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Effect of silica aerosils on the nematic to isotropic transition: A theoretical treatment

A. V. Zakharov* and J. Thoen†

Laboratorium voor Akoestiek en Thermische Fysica, Departement Natuurkunde en Sterrenkunde, Katholieke Universiteit Leuven,
Celestijnenlaan 200D, B-3001 Leuven, Belgium

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The effect of silica aerosils on a first-order nematic-isotropic (NI) transition temperature shift $\Delta T_{NI}(\rho_s)$ and on the enthalpy jump $\Delta H(\rho_s)$ is phenomenologically described in the framework of the Landau–de Gennes theory. It is shown that the aerosil network dispersed in the liquid crystal phase creates an additional curvature perturbation, resulting in linear and nonlinear slopes both in the transition temperature shift $\Delta T_{NI}(\rho_s) = -T_{NI}(0)\alpha\rho_s$ and in the enthalpy jump $\Delta H(\rho_s) = \frac{1}{4}\Delta H(0)(1+\sqrt{1-\kappa\rho_s})^2(1-\alpha\rho_s)$, where ρ_s is the aerosil density, and both α and κ are constants of the theory. In the low $\rho_s(\leqslant 0.2\ \mathrm{g/cm^3})$ regime, both the calculated and the measured values of $\Delta H(\rho_s)$ for polar liquid crystals, such as 4-*n*-octyl-4′-cyanobiphenyl (8CB) and 4-*n*-heptyl-4′-cyanobiphenyl (7CB) show a good agreement between theory and experiment. The comparisons between the calculated and measured values of $\Delta T_{NI}(\rho_s)$, in the low-ρ_s regime, show a better agreement in the 7CB+aerosil than in the 8CB+aerosil systems.

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I. INTRODUCTION

In the past few years a great deal of attention has been focused on the problem of the phase behavior of liquid crystals (LCs) confined in randomly interconnected porous media, such as aerosils [1–7]. This attention resulted in several calorimetric [1–3], photopyroelectric [5], NMR [6], high-resolution *x*-ray diffraction [4], and dielectric spectroscopy [7] investigations of the nematic-isotropic (NI) and smectic *A*-nematic phase transitions in LC+aerosil samples. Aerosil systems are particularly attractive since random disorder is introduced in a controlled fashion. These dispersions consisting in most cases of hydrophilic aerosil particles [small quartz spheres with radius $R_s \sim 3.5$ nm and surface area $\mathcal{S} \sim 300\ \mathrm{m^2/g}$ (type 300 [8])] with hydroxyl groups covering their surfaces are suitable to study quenched disorder effects on LC environment. For instance, these particles can form, due to hydrogen bonding, a network in the host LC phase. The hydroxyl groups on the surface and the polar nature of the LC environment yield a homeotropic LC alignment at the silica surfaces, while the director field $\mathbf{n}(\mathbf{r})$ in the void volume is parallel to the silica strands. In addition to introducing a random distribution of surfaces, the LC-surface interaction results in two primary effects altering the orientational ordering. First, there is surface-induced order that decays with distance far from the surface and yields a local ordering. The magnitude of this disturbing effect is fixed by the intrinsic properties of the surface and LC phase, which induces an additional long-range interaction of dipolar or quadrupolar type, depending on the symmetry of the director configuration $\mathbf{n}(\mathbf{r})$ around a single silica particle [9]. Second, there is elastic strain arising from competing surface interactions, whose magnitude is likely to increase with silica density $\rho_s = m_s/V_{LC} = (m_s/m_{LC})\rho_{LC} = \Phi\rho_{LC}$, where m_s, m_{LC}, and V_{LC} are the mass of aerosils, the mass and the volume of the LC, respectively. On increasing the aerosil particle concentration ρ_s (or Φ), the degree of disordering enforced on a host LC phase can be relatively well controlled, and the organization of aerosil particles undergoes two qualitatively different regimes [2,3,5,7]. Below $\rho_s < 0.05\ \mathrm{g/cm^3}$ a gel-like aerosil structure is formed (labeled as ‘‘soft’’), meaning that the bonds among the hydrophilic aerosil particles can easily break, allowing a rearrangement of the particles to form a network in which the elastic strain imposed by the surround LC phase is minimized. In this regime, a rapid $\Delta T_{NI}(\rho_s) = T_{NI}(\rho_s) - T_{NI}(0)$ shift to lower temperature is observed, both from calorimetric [2,3] and dielectric spectroscopy [7] studies. In the high-ρ_s ($> 0.1\ \mathrm{g/cm^3}$) regime, the gel is ‘‘stiff’’ or rigid, having similarities with the aerogel system [10], which is dominated by quenched elastic-strain smearing effects that destroy long-range order, and the residual order is a quasi-long-range order [11]. In this regime, the decrease of the transition temperature shift $\Delta T_{NI}(\rho_s)$ shows a complicated behavior as a function of ρ_s. So, such dispersions are suitable for testing existing and future theoretical models.

