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Molecular statistical description of nematics in terms of the random-phase approximation

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A calculation of the Maier-Saupe model is given in terms of the random-phase approximation. The influence of the range of the intermolecular potential is analyzed. Notably, attention is paid to short-range-order effects in the isotropic phase. It appears that light-scattering data can be understood using a short-range potential.

I. INTRODUCTION

Short-range-order effects in the isotropic phase of nematics and cholesterics have been extensively discussed by de Gennes.[1] The starting point of his discussion is the Landau expansion of the free energy; the next point is the equipartition theorem in order to obtain the temperature dependence of the relevant fluctuations. This phenomenological approach gives a satisfactory description of both the ordered and disordered state of nematics.

In order to gain insight into the type of interaction that produces the first-order nematic-isotropic transition, Maier and Saupe[2] developed a molecular model based upon anisotropic dispersion forces. According to their theory, the origin of nematic order is due to the interaction between the anisotropic polarizabilities of the molecules; the molecules themselves are considered to be spherical. Taking into account the liquid character of nematics, they arrived at the following Hamiltonian:

$$H=-\frac{1}{2}\sum_{\substack{i,j\\ i\neq j}} J(R_{ij})P_2(\vec{a}_i\cdot\vec{a}_j)\ , \tag{1.1}$$

where $\vec{a}_i$ and $\vec{a}_j$ are unit vectors pointing in the direction of the long axis of the molecules i and j being situated at $\vec{R}_i$ and $\vec{R}_j$. The coupling constant $J(R_{ij})$, $R_{ij}=|\vec{R}_i-\vec{R}_j|$, denotes the interaction strength between these molecules and P_2 is the second Legendre polynomial. Maier and Saupe solved their model in the molecular-field approximation (MFA) and obtained a qualitatively correct temperature dependence of the order parameter.

The physical interpretation of the coupling constant $J(R_{ij})$ in terms of anisotropic polarizabilities of spherical molecules should not be taken seriously, as shown by Gelbart and Gelbart.[3] They demonstrated that the orientational dependence of the intermolecular interaction originates mainly from the coupling between isotropic attractions and anisotropic hard-core repulsions. Nevertheless, the form of the interaction seems relevant for the discussion of the behavior of nematics.

A proper description of the behavior of nematics in the isotropic phase can not be given in the MFA, because this approximation neglects the fluctuations. In order to discuss the local order in the isotropic phase, a nearest-neighbor lattice version of the Maier-Saupe model was calculated recently by means of a cluster variation method[4,5] and a Bethe-Peierls approximation.[6,7] Because these approximations calculate only the nearest-neighbor-correlation function, expressions for the relevant fluctuations, which describe pretransitional effects, e.g., the scattering of light, cannot be obtained directly. In that case approximate summations have to be carried out.[7]

It is the purpose of this paper to give an approximate solution of the Maier-Saupe model in terms of the random-phase approximation (RPA), a method well known in the field of magnetism.[8] The advantage of this method is that it is applicable to both long- and short-range potentials and that it is directly based upon the fluctuations, i.e., it provides a link with the treatment of de Gennes.

II. RANDOM-PHASE APPROXIMATION

In order to apply the RPA the original Hamiltonian (1.1) is split up into two parts

$$H=H_0+V\ , \tag{2.1}$$

with

$$H_0=\tfrac{1}{2}NJ(0)S^2-J(0)S\sum_i P_2(a_{iz})\ , \tag{2.1a}$$

$$V=-\frac{1}{2}\sum_{\substack{i,j\\ i\neq j}} J(R_{ij})\sum_{\mu=1}^{5} Q_\mu(\vec{R}_i)Q_\mu(\vec{R}_j)\ , \tag{2.1b}$$

where

$$Q_1(\vec{R}_i) = P_2(a_{iz}) - S,\ Q_2(\vec{R}_i) = \tfrac{1}{2}\sqrt{3}\,(a_{ix}^2 - a_{iy}^2)\ ,$$

