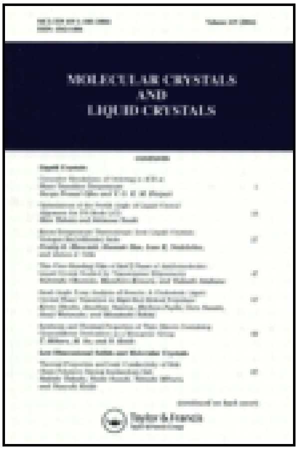

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Cluster Integral Expansion of the Cotton-Mouton Constant in Suspensions

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Cluster Integral Expansion of the Cotton-Mouton Constant in Suspensions

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We consider suspensions of anisotropic (rigid) particles, e.g., polymer solutions or micellar solutions, of relatively low particle concentrations. The magnetic-field induced alignment of the particles is treated theoretically, assuming that the particles have cylindrical symmetry. The inverse Cotton-Mouton constant for this alignment can be given as an expansion in powers of the particle density, analogous to the expansion used in the equation of state for non-ideal gases. Explicit expressions for the coefficients of the expansion are obtained in terms of cluster integrals. The results allow the interpretation of the Cotton-Mouton effect in terms of particle interactions.

INTRODUCTION

A magnetic field applied normal to a light beam propagating through an isotropic medium, induces birefringence. This is known as the Cotton-Mouton effect. The induced birefringence depends on the applied external field, the wave length, the temperature and the nature of the system. The difference between the indexes of refraction corresponding to the two normal modes of polarization is given by

$$n_1 - n_2 = \lambda C H^2 \qquad (1)$$

where λ is the wave length, H is the magnetic field and C is the Cotton-Mouton constant.

In suspensions of anisometric particles, the action of a magnetic field induces orientational order. This orientational ordering of the anisometric particles makes a contribution to the induced birefringence. In what follows we will be concerned with this contribution only.

The magnitude of the induced birefringence increases with the concentration of the anisometric particles. At sufficiently high concentrations, the particles may exhibit spontaneous orientational order (nematic order) and thus spontaneous birefringence. Here we will consider concentrations that are lower than the concentration corresponding to the nematic transition. Thus in the absence of the external field the system is isotropic.

We consider a sample of index of refraction n, containing N cylindrically symmetric particles in volume V and at temperature T. We define

$$\Delta\alpha = \alpha_{\parallel} - \alpha_{\perp} \tag{2}$$

and

$$\Delta\chi = \chi_{\parallel} - \chi_{\perp} \tag{3}$$

where $\alpha_{\parallel}$ and $\alpha_{\perp}$ are the principal values of the polarizability tensor of the particle, and $\chi_{\parallel}$ and $\chi_{\perp}$ are the principal values of the susceptibility tensor of the particle. Then using the Lorentz-Lorenz[1] equation, one can express the Cotton-Mouton constant in terms of these parameters as follows

$$\lambda C = \frac{2\pi}{27}\frac{(n^2+2)^2}{nkTV}\Delta\alpha\Delta\chi\sum_{i,j}^{N}\langle P_2(\cos\theta_i)P_2(\cos\theta_j)\rangle \tag{4}$$

where $P_2(\cos\theta_i)$ are the Legendre polynomials of order 2, θ_i is the angle formed by particle i and the direction of the magnetic field, and k is the Boltzmann constant.

The average value in Eq. (4) can be evaluated from the induced orientational order. In the present work we derive a density expansion for the induced order, extending the first order expansion already presented by Straley.[2] Our formulation follows Onsager's theory of solutions of anisometric particles.[3] This theory provides a density expansion for the free energy. The coefficients of the expansion, known as the cluster integrals, are essentially volume integrals of the Ursell functions, involving the interaction potential. The method of cluster integrals was introduced by Mayer in connection with imperfect gases.[4]

Retaining only the first order term in the cluster expansion, Onsager determined that a dispersion of anisometric particles can exhibit spontaneous orientational order when the number of particles per unit volume is sufficiently increased. Among the predictions of Onsager's model, was that the nematic phase becomes stable at rather low concentrations (about 4% by volume for hard rods with a length to diameter ratio of 100) and that the orientational order of the nematic phase is well developed ($S = 0.8$ at the onset).

