Generating moment equations in the Doi model of liquid-crystalline polymers

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We present a self-consistent method for deriving moment equations for kinetic models of polymer dynamics. The Doi model [J. Polym. Sci., Polym. Phys. Ed. **19**, 229 (1981)] of liquid-crystalline polymers with the Onsager excluded-volume potential is considered as an example. To lowest order, this method amounts to a simple effective potential different from the Maier-Saupe form. Analytical results are presented which indicate that this effective potential provides a better approximation to the Onsager potential than the Maier-Saupe potential. Corrections to the effective potential are obtained. [S1063-651X(99)09511-2]

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I. INTRODUCTION

Kinetic theory is a powerful analytical tool for describing the dynamics of dilute and semidilute solutions of polymers in terms of a diffusion equation for the particle distribution function or, equivalently, by the full system of moment equations. In general, the moment system has to be truncated at some level. The problem of the "closure approximation" is very well-known in the literature, and an enormous amount of suggestions has been analyzed in the case where each moment couples only to a few higher-order moments. However, for some kinetic equations, the time evolution of each moment couples to an infinite set of higher moments, so that further analytical work is often precluded since closure approximations are less studied for this case. In this paper we present a simple method that allows us to derive moment equations with a finite coupling valid for a wide class of kinetic equations.

In order to be specific, we consider a particularly important example: the Doi theory of liquid-crystalline polymers (LCP), subject to the Onsager excluded-volume potential [1]. As it is well-known, in this model each moment equation depends on an infinite set of higher-order moments. In the original work [1], this problem was treated in two steps: First, the Onsager potential was replaced by a different, phenomenological potential of the Maier-Saupe type [2], which gives rise to a coupling to the next higher moment only. In the second step, the "decoupling" approximation was used to solve the resulting closure problem for the second moment. Subsequent extensive studies were focused on improvements of the second step [3–6]. At the same time, we are not aware of improvements on the first step and closure approximations are limited to the Maier-Saupe potential up to now. However, it would be desirable to deal with the true Onsager potential, not only because it becomes exact in the limit of low concentrations of perfectly rigid rodlike molecules, but also because it contains no phenomenological parameters and therefore gives more quantitative predictions. In addition, the Onsager potential is preferred in the study of the influence of flow on the isotropic-nematic transition,

since it gives a clear-cut prediction of the range of coexistence of the equilibrium isotropic and nematic phase, both in stationary [7] and nonstationary [8] flows. The method that we propose in this work leads to an approximation of the Onsager potential, which, to the lowest order, is at the same time as simple as the Maier-Saupe potential but also closer to the true Onsager potential. Moreover, corrections to this approximation can be obtained in a systematic manner.

II. DOI MODEL

Let $\psi(\boldsymbol{u};t)$ be the probability distribution function for a rigid rodlike polymer molecule to be oriented parallel to the unit vector $\boldsymbol{u}$. The time evolution of ψ in the presence of flow and the Onsager excluded-volume potential was given by Doi [1] and may be written as

$$\partial_t \psi = -\mathcal{R} \cdot [\boldsymbol{u} \times (\boldsymbol{\kappa} \cdot \boldsymbol{u} \psi)] + \mathcal{R} \cdot \hat{D}_r \psi \mathcal{R} \left(\frac{\delta A}{\delta \psi(\boldsymbol{u})} \right). \quad (1)$$

Here $\mathcal{R} = \boldsymbol{u} \times \partial/\partial \boldsymbol{u}$ is the rotational operator, $\partial/\partial \boldsymbol{u}$ the gradient on the unit sphere, $\boldsymbol{\kappa}$ the gradient of the velocity, $\hat{D}_r$ the rotational diffusivity, $\delta/\delta\psi$ the functional derivative, and $A = A_0 + A_1$ the free energy functional per molecule divided by $k_B T$,

$$A_0 = \ln \nu - 1 + \langle \ln \psi(\boldsymbol{u}) \rangle, \quad (2a)$$

$$A_1 = \frac{U}{2} \langle\langle \sqrt{1 - (\boldsymbol{u} \cdot \boldsymbol{w})^2} \rangle\rangle. \quad (2b)$$

