicker to thinner nanotubes), W_{aggr} is growing rapidly, while the volume with nematic molecules "captured" by the skeleton of nanotubes (the volume of the "coat") increases much slower. The coefficient A is determined by the specific geometry of the skeleton, and its values can vary within $10^{-1} > A > 10^{-2}$ ($A = 1/3\pi \sim 0.1$ for cubic cells, $A \sim 0.025$ for tetrahedral cells).

Thus, W_{aggr} is the ratio of the volume of an S-aggregate (i.e., of a loose skeleton formed by nanotubes including "captured" molecules of the dispersion medium (nematic LC) both "inside" the skeleton and in the nearest coordination layers around it) and the total volume of the nanotubes forming the skeleton. If $c = V_{nt}/V$ is the volume fraction of nanotubes that were introduced into the matrix, $C_{aggr} = cW_{aggr}$ can be considered as the effective volume concentration of S-aggregates in the matrix (solvent, dispersion medium) where these aggregates are formed. At small volume fraction, $c \ll 1$, the mass fraction c_m may be estimated as $c_m = (1 + (\rho_c/\rho)(c^{-1} - 1))^{-1} \approx c\rho_c/\rho$, where $\rho_c = 2045\ \text{kg/m}^3$ is the density of the MWCNTs (it was assumed to be the same as the density of pure graphite), and ρ is the density of the matrix ($\rho = 1008\ \text{kg/m}^3$ for 5CB).

In the case of fractal geometry, both the surface of the skeleton formed by the nanotubes and the outer surface of an S-aggregate formed by the aggregated nanotubes and captured molecules of the dispersion phase will be of fractal character. Accounting for the fact that S-aggregates in the orientationally ordered matrix are formed by the orientationally ordered nanotubes, it is reasonable to expect that S-aggregates are essentially oblate (flattened). This leads us to a heuristic formula

$$W_{aggr} = \frac{V_{cl}}{V_{nt}} = Ar^{d_f} \tag{1}$$

Correspondingly, the effective concentration of aggregates in the LC + NT dispersion is

$$C_{aggr} = cW_{aggr} = c\frac{A_{cl}}{B_{nt}} r^{d_f} = cAr^{d_f} \tag{2}$$

Thus, the effective concentration of S-aggregates at a given initial concentration of nanotubes appears to be a universal function of the aspect ratio. The proportionality coefficient A is determined by specific geometries of the nanotubes and the fractal skeleton structure formed by them; it can be considered as constant for a given type of the nanotube dispersions. As noted above, its value can be taken within 0.025–0.1.

This formula accounts at a semi-empirical level for all the main factors affecting aggregation of the nanotubes: the initial concentration of nanotubes c, their aspect ratio r, geometry of cluster formation A and fractal dimensionality of the formed aggregates d_f. This formula can be easily verified experimentally: thus, for two different NT + LC dispersions prepared and studied under the same conditions but

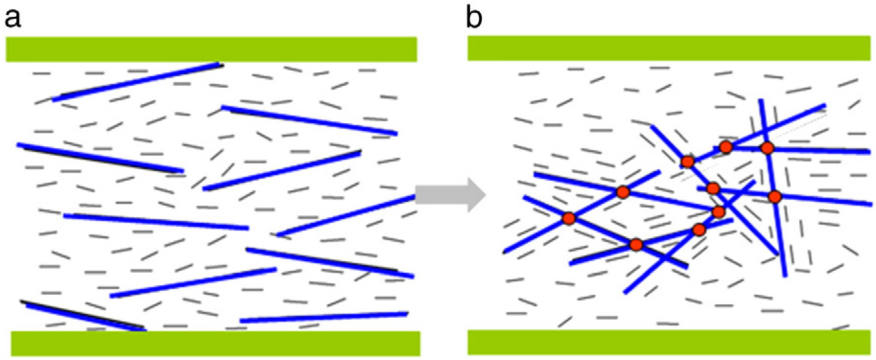

Fig. 1. A simplified scheme of aggregation of the carbon nanotubes dispersed in nematic liquid crystalline medium. The nanotubes are initially dispersed homogeneously by intensive ultrasonication (a); and then, the ramified aggregates of fractal nature with a large number of nematic molecules incorporated into the nanotube "skeleton" appear (b).