In obtaining the above mentioned results, the assumption is made that the cluster integrals are independent of the volume of the system. It has been pointed out,[5] however, that for densities close to the nematic transition of such systems, the assumption that the cluster integrals are independent of the volume of the system is not justified, and that the errors thus introduced tend to favor the formation of the nematic order. This in turn would account for the rather high value predicted for the degree of order.

The Induced order

In what follows we focus our discussion to cylindrically symmetric particles, although less symmetrical shapes can be handled along the same lines.

The interaction of the N particles with the applied magnetic field results in an angle dependent contribution to the total energy

$$-JkT \sum_{i}^{N} P_2(\cos \theta_i) \tag{5}$$

where

$$J = \Delta\chi H^2/3kT. \tag{6}$$

For the orientational order parameter $S = \langle P_2 \rangle$, we can write

$$S = S_0 + J(\partial S/\partial J)_0 + \frac{1}{2} J^2(\partial^2 S/\partial J^2)_0 + \dots \tag{7}$$

where the suffix o indicates that the quantities are taken at $J = 0$. Since the field is applied on an isotropic phase, the first term in the series vanishes. In view of Eq. (5)

$$S = \frac{1}{N}\sum_i \frac{\int P_2(\cos\theta_i)e^{-E/kT}\prod_j^N e^{JP_2(\cos\theta_j)}\,d\cos\theta_j}{\int e^{-E/kT}\prod_j^N e^{JP_2(\cos\theta_j)}\,d\cos\theta_j} \tag{8}$$

thus

$$(\partial S/\partial J)_0 = \frac{1}{N}\sum_{i,j}\langle P_2(\cos\theta_i)P_2(\cos\theta_j)\rangle_0. \tag{9}$$

Since $S = 0$ at $J = 0$, $P_2(\cos\theta_i)$ measures the orientational fluctuation of molecule i about its equilibrium position. Thus the above equation relates $(\partial S/\partial J)_0$ to the orientational fluctuations arising from the interaction of the N particles with the external field. This result is in agreement with the fluctuation-dissipation theorem. Indeed, following the formulation of Ref. 6, $(\partial S/\partial J)_0$ can be identified in our case as the generalized susceptibility at zero frequency.

Retaining up to second order terms in H, we have

$$S = \frac{J}{N}\sum_{i,j}\langle P_2(\cos\theta_i)P_2(\cos\theta_j)\rangle_0. \tag{10}$$

Cluster expansion

Following the development by Onsager mentioned earlier, we express the free energy in terms of a power series of the particle density:

$$-F/NkT = 1 + \phi(T) - \ln\rho + J\int w(\theta)P_2(\cos\theta)d\Omega$$
$$- \int w(\theta)\ln w(\theta)d\Omega + \sum_{\kappa\geq 1}\frac{\rho}{\kappa+1}\int\beta(\Omega_1,\ldots\Omega_{\kappa+1})\prod_{j=1}^{\kappa+1} w(\theta_j)d\Omega_j. \tag{11}$$

Except for the term proportional to J, which is a contribution arising from the interaction of the particles with the external field, the above equation is identical to the expression derived by Onsager.[3] Here ϕ is a function of the temperature, ρ is the number of particles per unit volume (the particle density) and w is the one particle distribution function. The quantities $\beta_\kappa(\Omega_1, \ldots \Omega_{\kappa+1})$ are volume integrals of products formed by the functions

$$f_{ij} \equiv \exp\left(-u_{ij}/kT\right) - 1 \tag{12}$$

where u_{ij} is the interaction potential between particles i and j. The products are to be taken over all $\kappa + 1$ particles that are contained in an irreducible cluster of order κ.[4] The equilibrium distribution function w minimizes the free energy, subject to the constraint

$$\int w(\theta) d\Omega = 1. \tag{13}$$

Thus we require that the quantity

$$-\frac{F}{NkT} + \lambda \int w(\theta) d\Omega \tag{14}$$

vanishes for a variation of w, i.e.

$$\int \delta w d\Omega \left\{ -\ln w(\theta_1) - 1 + \sum_{\kappa \geq 1} \rho^\kappa \int \beta_\kappa(\Omega_1 \ldots \Omega_{\kappa+1}) \prod_{j=2}^{\kappa+1} w(\theta_j) d\Omega_j + \lambda \right\} = 0 \tag{15}$$

or

$$w(\theta_1) = \exp\left\{ -1 + \lambda + \sum_{\kappa \geq 1} \rho^\kappa \int \beta_\kappa(\Omega_1 \ldots \Omega_{\kappa+1}) \prod_{j=2}^{\kappa+1} w(\theta_j) d\Omega_j \right\} \tag{16}$$