$U = 2bL^2\nu$ is the reduced excluded-volume, $2b$ and L are the diameter and the length of the rodlike polymeric molecules, respectively, and ν is the number of molecules per unit volume. Here and below we use the following notations for averages: $\langle f(\boldsymbol{u}) \rangle = \int f(\boldsymbol{u}) \psi(\boldsymbol{u}) d\boldsymbol{u}$, and $\langle\langle f(\boldsymbol{u},\boldsymbol{w}) \rangle\rangle = \int\int f(\boldsymbol{u},\boldsymbol{w}) \psi(\boldsymbol{u}) \psi(\boldsymbol{w}) d\boldsymbol{u} \, d\boldsymbol{w}$. A_0 describes the loss of entropy with molecular alignment, while A_1 expresses the Onsager free energy of steric interaction in the second virial approximation [9]. Following Doi and Edwards [10], the rotational diffusivity is approximated by

$$\hat{D}_r \approx \bar{D}_r = D_r \left[\frac{4}{\pi} \langle\langle \sqrt{1 - (\boldsymbol{u} \cdot \boldsymbol{w})^2} \rangle\rangle \right]^{-2}, \quad (3)$$

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where D_r, the rotational diffusion coefficient for a rod in an isotropic, semidilute solution of like rods, is related to the rotational diffusion constant for a dilute solution, D_{r0}, by $D_r = c D_{r0} (\nu L)^{-2}$ with an empirical coefficient c. Nonlinearity of Eq. (1) in ψ brought about by the potential (2b) reflects the mean-field nature of the Onsager theory of the excluded-volume effect. The self-consistent potential, identified by Doi [10], is related to the free energy of interaction, $V(\boldsymbol{u}) = k_B T \delta A_1 / \delta \psi(\boldsymbol{u})$. Various phases of the LCP are conveniently described by the order parameter $\boldsymbol{S} = \langle \boldsymbol{uu} - (1/3)\boldsymbol{1} \rangle$, where $\boldsymbol{1}$ is the unit tensor. It is reasonable therefore to look for approximate formulations of the dynamics in terms of the order parameter alone. However, as mentioned above, the time evolution equation for $\boldsymbol{S}$ couples to an infinite number of moments of ψ. In the derivation given by Doi, this difficulty was circumvented by replacing the Onsager potential (2b) by a different, phenomenological expression of the Maier-Saupe type [2]

$$A_1^{MS} = a_0 - \frac{a_1}{2} U \boldsymbol{S} : \boldsymbol{S}, \tag{4}$$

where a_0 and a_1 are parameters independent of ψ. A further separate treatment of the diffusivity (3) is also necessary. A compact presentation of the entire development is given by Doi and Edwards [10]. The Doi model with the Maier-Saupe potential (4) constitutes the basic kinetic model of LCP used by many authors for analytical studies to derive equations for the order parameter. As is well-known, the kinetic equation (1) with the potential (4) does not give a closed equation for the order parameter but contains also the higher-order moment $\langle \boldsymbol{uuuu} \rangle$, and therefore constitutes a further problem of closure. The original Doi approach was based on the decoupling approximation for the fourth-order moments of ψ in terms of $\boldsymbol{S}$. Improvements on the decoupling approximation are currently under active research [5].

III. GENERATING MOMENT EQUATIONS

In this paper we demonstrate that a different self-consistent treatment of the kinetic equation (1) is possible. Modifications concern only the relaxational part of Eq. (1), specifically, the excluded-volume potential (2b) and the diffusivity (3), and therefore we consider the case $\boldsymbol{\kappa} = 0$ in the sequel to simplify notations. Specifically, we employ the cumulant expansion of the potential (2b) and the diffusivity (3). The leading term of this expansion results in an effective potential that differs from the Maier-Saupe potential (4), and which contains a nonpolynomial dependence on the order parameter $\boldsymbol{S}$.