The three related theories to consider at the present moment for dealing with the density dependence of the first-order NI transition enthalpy $\Delta H(\rho_s)$ are a pinned-boundary-layer (PBL) [2], a random-field (RF) [2], and a surface-induced order (SIO) [2,12] model. In the first two models (PBL and RF) one assumes that a fraction of the LC molecules anchored by the silica surface $p(\sim\rho_s)$ is quenched and does not participate in any ordering transition. Moreover, for the PBL model, the orientational anchoring at the silica surface is so strong that only the LC material in the boundary layer is quenched, whereas the remaining LC behaves as pure bulk material. Consequently, the transition enthalpy $\Delta H(\rho_s)$ given by the PBL model is proportional to $\Delta H(0)(1-\rho_s)$, while the transition temperature $T_{NI}(\rho_s)$ remains unaltered. For the RF model, the quenched LC is sim-

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*Corresponding author. Permanent address: St. Petersburg Institute for Machine Sciences, The Russian Academy of Sciences, St. Petersburg 199178, Russia. Electronic address: Alexandre.Zakharov@fys.kuleuven.ac.be

†Electronic address: Jan.Thoen@fys.kuleuven.ac.be

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ply distributed randomly in space leading to an additional reduction of the average order in the remaining material affecting the latent heat of the NI transition. Although the RF model predicts a somewhat weaker decrease in $\Delta H(\rho_s)$ than the PBL model, both models suffer from the same difficulties: the decrease of the $\Delta H(\rho_s)$ follows a behavior which is not observed experimentally [3]. Also, the transition temperature shift is zero for the PBL model, while the RF model predicts a far too rapid NI transition temperature decrease with increasing ρ_s than observed for $\rho_s > 0.1$ g/cm^3 [3]. Thus, neither the PBL nor the RF model provides us a physically reasonable description of aerosil perturbations on the NI phase transition enthalpy. The difficulties of these two models have been particularly avoided in the third SIO model, based on surface-induced order that converts the isotropic phase into a paranematic phase at the aerosil surfaces. This model does not suppose a nonordering, quenched fraction of the LC, but gives an expression for the latent heat decrease, which involves a number of adjustable parameters. So, the problem of predicting the influence of ρ_s on LC phase behavior in the vicinity of the NI phase transition is far from being trivial, and more realistic theoretical treatments which can elucidate the role of the quantitative changes in the aerosil arrangement on the LC environment are needed.

II. THEORETICAL TREATMENT

To understand the effect of the aerosil network on the NI transition temperature shift $\Delta T(\rho_s)$ as well as on the NI latent heat $\Delta H(\rho_s)$ in such system, it is necessary to first consider how the disorder disrupts the orientationally ordered nematic phase. Let us consider the behavior of a system of small spherical particles dispersed in the LC phase undergoing a direct NI transition on cooling. That transition is weakly first order, so the latent heat $\Delta H(\rho_s)$ and the jump of the order parameter $\Delta Q(T(\rho_s))$ are small at the NI transition. The full free energy of the LC+aerosils system close to the NI transition can be written as the sum of the Landau–de Gennes free energy $\mathcal{F}_n$, the Frank curvature elastic energy $\mathcal{F}_{el}$ due to a system of small spherical particles dispersed in the LC phase, and a contribution due to a system of hard spheres $\mathcal{F}_s$. The aerosil network dilutes $(\Phi \ll 1)$ the nematogens and additionally creates a curvature perturbation in the nematic phase. Taking into account that the orientational symmetry is broken in the vicinity of the silica surface, a closed inner silica surface creates a topological mismatch between the director field $\mathbf{n}(\mathbf{r})$ on the particle surface and the uniform director at large distances away from it. This mismatch leads to topological defects, i.e., regions where the LC order and the continuity $\mathbf{n}(\mathbf{r})$ break down [9]. So, a strong director anchoring on the particle surfaces gives an additional curvature elastic energy in the LC microconfined by such interfaces and should have a profound effect on the whole process of phase ordering. The latter effect is the most important and contributes to the total free energy as