$$Q_3(\vec{R}_i) = \sqrt{3}\,a_{ix}a_{iy},\ Q_4(\vec{R}_i)$$

$$= \sqrt{3}\,a_{ix}a_{iz},\ Q_5(\vec{R}_i) = \sqrt{3}\,a_{iy}a_{iz},$$

and

$$J(0) = \sum_j J(R_{ij})\ .$$

N denotes the total number of molecules. Obviously the functions $Q_\mu(\vec{R}_i)$ are related with the five spherical harmonics $Y_{2m}(\vec{a}_i)$ $(m = -2, \ldots, 2)$ in a simple way. It follows easily that the Helmholtz free energy F can be written

$$-\beta F = -\beta F_0 + \ln\langle\exp(-\beta V)\rangle_0\ , \tag{2.2}$$

with

$$-\beta F_0 = -\tfrac{1}{2}N\beta J(0)S^2 + N\ln Z_0\ , \tag{2.2a}$$

$$\langle A\rangle_0 = [\mathrm{Tr}\exp(-\beta H_0)]^{-1}\,\mathrm{Tr}A\exp(-\beta H_0)\ , \tag{2.2b}$$

$$Z_0 = \mathrm{Tr}\exp(-\beta H_0)$$

$$= 2\pi\int_0^\pi d(\cos\theta)\exp[\beta J(0)SP_2(\cos\theta)]\ . \tag{2.2c}$$

Cluster-variation methods treat S as a variation parameter. After decoupling the fluctuation term $\langle\exp(-\beta V)\rangle_0$ into clusters the parameter S is determined by minimizing the free energy F with respect to variations of S.

The RPA takes a different point of view and considers S still to be determined by the requirement of translational invariance, i.e., S is the long-range order parameter satisfying the well-known self-consistency relation

$$S = \langle P_2(\cos\theta)\rangle_0\ . \tag{2.3}$$

The criterion of the lowest free energy selects the solution of S that corresponds to thermodynamic equilibrium. If we neglect the fluctuations we simply obtain the Maier-Saupe result.

In order to calculate the free energy in the RPA we put

$$Q_\mu(\vec{R}_i) = \frac{1}{\sqrt{N}}\sum_{\vec{q}} Q_\mu(\vec{q})\exp(-i\vec{q}\cdot\vec{R}_i)\ ; \tag{2.4}$$

the vectors $\vec{q}$ are determined by the boundary conditions. In the case of a Maier-Saupe model on a simple-cubic lattice the vectors $\vec{q}$ belong to the first Brillouin zone and the Fourier components $Q_\mu(\vec{q})$ are independent, for we have only N components. If we deal with a liquid, however, we have an infinite number of Fourier components $Q_\mu(\vec{q})$ and only N of them can be taken to be independent. In the following we select the independent components according to the Debye procedure, a quite natural choice, and the influence of the remaining ones is neglected.

Realizing that the $\vec{q} = 0$ mode already appears in H_0 as far as the anisotropic phase is concerned, the fluctuation term reads

$$V = -\frac{1}{2}\sum_{\vec{q},\mu}{}' J(\vec{q})Q_\mu^\dagger(\vec{q})Q_\mu(\vec{q})\ , \tag{2.5}$$

with

$$J(\vec{q}) = \sum_j J(R_{ij})\exp(i\vec{q}\cdot\vec{R}_{ij})\ . \tag{2.6}$$

The prime in the summation appearing in expression (2.5) denotes that we have to exclude the $\vec{q} = 0$ term in the nematic phase. The RPA assumes that each Fourier component $Q_\mu(\vec{q})$ fluctuates independently, except the $\vec{q}$ and $-\vec{q}$ terms that fluctuate in the same way. This means

$$\ln\langle\exp(-\beta V)\rangle_0 = \frac{1}{2}\sum_{\vec{q},\mu}{}' \ln\langle\exp[\beta J(\vec{q})Q_\mu^\dagger(\vec{q})Q_\mu(\vec{q})]\rangle$$

$$+\sum_\mu \ln\langle\exp[\tfrac{1}{2}\beta J(0)Q_\mu^\dagger(0)Q_\mu(0)]\rangle, \tag{2.7}$$

where the $\vec{q}$-mode spectrum is cut off on a spherical surface of radius q_D and the $\vec{q} = 0$ term only appears in the isotropic phase. It holds

$$q_D = (6\pi^2\rho)^{1/3}\ , \tag{2.8}$$

where $\rho = N/V$ denotes the density of the system with volume V.