In the second virial approximation, the free energy of interaction A_1 can be written as $A_1 = (\nu/2)\langle\langle \beta(\boldsymbol{u},\boldsymbol{w}) \rangle\rangle$. If only excluded-volume interactions are present, the second virial coefficient β corresponding to the Onsager expression (2b) is of the form $\beta(\boldsymbol{u},\boldsymbol{w}) = \beta[(\boldsymbol{u} \cdot \boldsymbol{w})^2]$, with $\beta(x) = 2bL^2\sqrt{1-x}$. Specifically, expanding $\beta(x)$ in a Taylor series and interchanging summation and averaging in this expansion, we get $\langle\langle \beta(x) \rangle\rangle = \Sigma_{n=0}^{\infty} a_n \langle\langle x^n \rangle\rangle$, where a_n are numerical coefficients. Each average $\langle\langle x^n \rangle\rangle$ can be represented in terms of cumulants $\langle\langle x^k \rangle\rangle_c$ of order $k \leq n$. Resummation of the series leads to

$$\langle\langle \beta(x) \rangle\rangle = \beta(\langle\langle x \rangle\rangle) + \sum_{m=1}^{\infty} \frac{1}{m!} \left(\frac{\langle\langle x^2 \rangle\rangle_c}{2} \right)^m \beta^{(2m)}(\langle\langle x \rangle\rangle)$$
$$+ \cdots, \tag{5}$$

where $\beta^{(2m)}$ is the $2m$th derivative of β and ellipses denote terms including third or higher-order cumulants as factors. Therefore, the functional A_1 (2b) can be split as $A_1 = A_1^{(1)} + B$, where $A_1^{(1)}$ is the free energy, corresponding to the total neglect of second and higher-order cumulants in each term of the expansion,

$$A_1^{(1)} = \frac{U}{2} \sqrt{1 - \langle \boldsymbol{uu} \rangle : \langle \boldsymbol{uu} \rangle}. \tag{6}$$

In terms of the order parameter $\boldsymbol{S}$, $A_1^{(1)}$ may be rewritten as $A_1^{(1)} = (U/\sqrt{6}) \sqrt{1 - (3/2)\boldsymbol{S} : \boldsymbol{S}}$. By the mean value theorem, it is easy to see that $A_1^{(1)}$ gives an upper bound to A_1, $A_1 \leq A_1^{(1)}$, for the present case of excluded-volume interactions. The functional B contains the higher-order cumulants. While all powers of the second cumulants are displayed in Eq. (5), in general it is not a priori clear whether it is more important to keep powers of the second cumulant or higher cumulants. However, we generally expect the linear term in the second order cumulant to be most important. The corresponding term $m=1$ in Eq. (5), $A_1^{(2)} = (1/2)\langle\langle x^2 \rangle\rangle_c \beta''(\langle\langle x \rangle\rangle)$, gives the first nonvanishing contribution to B,

$$A_1^{(2)} = -\frac{U}{16} \langle\langle [(\boldsymbol{u} \cdot \boldsymbol{w})^2 - \langle \boldsymbol{uu} \rangle : \langle \boldsymbol{uu} \rangle]^2 \rangle\rangle (1 - \langle \boldsymbol{uu} \rangle : \langle \boldsymbol{uu} \rangle)^{-3/2}. \tag{7}$$

Keeping only the first N cumulants in the expansion (5), the functional (2b) is approximated by nonlinear functions of the first $2N$ moments of ψ. Inserting this approximation in the time evolution equation (1) amounts to an approximation of the self-consistent Onsager potential V in terms of a polynomial of order $2N$ in $\boldsymbol{u}$ but with nonlinear coefficients. In this approximation, the time evolution of the $2n$th moment contains only the first $(2n+2N)$th moments. With this, moment equations can be generated that approach the original equations in a systematic way, thereby containing only a finite number of moments at each stage.

IV. TESTING THE APPROXIMATION

Clearly, the above procedure is most valuable if the first terms, $A_1^{(1)}$, etc., already provide a good approximation to the full expression A_1. While the general validity of $A_1^{(1)}$ as a good approximation to A_1 is a rather delicate problem, it should be mentioned that it is so at least in two limiting cases. Namely, for the isotropic state, the value of $A_1^{(1)}$ differs from A_1 for less than 5%, while in the fully ordered state the approximation (6) becomes exact. Moreover, on the submanifold of distribution functions of the form