$$\mathcal{F}_{el}=\frac{\Phi}{2}\left(K\sum_{ij}\int d^3r\,\partial_i n_j \partial_i n_j - W\int d\mathcal{S}(\mathbf{n}\cdot\mathbf{n}_0)^2\right), \quad (1)$$

where the integrals are over the volume V_{LC} of the nematic LC and the surface $\mathcal{S}$ of silica spherical particle, respectively; $i,j=x,y,z$; n_i is the ith component of the director, $\partial_i = \partial/\partial x_i$, $K=K_1=K_2=K_3$ is the isotropic elastic constant (one-constant approximation), $\mathbf{n}_0$ is the surface director orientation, to be normal to the surface of the spherical particle, and W is the anchoring energy on the aerosil particle surface. According to the experimental data for elastic coefficients K_i $(i=1,2,3)$, determined by the Freedericksz transition method [13], the values of these coefficients are approximately equal in the vicinity of NI phase transition, at least for *cyanobiphenyls*, and that approximation seems quite reasonable. The system of hard spheres has been extensively studied using computer methods, and the numerical results are described quite well, at small concentrations of the volume fraction of particles $\Phi < \Phi^*$ (~ 0.5), by the free energy of the following form [14]:

$$\mathcal{F}_s = k_B T\left(\Phi \ln \Phi + \Phi^2 \frac{4-3\Phi}{(1-\Phi)^2}\right), \quad (2)$$

where k_B is the Boltzmann constant and T is the temperature. The phase transition from the isotropic to the nematic is phenomenologically described in terms of the Landau–de Gennes theory as [15]

$$f_n = \tfrac{1}{2}a_0[T - T_{NI}(0)]Q^2 - \tfrac{1}{3}bQ^3 + \tfrac{1}{4}cQ^4, \quad (3)$$

where $f_n = \mathcal{F}_n / v_s$ is the Landau–de Gennes free energy density per particle volume, Q is the order parameter at $T_{NI}(0)$, and a_0, b, and c are the positive constants.

In order to calculate the deformation energy created by the spherical particles in the host LC phase, one needs the director field $\mathbf{n}(\mathbf{r})$ around these particles. Generally, that problem cannot be resolved analytically, because it is a highly nonlinear problem in a complex geometry. However, in the case of "weak" ($W \leq 10^{-5}$ J/m^2) or "strong" ("rigid") ($W \geq 10^{-4}$ J/m^2) anchoring on the particle surface the problem can be linearized, and an exact analytical solution is possible and the energy of deformation, created by the spherical particles, can be written in the following form [9]:

$$\mathcal{F}_{el} = \alpha_i \Phi Q_{NI}^2(\rho_s), \quad (4)$$

where

$$\alpha_i = \begin{cases} 0.2\ \ (W^2 R_s^3/K), & i=1\ \ \text{(weak anchoring)} \\ 6.7\ \ (K a^6/R_s^5), & i=2\ \ \text{(rigid anchoring)}. \end{cases}$$

Here a is the disclination ring size, which in the case of radial hedgehog (rigid anchoring) attains a value $a \approx 1.25 R_s$ (R_s is the radius of the spherical particle), showing that the hyperbolic hedgehog sits close to the spherical particle.

It should be pointed out that the dimensionless parameter $\lambda = W R_s / K$ which controls the outcome of the nonuniform distortion of $\mathbf{n}(\mathbf{r})$ around a single spherical particle can be large or small, and the exact solution for the angle $\theta(\mathbf{r})$ of the director deviation from the uniform direction $\mathbf{n}_0$ can be obtained in terms of multipole expansion [16] $\theta(r)$

$=(\lambda/4)(R_s/r)^3\sin 2\beta$ ($\lambda \ll 1$ or weak anchoring) or $\theta(r)=\beta-\frac{1}{2}\tan^{-1}[r^3\sin 2\beta/(r^3\cos 2\beta+a^3)t]$ ($\lambda \gg 1$ or strong anchoring), where β and r are the polar angle and position of the spherical coordinate system, respectively. In both situations the far field behavior of the director is identical and described by the cubic power decay of deformations. The convention of weak anchoring usually corresponds to values $W \leqslant 10^{-5}$ J/m^2, whereas the strong anchoring usually corresponds to values $W \geqslant 10^{-4}$ J/m^2.