In the unperturbed isotropic phase (i.e., without fluctuations) the distribution of $Q_\mu(\vec{q})$ is Gaussian with $\langle Q_\mu(\vec{q})\rangle_0 = 0$ and $\langle Q_\mu^\dagger(\vec{q})Q_\mu(\vec{q})\rangle_0 = \frac{1}{5}$. This means

$$\langle\exp[\beta J(\vec{q})Q_\mu^\dagger(\vec{q})Q_\mu(\vec{q})]\rangle = \int_0^\infty dx^2\exp\{-[5 - \beta J(\vec{q})]x^2\}\ \int_0^\infty dx^2\exp(-5x^2) = [1 - \tfrac{1}{5}\beta J(\vec{q})]^{-1}\ , \tag{2.9a}$$

$$\langle\exp[\tfrac{1}{2}\beta J(0)Q_\mu^\dagger(0)Q_\mu(0)]\rangle = \int_0^\infty dx\exp\{-\tfrac{1}{2}[5 - \beta J(0)]x^2\}\ \int_0^\infty dx\exp(-\tfrac{5}{2}x^2) = [1 - \tfrac{1}{5}\beta J(0)]^{-1/2}\ . \tag{2.9b}$$

Using expression (2.9) the RPA gives rise to the following free energy in the isotropic phase $(S = 0)$:

$$F_{\mathrm{iso}} = -\frac{N\ln 4\pi}{\beta} + \frac{5}{2\beta}\sum_{\vec{q}}\ln[1 - \tfrac{1}{5}\beta J(\vec{q})]\ , \tag{2.10}$$

where the sum on $\vec{q}$ is limited to the Debye sphere. The expectation value of $Q_\mu^\dagger(\vec{q})Q_\mu(\vec{q})$ in the perturbed isotropic phase, $\langle Q_\mu^\dagger(\vec{q})Q_\mu(\vec{q})\rangle$, can be calculated in an analogous way. It holds

$$\langle Q_\mu^\dagger(\vec{q})Q_\mu(\vec{q})\rangle = [5-\beta J(\vec{q})]^{-1} \,, \tag{2.11}$$

i.e., the fluctuation $\langle Q_\mu^\dagger(0)Q_\mu(0)\rangle$ diverges at $k_B T_c^* = \frac{1}{5}J(0)$.

In order to determine T_c we have to calculate the free energy of the nematic phase. In the unperturbed nematic phase, i.e., without fluctuations, the distribution of $Q_\mu(\vec{q})$ is also Gaussian with $\langle Q_\mu(\vec{q})\rangle_0 = 0$ and $\langle Q_\mu^\dagger(\vec{q})Q_\mu(\vec{q})\rangle_0 = \frac{1}{5}\sigma_\mu^2$, where

$$\sigma_1^2 = \tfrac{5}{2} - 15/2\beta J(0) + \tfrac{5}{2}S - 5S^2 \,, \tag{2.12a}$$

$$\sigma_2^2 = \sigma_3^2 = \tfrac{5}{4} - 5/4\beta J(0) - \tfrac{5}{4}S \,, \tag{2.12b}$$

$$\sigma_4^2 = \sigma_5^2 = 5/\beta J(0) \,. \tag{2.12c}$$

Then the RPA gives the following expression for the free energy of the nematic phase:

$$F_{\text{nem}} = F_0 + \frac{1}{2\beta}\sum_{\mu=1}^{5}\sum_{\vec{q}}{}' \ln[1 - \tfrac{1}{5}\beta J(\vec{q})\sigma_\mu^2] \,, \tag{2.13}$$

while the expectation value of $Q_\mu^\dagger(\vec{q})Q_\mu(\vec{q})$ in the perturbed nematic phase equals

$$\langle Q_\mu^\dagger(\vec{q})Q_\mu(\vec{q})\rangle = \sigma_\mu^2[5 - \beta J(\vec{q})\sigma_\mu^2]^{-1} \,. \tag{2.14}$$