$$\psi_\alpha(\boldsymbol{u}) = \frac{\alpha}{4\pi \sinh \alpha} \cosh(\alpha \boldsymbol{u} \cdot \boldsymbol{n}), \tag{8}$$

where $\boldsymbol{n}$ is an arbitrary unit vector, and $0 \leq \alpha \leq \infty$, the functional $A_1^{(1)}$ turns out to approximate A_1 very well for all
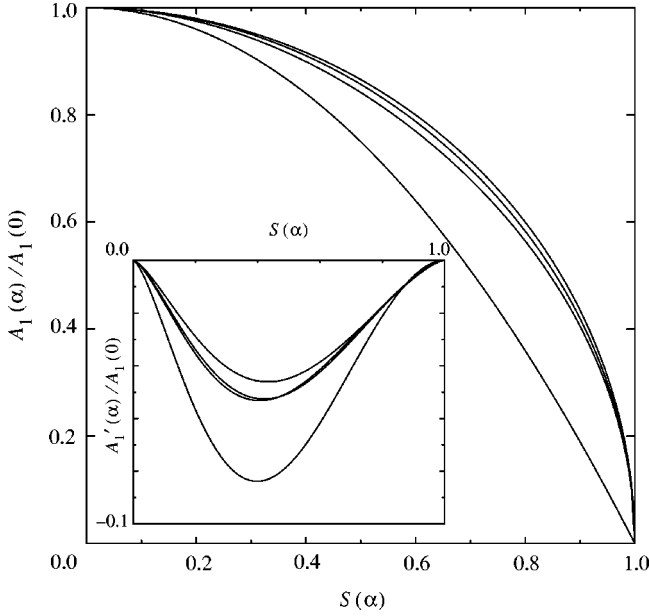
FIG. 1. Free energy of excluded-volume interaction for distribution functions (8) plotted against the scalar order parameter $S(\alpha)$. From top to bottom: approximation $A_1^{(1)}$ (6), with first correction $A_1^{(1)} + A_1^{(2)}$ (7), true Onsager expression A_1 (2b), and the Maier-Saupe free energy A_1^{MS} (4), when the limits $S=0$ and $S=1$ are matched. In the inset, the derivative of the above functions is shown as a function of $S(\alpha)$. The order of the curves from top to bottom is the same.

values of the parameter α between the isotropic state, $\alpha = 0$, and the fully ordered state, $\alpha = \infty$. To show this, we plot in Fig. 1 the functions $A_1(\alpha)$, $A_1^{(1)}(\alpha)$, and $A_1^{(1)}(\alpha) + A_1^{(2)}(\alpha)$, what result upon inserting the ansatz (8) into Eqs. (2b), (6), and (7), respectively. Note that $A_1(\alpha)$, $A_1^{(1)}(\alpha)$, and $A_1^{(2)}(\alpha)$ can be calculated analytically. For convenience, we plot the functions against the scalar order parameter, defined as $S = \sqrt{(3/2)\boldsymbol{S}:\boldsymbol{S}}$. Including $A_1^{(2)}$ does not only reduce the error of the approximate value of A_1 in the isotropic state to 1.5%, but improves the accuracy of the approximation over the whole range of S. For comparison, we included in Fig. 1 also the free energy A_1^{MS}, corresponding to the Maier-Saupe expression (4), thereby choosing the undetermined constant so that the limit of the fully ordered state is matched correctly. Note, however, that in any case A_1^{MS} decays asymptotically like $1/\alpha$, for $\alpha \gg 1$, whereas A_1 and $A_1^{(1)}$ behave like $1/\sqrt{\alpha}$ in this regime. We included in Fig. 1 also the derivative of the above functions, since they are related to the self-consistent potential V. Figure 1 shows that also the derivative of $A_1^{(1)}$ provides a good approximation to the derivative of A_1, with correct limiting behavior near the isotropic and fully ordered state. Note that including the first correction $A_1^{(2)}$ yields excellent agreement to the true Onsager prediction. The Maier-Saupe potential captures the main features but, besides an undetermined constant, shows the wrong behavior near the fully ordered state. The ansatz (8), originally proposed by Onsager [9], is known to approximate the equilibrium distribution very well. Therefore, we conclude that $A_1^{(1)}$ represents a good approximation to A_1, at least on a representative subset of distribution functions.