This makes an addition to the Landau–de Gennes free energy density $\mathcal{F}_n$ describing the nematic transition to be proportional to $\alpha_i \Phi Q_{NI}^2/v_s$, where $v_s=\frac{4}{3}\pi R_s^3$ is the particle volume. The full free energy density of LC+aerosils then takes the dimensionless form

$$f_{tot}^{(n)}=\tfrac{1}{2}a_0[T-T_{NI}(\rho_s)]Q_{NI}^2-\tfrac{1}{3}bQ_{NI}^3+\tfrac{1}{4}cQ_{NI}^4+f_s, \qquad (5)$$

where

$$T_{NI}(\rho_s)=T_{NI}(0)(1-\overline{\alpha_i}\rho_s) \qquad (6)$$

gives the transition temperature shift due to aerosils,

$$Q_{NI}(\rho_s)=\frac{b}{4c}(1+\{1-[4a_0T_{NI}(0)c/b^2]\overline{\alpha_i}\rho_s\}^{1/2}), \qquad (7)$$

is the equilibrium order parameter of the nematic+aerosils system at the NI transition temperature, $\overline{\alpha_i}=\alpha_i/[v_s a_0 T_{NI}(0)\rho_{LC}]$, and $f_s=\mathcal{F}_s/v_s$.

The difference in entropy density between the nematic phase ($f_{tot}^{(n)}$) and the isotropic phase ($f_{tot}^{(i)}$) at $T_{NI}(\rho_s)$ is given by

$$\Delta\Sigma=-\frac{\partial(f_{tot}^{(n)}-f_{tot}^{(i)})}{\partial T}_{T=T_{NI}(\rho_s)}=\frac{1}{2}a_0Q_{NI}^2(\rho_s). \qquad (8)$$

This means that the latent heat per unit volume, $\Delta H(\rho_s)$, is given by

$$\Delta H(\rho_s)=\tfrac{1}{2}a_0\, Q_{NI}^2(\rho_s)T_{NI}(\rho_s). \qquad (9)$$

Combining Eqs. (6) and (7) with Eq. (9) yields the NI transition enthalpy jump

$$\Delta H(\rho_s)=\frac{\Delta H(0)}{4}\left[1+\sqrt{1-\frac{4c\alpha_i}{b^2v_s\rho_{LC}}\rho_s}\right]^2(1-\overline{\alpha_i}\rho_s). \qquad (10)$$

III. COMPARISON WITH EXPERIMENTS

Recently, several high-resolution calorimetric investigations of different *cyanobiphenyls* LC+aerosil systems have been conducted [2,3]. So, the NI transition enthalpy jump $\Delta H(\rho_s)$ in the pure 4-*n*-octyl-4′-*cyanobiphenyl* (8CB) and 4-*n-heptyl*-4′-*cyanobiphenyl* (7CB) have been found to be $\Delta H(0)\sim 2070$ J/kg, for 7CB and $\Delta H(0)\sim 2091$ J/kg, for 8CB. Having obtained the values of the $T_{NI}(0)$ to be equal to 313.8 K and 315.8 K, for 8CB and 7CB [17], and the data for Q_{NI}, to be equal to ~ 0.27 and ~ 0.29, derived from polarized laser Raman scattering [18], one can calculate, using Eq. (9), the phenomenological coefficient a_0 and the ratio of the coefficients b and c; $a_0 \sim 18\times 10^4$ J/Km^3 and $b/c\sim 0.546$ for 8CB, and $a_0\sim 15\times 10^4$ J/Km^3 and $b/c \sim 0.591$ for 7CB. In both these cases the density of the LC compounds has been fixed to the value $\sim 10^3$ kg/m^3. In order to calculate the separate values of b and c, one can use the interval between the NI transition temperature $T_{NI}(0)$ and the critical temperature $T^*(0)$, which can be determined by extrapolating the inverse intensity of the scattering light in the isotropic phase. In the case of cyanobiphenyls, this interval is ~ 1 K [19], so $T_{NI}(0)-T^*(0)=2b^2/(9ca_0)$ gives $b\sim 1.48\times 10^6$ J/m^3, for 8CB and $b \sim 1.14\times 10^6$ J/m^3 for 7CB.