The multiplier λ can be eliminated from Eq. (16) by applying the normalization condition, Eq. (13), to $w(\theta)$ of Eq. (16). This leads to

$$w(\theta_1) = Q \exp\left[J P_2(\cos\theta_1) + \epsilon(\theta_1)\right] \tag{17}$$

where

$$\epsilon(\theta_1) = \sum_{\kappa\geq 1} \rho^\kappa \int \beta_\kappa(\Omega_1, \ldots \Omega_{\kappa+1}) \prod_{j=2}^{\kappa+1} w(\theta_j) d\Omega_j \tag{18}$$

and

$$Q^{-1} = \int \exp\,[JP_2(\cos\theta_1) + \epsilon(\theta_1)]d\Omega_1. \tag{19}$$

Since the system has rotational symmetry about the direction of the applied magnetic field, the one particle distribution function can be expanded in terms of Legendre polynomials:

$$w(\theta) = \frac{1}{4\pi}\left[1 + \sum_{l=1}^{\infty} (4l + 1)\langle P_{2l}\rangle P_{2l}(\cos(\theta)\right]. \tag{20}$$

As in Eq. (7), we can write

$$\langle P_n\rangle = J\left(\frac{\partial\langle P_n\rangle}{\partial J}\right)_0 + \frac{1}{2}J^2\left(\frac{\partial^2\langle P_n\rangle}{\partial J^2}\right)_0 + \ldots \tag{21}$$

The coefficient of the term linear in J is evaluated in Appendix A. This coefficient vanishes, unless $n = 2$. Thus from Eq. (A7)

$$\left(\frac{\partial S}{\partial J}\right)_0 = \frac{1}{5}\left[1 - 5\sum_{\kappa\geq 1} \kappa B_\kappa \rho^\kappa\right]^{-1}. \tag{22}$$

The quantities B_κ are given by Eq. (A8) in Appendix A. We note that for $n > 2$ the lowest order terms in the expansion of Eq. (21), will be proportional to J^2. Consequently, their contribution to the distribution function, Eq. (20), will be of the order of J^2 or higher, and only the average $\langle P_2\rangle$ will contribute a term linear in J.

In practice the second order terms in J. (i.e. fourth order in H) are negligible, thus the dominant contribution is that corresponding to the P_2 term, and one can write:

$$w(\theta) = \frac{1}{4\pi}\left[1 + J\left(\frac{\partial S}{\partial J}\right)_0 P_2(\cos\theta)\right]. \tag{23}$$

The degree of (induced) order is

$$S = \frac{J}{5}\left[1 - 5\sum_{\kappa\geq 1}\kappa B_\kappa \rho^\kappa\right]^{-1}. \tag{24}$$

Retaining the first term in the series, Eq. (24) reduces to the result obtained by Straley.[2]

Combining Eqs. (4), (9) and (22) we obtain an expression for the inverse Cotton-Mouton constant, in terms of a power series in the particle density:

$$\frac{1}{\lambda C} = \frac{135}{2\pi}\frac{nkT}{(n^2+2)^2\rho\Delta\alpha\Delta\chi}\left[1 - 5\sum_{\kappa\geq 1}\kappa B_\kappa \rho^\kappa\right]. \tag{25}$$

Discussion

In comparing Eq. (25) with experimental data, it should be remembered that since the equation refers to the contribution made by orienting the anisometric particles, one has to appropriately separate the contribution of the solvent. This separation should become easier as the particle concentration is increased. The proper choice of solvent, optical path and magnetic field strength should permit measurement of C in a useful range of concentrations below the nematic-isotrophic phase transition.