V. THERMODYNAMIC CONSISTENCY

It is worth mentioning that the presentation given so far can easily be cast into the recently developed formalism of nonequilibrium thermodynamics, called general equation for the nonequilibrium reversible-irreversible coupling (GENERIC) [11,12]. In the absence of potential forces, the example of rigid dumbbells, which are equivalent to the model of rigid rods, is formulated within the GENERIC formalism in Ref. [13]. The mean field potentials considered above can be included in a straightforward manner, if we recognize that $A_1 = -S_1$, where S_1 is the entropic contribution per molecule to the free energy of interaction divided by k_B. Formulating the original model as well as the approximations within the GENERIC formalism guarantees that our treatment is in accordance with the principles of nonequilibrium thermodynamics. This becomes especially important if the present model is considered in nonisothermal situations. For example, the structure of the GENERIC formalism requires the polymeric contribution to the elastic stress to be

$$\sigma_{\alpha\beta}^e = 3\nu k_B T S_{\alpha\beta} - \nu k_B T \left\langle \left(\boldsymbol{u} \times \mathcal{R} \frac{\delta S_1}{\delta \psi} \right)_\alpha u_\beta \right\rangle. \quad (9)$$

Equation (9) agrees with the result of Doi [10], obtained upon varying the free energy functional.

VI. LOWEST ORDER APPROXIMATION

In the sequel, we will adopt the lowest order approximation $A = A^{(1)} = A_0 + A_1^{(1)}$, where $A_1^{(1)}$ is given by Eq. (6), and A_0 is given by Eq. (2a). This amounts to neglect of all higher order correlations in Eq. (5), or, equivalently, setting $B = 0$. Substituting $A^{(1)}$ instead of A into Eq. (1), we derive

$$\partial_t \psi = \mathcal{R} \cdot \hat{D}_r \left[\mathcal{R}\psi - \psi \mathcal{R} \left(\frac{U \boldsymbol{u}\boldsymbol{u}:\langle \boldsymbol{u}\boldsymbol{u} \rangle}{2\sqrt{1 - \langle \boldsymbol{u}\boldsymbol{u} \rangle : \langle \boldsymbol{u}\boldsymbol{u} \rangle}} \right) \right]. \quad (10)$$

It is now possible to identify the self-consistent potential as

$$V^{(1)}(\boldsymbol{u}) = \left(\frac{U k_B T}{2} \right) \frac{1 - \boldsymbol{u}\boldsymbol{u}:\langle \boldsymbol{u}\boldsymbol{u} \rangle}{\sqrt{1 - \langle \boldsymbol{u}\boldsymbol{u} \rangle : \langle \boldsymbol{u}\boldsymbol{u} \rangle}}, \quad (11)$$

which can be compared to the expression obtained from inserting the Maier-Saupe free energy (4) into Eq. (1),

$$V_{MS}(\boldsymbol{u}) = a_2 - a_1 U k_B T \boldsymbol{u}\boldsymbol{u}:\langle \boldsymbol{u}\boldsymbol{u} \rangle, \quad (12)$$

where a_2 is an arbitrary constant. The normalized equilibrium solutions to Eq. (10) are $\psi_{eq}^{(1)} = Z^{-1} \exp[-V^{(1)}/k_B T]$.

The rotational diffusivity (3) is related to the free energy of interaction, since $\bar{D}_r = D_r [8A_1/(\pi U)]^{-2}$. Substituting $A_1 = A_1^{(1)}$ gives

$$\bar{D}_r^{(1)} = (3\pi^2/32) D_r [1 - (3/2)\boldsymbol{S}:\boldsymbol{S}]^{-1}. \quad (13)$$

The diffusion coefficient $\bar{D}_r^{(1)}$ (13) is positive in the entire physically meaningful range of the order parameter S. Expression (13) should be compared with the Doi phenomenological result,

$$\bar{D}_{rD} = D_r[1 - (3/2)S:S]^{-2}. \tag{14}$$

While we have not found an argument which of the two powers, -1 or -2, is more consistent, it should be stressed that our derivation of the diffusion coefficient does not need any further assumptions or adjustable parameters, while the derivation of Eq. (14) [1,10] requires the matching of $\bar{D}_r$, respectively A_1^{MS}, in both the isotropic and the fully ordered state. Due to its relation to $A_1^{(1)}$, the diffusion coefficient $\bar{D}_r^{(1)}$ (13) has a correct limit in the fully ordered state ($D_r/\bar{D}_r^{(1)} = 0$ as soon as $S:S = 2/3$ in the ordered state), while the opposite limit of the isotropic state ($\bar{D}_r = D_r$) is matched within 8%. Again, the first correction (7) reduces the error in this limit to less than 3%.