The transition temperature T_c and the jump of the order parameter S_c at T_c are obtained by simultaneously solving the self-consistency equation for the order parameter S (2.3) and the equation $F_{\text{nem}} - F_{\text{iso}} = 0$. It follows directly that, in contrast to the case of second-order phase transitions, the fluctuations already influence the location of T_c; only T_c^* remains unaltered. This shift of T_c depends on the range of the interaction between the molecules. Although the shift is rather small the ratio $(T_c - T_c^*)/T_c$ can be changed drastically. This fact is of interest because there is quite a discrepancy between the theoretical and experimental values. Experimentally this ratio is 0.003 for MBBA,[9] while theory predicts a value of 0.092 in the MFA and, at the best, 0.028 in the two-site cluster approximation,[4] as far as the nearest neighbor Maier-Saupe model is concerned. Data of Monte Carlo simulations, however, indicate that this cluster variation method also overestimates the value of $(T_c - T_c^*)/T_c$ considerably.[10] In the following we will study the effect of the range of the potential on the ratio $(T_c - T_c^*)/T_c$.

III. EFFECT OF THE RANGE OF THE POTENTIAL

The influence of the range of the potential on the ratio $(T_c - T_c^*)/T_c$ can be quite suitably studied by using the Kac potential[11]

$$J(R_{ij}) = \frac{J}{4\pi b^2 R_{ij}} \exp\left(-\frac{R_{ij}}{b}\right) . \tag{3.1}$$

The parameter b is a measure for the range of the potential and J is a coupling constant. In the limit $b \to \infty$ this potential is a molecular-field potential and the original Maier-Saupe result is exact; the short-range character of the potential increases with decreasing b. It holds, using (2.6),

$$J(\vec{q}) = \rho J/[1 + (bq)^2] \,, \tag{3.2}$$

with $q = |\vec{q}\,|$. Changing summations into integrations via

$$\sum_{\vec{q}} = \frac{V}{2\pi^2}\int_0^{q_D} q^2 dq$$

we obtain

$$F_{\text{nem}} - F_{\text{iso}} = F_0 + \frac{N\ln 4\pi}{3} + \frac{15N}{\beta}\sum_{\mu=1}^{5}\int_0^1 dx\, x^2 \ln\left(\frac{1 + (bq_D)^2x^2 - \frac{1}{5}\beta\rho J\sigma_\mu^2}{1 + (bq_D)^2x^2 - \frac{1}{5}\beta\rho J}\right) . \tag{3.3}$$

After some numerical calculations we find that $(T_c - T_c^*)/T_c$, where $k_B T_c^* = \frac{1}{5}\rho J$, decreases with decreasing b, while S_c increases. The ratio $(T_c - T_c^*)/T_c$ can be made arbitrarily small, if the parameter b is suitably chosen; in that case T_c is approximately equal to T_c^* and S_c approaches $S(T_c^*) = 0.615$. The exact data are given in Table I, where we have expressed b in terms of an average intermolecular distance a defined by $aq_D = (6\pi^2)^{1/3}$.

