Validity of a macroscopic description in dilute polymeric solutions

P. Ilg and I. V. Karlin*
ETH-Zürich, Department of Materials, Institute of Polymers, CH-8092 Zürich, Switzerland
(Received 2 February 2000)

Derivation of macroscopic equations from the simplest dumbbell models is revisited. It is demonstrated that the onset of the macroscopic description is sensitive to the flows. For Peterlin's approximation [Makromol. Chem. **338**, 44 (1961)] to Warner's finitely extensible nonlinear elastic spring-force model [Ind. Eng. Chem. Fundam. **11**, 379 (1972)] (FENE-P), small deviations from the Gaussian solution undergo a slow relaxation before the macroscopic description sets on. Some consequences of these observations are discussed.

PACS number(s): 83.20.Di, 05.20.Dd, 05.10.Gg

Dumbbell models of dilute polymeric solutions are the simplest kinetic (microscopic) models of complex fluids [1]. The macroscopic description in this context is an equation for the stress tensor (the constitutive equation). Since simple models form a basis for our understanding of how the macroscopic description sets on within the kinetic picture, it makes sense to study the derivation of the macroscopic description in every detail for those cases.

In this paper, we revisit the derivation of the constitutive equation from the simplest (solvable) dumbbell models. We focus our attention on the following question: *How well is the macroscopic description represented by the classical Gaussian solution?* It appears that the answer to this question is sensitive to the flow. For weak enough flows, all microscopic solutions approach rapidly the Gaussian solution, which manifests validity of the standard macroscopic description. However, for strong flows, relaxation to the Gaussian solution becomes much slower, significant deviations persist over long times, in which case the macroscopic description is less valid. We discuss a possible impact of this observation on the statement of the problem of macroscopic description in related more complicated problems.

We consider the following simplest one-dimensional kinetic equation for the configuration distribution function $\Psi(q,t)$, where q is the reduced vector connecting the beads of the dumbbell:

$$\partial_t \Psi = -\partial_q \{\alpha(t) q \Psi\} + \frac{1}{2}\partial_q^2 \Psi. \quad (1)$$

Here

$$\alpha(t) = \kappa(t) - (1/2) f(M_1(t)), \quad (2)$$

$\kappa(t)$ is the given time-dependent velocity gradient, t is the reduced time, and the function $-fq$ is the reduced spring force. Function f may depend on the second moment of the distribution function $M_1 = \int q^2 \Psi(q,t) dq$. In particular, the case $f \equiv 1$ corresponds to the linear Hookean spring, while $f = [1 - M_1(t)/b]^{-1}$ corresponds to Peterlin's approximation to Warner's finitely extensible nonlinear elastic spring-force model (FENE-P, Ref. [2]). The second moment M_1 occurring in the FENE-P force f is the result of the preaveraging approximation to the original FENE model (with nonlinear spring force $f = [1 - q^2/b]^{-1}$). Leading to closed constitutive equations, the FENE-P model is frequently used in simulations of complex rheological flows as well as the reference for more sophisticated closures to the FENE model [3]. The parameter b changes the characteristics of the force law from Hookean at small extensions to a confining force for $q^2 \to b$. Parameter b is roughly equal to the number of monomer units represented by the dumbbell and should therefore be a large number. In the limit $b \to \infty$, the Hookean spring is recovered. Recently, it has been demonstrated that the FENE-P model appears as first approximation within a systematic self-consistent expansion of nonlinear forces [4].

Equation (1) describes an ensemble of noninteracting dumbbells subject to a pseudoelongational flow with fixed kinematics. As it is well known, the Gaussian distribution function,

$$\Psi^{\mathrm{G}}(M_1) = (1/\sqrt{2\pi M_1}) \exp[-q^2/(2M_1)], \quad (3)$$

solves Eq. (1) provided the second moment M_1 satisfies

$$\frac{dM_1}{dt} = 1 + 2\alpha(t) M_1. \quad (4)$$

Solution (3) and (4) is the valid macroscopic description if all other solutions of Eq. (1) are rapidly attracted to the family of Gaussian distributions (3). In other words [5], the special solution (3) and (4) is the macroscopic description if Eq. (3) is the stable invariant manifold of the kinetic equation (1). If not, then the Gaussian solution is just a member of the family of solutions, and Eq. (4) has no meaning of the macroscopic equation. Thus, the complete answer to the question of validity of Eq. (4) as the macroscopic equation requires a study of dynamics in the neighborhood of the manifold (3). Because of the simplicity of model (1), this is possible to a satisfactory level even for M_1-dependent spring forces.