To get an estimate of the magnitudes involved, we consider a 2% suspension of the polypeptide poly-γ-benzyl-L-glutamate (PBLG). In the extended α-helix conformation, and for M.W. = 310,000 we have particles with a length to diameter ratio of about 85 (L = 2150 Å and D = 25 Å). Using $\kappa = 1$ in Eq. (24) and values from Ref. 7, we find that for a field of 10 kG, $S = 3.2\ 10^{-5}$ and

$$n_1 - n_2 = 0.02(n_\parallel - n_\perp)S = 1.8 \times 10^{-8}. \tag{26}$$

Thus, for a path length of 1 cm and $\lambda = 6328$ Å, the induced phase shift is about 0.1 degrees. Taking $C = 10^{-13}\ \mathrm{G}^{-2}\ \mathrm{cm}^{-1}$, for the solvent and using Eq. (1), we find that the contribution of the solvent would amount to 0.004 degrees.

As mentioned earlier, the coefficients of the derived expansions are integrals involving the interaction potential between the particles of the system. The multitude of integrations involved makes the evaluation of coefficients higher than second order, a rather formidable task.[8] Nevertheless, for systems that can be adequately described by retaining up to first or second order terms of the cluster expansion, one can elucidate the interparticle interaction in such systems. This can be accomplished by comparing the experimental values of the Cotton-Mouton constant and the values resulting from our expansion, using various forms of interparticle potentials.

An additional useful aspect of Eq. (25) is that it provides an experimental check of the range of validity of Onsager's model which neglects terms with $\kappa > 1$.

Finally, it should be noted that the induced order can be evaluated using the pair distribution function. By extending the work of Mayer and Montroll[9] to anisometric particles, one can expand the distribution function in terms of cluster integrals of the second kind. The procedure is outlined in Appendix B.

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APPENDIX A

Evaluation of $(\partial\langle P_n\rangle/\partial J)$ at $J = 0$

Forming the average

$$\langle P_n\rangle = \int P_n(\cos\theta_1) w(\theta_1) d\Omega_1 \tag{A1}$$

and using $w(\theta_1)$ from Eq. (17), and taking the derivative with respect to J at $J = 0$ we have

$$\left(\frac{\partial\langle P_n\rangle}{\partial J}\right)_0 = \frac{\delta_{n2}}{5} + \int P_n(\cos\theta_1) \sum_{\kappa\geqslant 1} \rho^\kappa \int \beta_\kappa(\Omega_1, \ldots \Omega_{\kappa+1}) \cdot \left[\frac{\partial}{\partial J} \sum_{j=2}^{\kappa+1} w(\theta_j) d\Omega_j\right]_0 \frac{d\Omega_1}{4\pi} \tag{A2}$$

where δ_{n2} is the Kronecker delta. The quantities $w(\theta_j)$ are then expanded using Eq. (20). This leads to derivatives of products of expansions having the form of Eq. (20), at $J = 0$. In taking these derivatives, it should be remembered that all the coefficients in Eq. (20) vanish at $J = 0$, and the differentiation yields

$$\left[\frac{\partial}{\partial J}\prod_{j=2}^{\kappa+1}\left[1 + \sum_{\nu}(4\nu + 1)\langle P_{2\nu}\rangle P_{2\nu}(\cos\theta_j)\right]\right]_0$$

$$= \sum_{j=2}^{\kappa+1}\sum_{\nu}^{\infty}(4\nu + 1)P_{2\nu}(\cos\theta_j)\left(\frac{\partial\langle P_{2\nu}\rangle}{\partial J}\right)_0. \quad \text{(A3)}$$

Substituting in Eq. (A2), and noting that the summation over j reduces to κ identical terms, we have

$$\left(\frac{\partial\langle P_n\rangle}{\partial J}\right)_0 = \frac{\delta_{n2}}{5} + \sum_{\kappa\geqslant 1}\kappa\rho^{\kappa}\sum_{\nu}^{\infty}(4\nu + 1)$$

$$\times\left(\frac{\partial\langle P_{2\nu}\rangle}{\partial J}\right)_0\int P_n(\cos\theta_1)\beta_\kappa(\Omega_1, \ldots, \Omega_{\kappa+1})P_{2\nu}(\cos\theta_2)\prod_{j=1}^{\kappa+1}\frac{d\Omega_j}{4\pi}. \quad \text{(A4)}$$

After integration over the angles of particles 3 to $\kappa + 1$, due to the symmetry of the particles, the result will depend only on the angle between particles 1 and 2. We call this angle γ_{12}, and the result of the integration $\beta_\kappa(\gamma_{12})$.