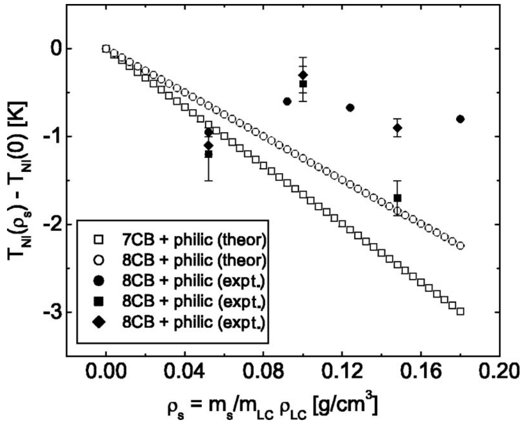

FIG. 1. Aerosil density ρ_s dependence of the NI transition temperature shift $\Delta T_{NI}(\rho_s)$ calculated using Eq. (6) [or Eq. (12)] for hydrophilic aerosils (diameter 7 nm) with 8CB (open circles) and with 7CB (open squares), and measured values for 8CB (solid circles, Ref. [2]), and for 7CB (solid squares, Ref. [7], and diamonds, Ref. [3]).

The values of $\Delta T_{NI}(\rho_s)$ and $\Delta H(\rho_s)$, in the case of strong anchoring for both cyanobiphenyl molecules on the particle surfaces, when $\alpha_i=\alpha_2$, as a function of aerosil density ρ_s are presented in Figs. 1 and 2. It is found that the

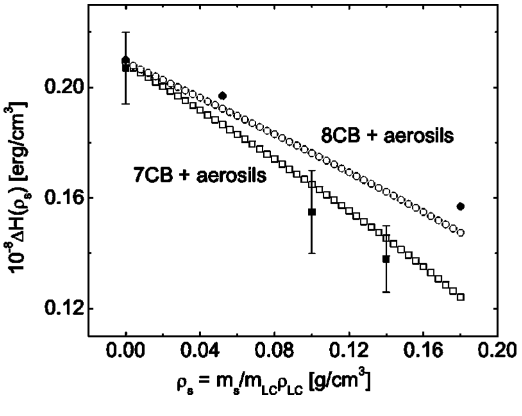

FIG. 2. Hydrophilic aerosil (diameter 7 nm) density ρ_s dependence of the NI transition enthalpy $\Delta H(\rho_s)$ calculated using Eq. (10) for 8CB (open circles) and 7CB (open squares), and measured values for 8CB (solid circles, Ref. [2]) and for 7CB (solid squares, Ref. [3]), respectively.

values of $\Delta T_{NI}(\rho_s)$ and $\Delta H(\rho_s)$ both decrease with increasing ρ_s. The experimental values of the temperature shift $\Delta T_{NI}(\rho_s)$ in Fig. 1 for 7CB and 8CB+hydrophilic $R_s \sim 3.5$ nm aerosil particles were obtained by direct high-resolution calorimetric [2,3] and dielectric spectroscopy [7] measurements, in the aerosil density range $0.02 \leqslant \rho_s \leqslant 0.45$ g/cm^3 for 7CB and 8CB+hydrophilic aerosil systems. In the low-ρ_s(<0.1 g/cm^3) regime the calculated values of $\Delta T_{NI}(\rho_s)$ show a good agreement between theory and experiment. With increasing ρ_s, the calculated values of $\Delta T_{NI}(\rho_s)$ show a faster shift to lower temperature than the one observed from calorimetric and dielectric spectroscopy studies. In this regime, the decrease of transition temperature shift, obtained experimentally, shows a complicated behavior as a function of ρ_s, whereas the calculated values result in linear slope in the transition temperature shift. The values of the temperature shift in the aerosil density range $0.05 \leqslant \rho_s \leqslant 0.4$ g/cm^3, for 7CB+phobic aerosil system, give a faster shift of $\Delta T_{NI}(\rho_s)$ to lower temperatures than calculated values. The results of our model for $\Delta H(\rho_s)$ are based on a physically reasonable description of aerosil perturbation on the NI phase transition, and show good agreement with the data obtained from calorimetric measurements [2,3] for the above-mentioned systems. It should be pointed out that the first two above-mentioned theories (PBL and RF) yield too slow a variation of the latent heat $\Delta H(\rho_s)$, whereas the third theory (SIO), involving a number of adjustable parameters, gives an expression which predicts a weaker density ρ_s decrease, but a possible mechanism, responsible for such choice of these parameters, is still not clear.