An important quantity in the isotropic phase is the correlation length ξ. Small q values of $\langle Q_\mu^\dagger(\vec{q})Q_\mu(\vec{q})\rangle$ correspond to the behavior of $\langle Q_\mu(\vec{R}_i)Q_\mu(\vec{R}_j)\rangle$ for large values of R_{ij}. Approximating the Kac potential by

$$J(\vec{q}) = \rho J(1 - b^2q^2) \tag{3.4}$$

we obtain for large values of R_{ij}

$$\langle Q_\mu(\vec{R}_i)Q_\mu(\vec{R}_j)\rangle \simeq (4\pi\beta\rho^2 b^2 J R_{ij})^{-1}\exp(-R_{ij}/\xi) \,, \tag{3.5}$$

where the correlation length ξ is given by

TABLE I. Ratio $1-T_c^*/T_c$ and the values of the order parameter S_c at $T=T_c$. The parameter b has been expressed in units of an average intermolecular distance $a=\rho^{-1/3}$.

b	$1-T_c^*/T_c$	S_c
∞	0.092	0.429
5	0.084	0.459
4	0.080	0.473
3	0.070	0.500
2	0.040	0.560
1.9	0.034	0.570
1.8	0.027	0.581
1.7	0.018	0.593
1.6	0.008	0.607

$$\xi = b[T/T_c^* - 1]^{-1/2} . \tag{3.6}$$

It follows directly that

$$\frac{1}{N}\sum_{\vec{q}}\langle Q_\mu^\dagger(\vec{q})Q_\mu(\vec{q})\rangle$$

diverges at $T=T_c^*$ in one and two dimensions for short-range potentials. Therefore the RPA already excludes nematic order in one and two dimensions. A mathematically rigorous proof of that statement has been given by Vuillermot and Romerio.[12]

Light scattering in the isotropic phase due to fluctuations of the polarizability tensor can be easily calculated, using expression (3.5). Neglecting the dependence of the intensity I on the scattering wave vector the expressions for the intensity of the outgoing light with polarization parallel ($I_\parallel$) and perpendicular ($I_\perp$) to the polarization of the incident light are

$$I_\parallel = \frac{4N(\Delta\alpha)^2}{9\lambda^4}\sum_i \langle Q_1(\vec{R}_0)Q_1(\vec{R}_i)\rangle , \tag{3.7a}$$

$$I_\perp = \frac{N(\Delta\alpha)^2}{3\lambda^4}\sum_i \langle Q_4(\vec{R}_0)Q_4(\vec{R}_i)\rangle , \tag{3.7b}$$

where λ is the wavelength of the incident light and $\Delta\alpha = \alpha_l - \alpha_t$, α_l and α_t are the longitudinal and transverse molecular polarizabilities, respectively. The index i runs over all molecules of the sample. Because $\langle Q_1(\vec{R}_0)Q_1(\vec{R}_i)\rangle = \langle Q_4(\vec{R}_0)Q_4(\vec{R}_i)\rangle$ we have $I_\parallel = \frac{4}{3}I_\perp$. Substitution of (3.5) into (3.7) gives us roughly the following temperature-dependent behavior of the intensities:

$$I_\parallel = \tfrac{4}{3}I_\perp = 4N(\Delta\alpha)^2\xi^2/9\lambda^4 b^2\beta\rho J . \tag{3.8}$$

This behavior has been verified experimentally by Stinson and Litster.[9]

IV. CONCLUSION

The RPA is a convenient and simple method to calculate the properties, notably the short-range-order effects, of molecular statistical models of nematics. In particular, the pretransitional effects are easy to calculate. The method is applicable to smectics as well. It has, however, one slight disadvantage. The order parameter is calculated using the MFA. This means that, in general, T_c, T_c^*, and the jump in the order parameter are too high and that the method breaks down if the range of the potential becomes too small ($b<1.55$). In that case, the contribution of the fluctuations can no longer be treated as a perturbation of the molecular field. A possible way to improve this situation is to use the spherical constraint.[13] However, a consistent way of using this constraint is not clear to us, as far as the nematic phase is concerned. The properties of the isotropic phase can be calculated using this constraint. The main result is that the spherical constraint brings down T_c^* considerably.

Our calculations show that a short-range intermolecular potential is needed in order to understand the experiments of Stinson and Litster in terms of the Maier-Saupe model. Clearly the structure of the molecules is reflected in the range of the potential, i.e., the parameter b. In particular, it might be expected that b is roughly proportional to the length minus the width of the molecule. It would be of interest to investigate the correlation between $1-T_c^*/T_c$ and molecular properties.

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