If we adopt (3) and approximate $\bar{D}_r$ by $\bar{D}_r^{(1)}$ (13), the time evolution of the order parameter S can be derived from Eq. (10) by the so-called Prager procedure,

$$\partial_t S = -6\bar{D}_r^{(1)}S + 6\bar{D}_r^{(1)}\frac{U'}{\sqrt{1-(3/2)S:S}}(S \cdot \langle uu \rangle - S:\langle uuuu \rangle), \tag{15}$$

with $U' = U/\sqrt{6}$. This expression differs from the result of Doi [1] not only in the diffusion coefficient and in the reduced excluded-volume U due to the undetermined constant in the Maier-Saupe potential (12), but contains a nonpolynomial dependence on the order parameter S, which becomes important in the nematic state.

VII. CONCLUSION

We have presented a systematic procedure that allows to derive approximate moment equations for the Doi model of LCP, which contain only a finite number of higher order moments. The first approximation for the Onsager excluded-volume interaction results in an effective potential (11) proportional to uu, but different from the Maier-Saupe form (12) and without free parameters. We find indications that Eq. (11) approximates the true Onsager potential better than the Maier-Saupe potential. For higher accuracy, the first correction seems to be the most important contribution. All these approximations are in accordance with nonequilibrium thermodynamics.

Note that we have not addressed the problem of solving the resulting kinetic equations or "closing" the moment equations. This work is currently under preparation. Nevertheless, for comparing Eq. (15) to the corresponding equation with the Maier-Saupe potential, we follow Refs. [1,10] and consider the decoupling approximation $S:\langle uuuu \rangle = S:\langle uu \rangle \langle uu \rangle$. If order parameter is assumed to be of the form $S_{\alpha\beta} = S(t)[n_\alpha n_\beta - \delta_{\alpha\beta}]$, the relaxation equation for the scalar parameter S is found to be as follows:

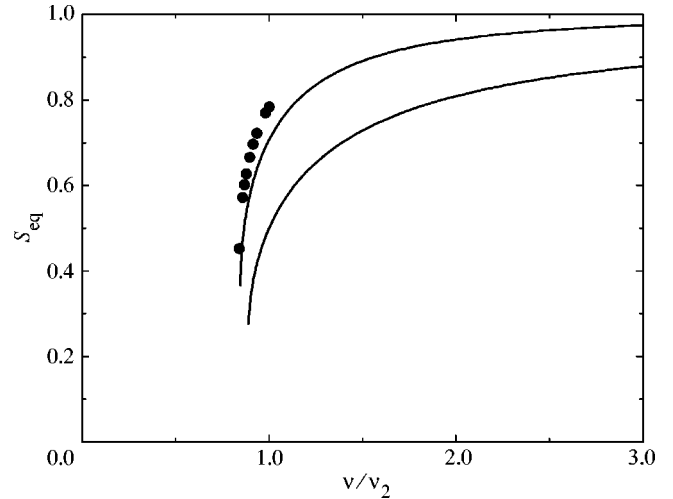$$\partial_t S = -6\bar{D}_r^{(1)}\frac{\partial A^{(1)}(S,U')}{\partial S}, \tag{16a}$$

FIG. 2. Equilibrium order parameter S_{eq} as a function of ν/ν_2. The figure shows the behavior due to the Maier-Saupe potential (17), lower curve, and the solution of (18) corresponding to $A^{(1)}$, upper curve, in the decoupling approximation. Solid circles indicate the order parameter for the true Onsager potential in the static case (from [15]).