In the framework of the elastic-strain approach, which describes the local distortion of the director field $\mathbf{n}(\mathbf{r})$, resulting in an elastic strain, the NI transition temperature shift is given by [2,20]

$$\Delta T_{NI}(\rho_s) = T_{NI}(\rho_s) - T_{NI}(0) = -\frac{1}{2}\frac{K}{a_0}\left(\frac{2\pi}{R}\right)^2, \qquad (11)$$

where R is the effective radius of curvature of the elastic strain. Taking R equal to the mean aerosil void size $R = l_0 = 2/(a_S\rho_s)$ yields a fast decrease of $\Delta T_{NI}(\rho_s)$. Here $l_0 = 2/(a_S\rho_s)$ is the mean LC length scale [2] and a_S is the specific silica area fixed to the value ~ 300 m^2/g, for De Gussa type 300 Aerosil [8]. A possible extension of Eq. (11) which yields a slower transition temperature shift can be achieved by varying the mean void size $R = nl_0$ [3], where n is an integer number. Obviously, by varying a parabola coefficient $A = \frac{1}{2}(K/a_0)(\pi^2/n^2)a_s^2$, (here only one changeable parameter n) one can yield a reasonable agreement of calculated $\Delta T_{NI}(\rho_s) = -A\rho_s^2$ with the results obtained experimentally, but only in very narrow ρ_s region. However, a possible mechanism responsible for obtaining such a void distribution is still not clear [3].

The influence of the aerosil density ρ_s both on the NI transition temperature shift $\Delta T_{NI}(\rho_s)$ and on the transition enthalpy jump $\Delta H(\rho_s)$, in the framework of the present theory, has originated from accounting for the elastic deformation of the host LC phase due to the aerosil particles immersed in the LC phase, which, in our case, is $\sim \alpha_2 \Phi Q_{NI}^2(\rho_s)$ (case of rigid anchoring). So, the NI transition temperature shift is determined to be equal to

$$\Delta T_{NI}(\rho_s) = -\mathcal{A}\frac{K}{a_0}\frac{1}{R_s^2\rho_{LC}}\rho_s, \qquad (12)$$

where coefficient $\mathcal{A}$, according to Eqs. (4) and (6), has been fixed at the value ~ 6.1. In order to apply Eq. (12) to our calculation, we use the $K \sim 5.2$ pN (in the vicinity of NI phase transition temperature [13]), $a_0 = 18 \times 10^4$ J/Km^3 (for 8CB molecules) and 15×10^4 J/Km^3 (for 7CB molecules), $R_s \sim 3.5$ nm, and $\rho_{LC} \sim 1$ g/cm^3. Calculation of the temperature shift gives $\Delta T_{NI}(\rho_s) \sim -0.72$ K (for 8CB+hydrophilic aerosil) and ~ -0.86 K (for 7CB+hydrophilic aerosil) at $\rho_s \sim 0.05$ g/cm^3, whereas the experimental values of the temperature shift from calorimetric measurements are ~ -0.95 K (for 8CB+hydrophilic aerosil [2]) and ~ -1.1 K (for 7CB+hydrophilic aerosil [3]). Note that the experimental value of $\Delta T_{NI}(\rho_s)$, obtained from dielectric spectroscopy measurements, is ~ -1.2 K [7] for 7CB +hydrophilic aerosil system at $\rho_s \sim 0.05$ g/cm^3.

It should also be noted here that in the case of weak anchoring of molecules on the particle surfaces, when $\alpha_i = \alpha_1$, the transition temperature shift $\Delta T_{NI}(\rho_s) = -\epsilon(W^2/Ka_0\rho_{LC})\rho_s$, where ϵ, according to Eqs. (4) and (6), has been fixed to the value ~ 0.0477. Taking into account the above values for K and a_0, and $W \sim 10^{-5}$ J/m^2, the downward shift $\Delta T_{NI}(\rho_s)$ remains practically zero for 8CB; this confirms a true choice (“strong” anchoring) of the boundary conditions at the silica particle surface.

Of course, the linear slope in the transition temperature shift $\sim -T_{NI}(0)\overline{\alpha_i}\rho_s$ means that the particles are regarded as noninteracting, and the present approach is valid only for dilute ($\Phi \ll 1$) aerosil network. With an increase of the aerosil density ρ_s, the small silica particles can aggregate into much bigger objects, producing a rich behavior due to topological-driven enhancement of dynamic elastic properties, which are not considered in our approach.

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