$$\left(\frac{\partial\langle P_n\rangle}{\partial J}\right)_0 = \frac{\delta_{n2}}{5} + \sum_{\kappa\geqslant 1}\kappa\rho^{\kappa}\sum_{\nu}(4\nu + 1)\left(\frac{\partial\langle P_{2\nu}\rangle}{\partial J}\right)_0$$

$$\times\int P_n(\cos\theta_1)P_{2\nu}(\cos\theta_2)\beta_\kappa(\gamma_{12})\frac{d\Omega_1 d\Omega_2}{(4\pi)^2} \quad \text{(A5)}$$

Next we expand $\beta_\kappa(\gamma_{12})$ as a series of Legendre polynomials. We assume that the interparticle interaction remains unchanged when one of the particles is rotated by π about the short axis. Thus the series will consist of even terms only, and using the addition theorem for spherical harmonics we can write:

$$\beta_\kappa(\gamma_{12}) = \sum_{l=\text{even}} \sum_{m=-l}^{l} \frac{4\pi}{2l+1} B_{\kappa l}\, Y^*_{lm}(\theta_1, \phi_1) Y_{lm}(\theta_2, \phi_2). \tag{A6}$$

Substituting into Eq. (A5) and making use of the orthogonality relations for spherical functions we obtain:

$$\left(\frac{\partial\langle P_n\rangle}{\partial J}\right)_0 = \frac{\delta_{n2}}{5}\left[1 - \frac{1}{2n+1}\sum_{\kappa\geq 1} \kappa B_{\kappa n}\rho^\kappa\right]^{-1}. \tag{A7}$$

Thus for $n \neq 2$, $\left(\frac{\partial\langle P_n\rangle}{\partial J}\right) = 0$.

For $n = 2$ we obtain Eq. (15), where

$$B_\kappa = B_{\kappa 2} = \frac{1}{(4\pi)^2}\int P_2(\cos\theta_1)P_2(\cos\theta_2)\beta_\kappa(\gamma_{12})d\Omega_1 d\Omega_2.$$

$$= \frac{1}{(4\pi)^{\kappa+1}}\int P_2(\cos\theta_1)P_2(\cos\theta_2)$$

$$\beta_\kappa(\Omega_1 \ldots \Omega_{\kappa+1})d\Omega_1 \ldots d\Omega_{\kappa+1}. \tag{A8}$$

APPENDIX B

Expansion using the distribution function

Following Mayer and Montroll,[9] we expand the pair distribution function

$$g^{(2)}(r_1, r_2, \Omega_1, \Omega_2) = e^{\frac{-u_{12}}{kT}}\left[1 + \sum_{\kappa\geq 1}\beta_{\kappa 2}\rho^\kappa\right] \tag{B1}$$

where $\beta_{\kappa 2}$ are the irreducible cluster integrals of the second kind, properly extended to include the orientational degrees of freedom. They are formed by integrating products of the quantities f_{ij} [defined by Eq. (12)], over the positions and angles of particles 3 to $\kappa + 1$, and thus depend on the positions and orientations of the remaining two particles (note than an irreducible cluster of order κ includes $\kappa + 1$ particles).

Thus effecting the average in Eq. (9), we find

$$\left(\frac{\partial S}{\partial J}\right)_0 = \langle (P_2(\cos\theta))^2\rangle_0$$

$$+ \frac{1}{(4\pi V)^2 N}\sum_{i=j}^{N}\int P_2(\cos\theta_i)P_2(\cos\theta_j)g^{(2)}dV_i dV_j d\Omega_i d\Omega_j. \quad \text{(B2)}$$

Using Eqs. (12) and (B2), we obtain, after some rearrangement

$$\left(\frac{\partial S}{\partial J}\right)_0 = \frac{1}{5} + \frac{\rho}{(4\pi)^2}\int P_2(\cos\theta_1)P_2(\cos\theta_2)\beta_1(\gamma_{12})d\Omega_1 d\Omega_2$$

$$+ \frac{N}{(4\pi V)^2}\sum_{\kappa\geqslant 1}\int (1 + f_{12})\beta_{\kappa 2}\rho^{\kappa}\, dV_1 d\Omega_1 dV_2 d\Omega_2. \quad \text{(B3)}$$

The equivalence of the above expansion to Eq. (22) can be readily verified to first order in ρ. To compare higher order terms, one has to express the various integrals of irreducible cluster products of the second kind, in terms of the ordinary β_κ. This task will not be pursued here.

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