$$A^{(1)}(S,U') = \frac{S^2}{2} - \frac{U'}{9}\sqrt{1-S^2}\left(1 - \frac{3S}{2} + 2S^2\right) - \frac{U'}{6}\arcsin(S), \tag{16b}$$

where $U' = U/\sqrt{6}$. Due to a nonpolynomial character of the function $A^{(1)}$ (16b), the relaxation equation (16a) differs formally from the Landau-de Gennes counterpart derived by Doi for the Maier-Saupe potential. Expansion of the function (16b) around $S = 0$ reproduces the result of Doi for the Maier-Saupe potential, subject to a renormalization of the strength of the excluded-volume potential, and a difference in the coefficient in front of the S^4 term. Moreover, the relaxation implied by $A^{(1)}$ (16b) is qualitatively similar to the one given by Doi result and distinguishes the same three regimes. For $U < U_1$, $A^{(1)}$ has only one minimum at $S = 0$, so that the system finally becomes isotropic. For $U_1 < U < U_2$, a second local minimum occurs. The system either becomes isotropic or nematic depending on the initial value of S. Finally, for $U > U_2$, the isotropic state becomes unstable and the system always approaches a nematic state.

Due to the undetermined constant a_1 in the Maier-Saupe potential (12), the Doi theory predicts the values U_1 and U_2 also in terms of a_1. On the contrary, the self-consistent potential (11) contains no free parameters, so that $U_1 = 3^{1/4}\sqrt{8}/(\sqrt{3}-1) \approx 6.22$ and $U_2 = 3\sqrt{6} \approx 7.34$ may directly be compared to the values in the Onsager theory $U_1 = 8.38$ and $U_2 = 10.67$. However, the values of the order parameter $S_1 = 1/4$ and $S_2 = 1/2$ at U_1 respectively U_2 in the Doi theory do not depend on a_1 and can therefore be compared to the values predicted by Eq. (11): $S_1 = (\sqrt{3}-1)/2 \approx 0.37$ and $S_2 = 1/\sqrt{2} \approx 0.71$.

In Fig. 2, the equilibrium order parameter S_{eq} is shown as a function of ν/ν_2. The lower solid line shows the prediction

of the Doi theory, whereas the upper solid line corresponds to the approximation (11). For the Maier-Saupe potential, $S_{eq} \neq 0$ is given by

$$S_{eq} = \frac{1}{4} + \frac{3}{4}\sqrt{1 - \frac{8\nu_2}{3\nu}}. \tag{17}$$

For the free energy (16b), S_{eq} is given implicitly as the solution to the algebraic equation

$$\frac{1 + S_{eq} - 2S_{eq}^2}{\sqrt{1 - S_{eq}^2}} = \frac{\nu_2}{\nu}. \tag{18}$$

For large values of ν/ν_2, the solution (18) approaches the value $S_{eq} = 1$ and asymptotically behaves like the solution of the Doi theory $S_{eq} \sim 1 - \nu_2/\nu$, for large ν. Note that the decoupling approximation corrects the asymptotic behavior of the Maier-Saupe potential near the fully ordered state.

As is well-known, the detailed form of the interaction potential can have a significant effect on the behavior of the order parameter in the nematic phase [14]. Specifically, the amount of order at the transition is known to be much smaller in the Maier-Saupe theory than in the Onsager model. For comparison, we included in Fig. 2 the values of the order parameter obtained from minimizing the true Onsager free energy numerically [15], where ν_2 now corresponds to the true nematic transition. Although the analysis of the phase transitions via the dynamical approach is affected by the use of the decoupling approximation, the prediction of the self-consistent approach is much closer to the true Onsager values than is the Maier-Saupe potential. Finally, it should be mentioned that approximations to the Onsager potential such as Eqs. (6) and (7) can also be used in the case of potential flows, following the approach of Thirumalai [7] without additional assumptions.

To summarize, we have developed a direct approach to the Doi model with the Onsager potential. We have demonstrated that the resulting kinetic equation has much in common with the Doi model with the phenomenological Maier-Saupe potential. Corrections to the approximation developed here can be found in a systematic way from Eqs. (5)–(7) by taking into account higher order correlations. The approach to derive self-consistent moment equations is applicable to other kinetic equations which can be cast into the form (1).

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