Let $M_n = \int q^{2n} \Psi dq$ denote the even moments (odd moments vanish by symmetry). We consider deviations $\mu_n = M_n - M_n^{\mathrm{G}}$, where $M_n^{\mathrm{G}} = \int q^{2n} \Psi^{\mathrm{G}} dq$ are moments of the

*Corresponding author. Electronic address: ikarlin@ifp.mat.ethz.ch

 ©2000 The American Physical Society

Gaussian distribution function (3). Let $\Psi(q,t_0)$ be the initial condition to Eq. (1) at time $t=t_0$. Introducing functions,

$$p_n(t,t_0)=\exp\left[2n\int_{t_0}^{t}\alpha(t')dt'\right], \tag{5}$$

where $t\geqslant t_0$, and $n\geqslant 2$, the *exact* time evolution of the deviations μ_n for $n\geqslant 2$ reads

$$\mu_2(t)=p_2(t,t_0)\mu_2(t_0), \tag{6}$$

and

$$\mu_n(t)=\left[\mu_n(t_0)+n(2n-1)\int_{t_0}^{t}\mu_{n-1}(t')p_n^{-1}(t',t_0)dt'\right]p_n(t,t_0), \tag{7}$$

for $n\geqslant 3$. Equations (5), (6), and (7) describe evolution near the Gaussian solution for arbitrary initial condition $\Psi(q,t_0)$. Notice that explicit evaluation of the integral in Eq. (5) requires solution to the moment equation (4), which is not available in the analytical form for the FENE-P model.

It is straightforward to conclude that any solution with a non-Gaussian initial condition converges to the Gaussian solution asymptotically as $t\to\infty$ if

$$\lim_{t\to\infty}\int_{t_0}^{t}\alpha(t')dt'<0. \tag{8}$$

However, even if this asymptotic condition is met, deviations from the Gaussian solution may survive for considerable *finite* times. For example, if for some finite time T, the integral in Eq. (5) is estimated as $\int_{t_0}^{t}\alpha(t')dt'>\alpha(t-t_0)$, $\alpha>0$, $t\leqslant T$, then the Gaussian solution becomes exponentially unstable during this time interval. If this is the case, the moment equation (4) cannot be regarded as the macroscopic equation. Let us consider specific examples.

For the Hookean spring ($f\equiv 1$) under a constant elongation ($\kappa=\text{const}$), the Gaussian solution is exponentially stable for $\kappa<0.5$, and it becomes exponentially unstable for $\kappa>0.5$. The exponential instability in this case is accompanied by the well-known breakdown of the solution to Eq. (4) due to infinite stretching of the dumbbell. Similar instability has been found numerically in three-dimensional flows for high Weissenberg numbers [6].

A more interesting situation is provided by the FENE-P model. As it is well known, due to the singularity of the FENE-P force, the infinite stretching is not possible, and solutions to Eq. (4) are always well behaved. Thus, in this case, nonconvergence to the Gaussian solution (if any), does not interfere with the collapse of the solution to Eq. (4).

Equations (4) and (6) were integrated by the fifth-order Runge-Kutta method with adaptive time step. The FENE-P parameter b was set equal to 50. The initial condition was $\Psi(q,0)=C(1-q^2/b)^{b/2}$, where C is the normalization (the equilibrium of the FENE model, notoriously close to the FENE-P equilibrium [7]). For this initial condition, in particular, $\mu_2(0)=-6b^2/[(b+3)^2(b+5)]$ which is about 4% of the value of M_2 in the Gaussian equilibrium for $b=50$. In Fig. 1 we demonstrate deviation $\mu_2(t)$ as a function of time for several values of the flow. Function $M_1(t)$ is also given for comparison. For small enough κ we find an adiabatic regime, that is, μ_2 relaxes exponentially to zero. For stronger flows, we observe an initial *fast runaway* from the invariant manifold with $|\mu_2|$ growing over three orders of magnitude compared to its initial value. After the maximum deviation has been reached, μ_2 relaxes to zero. This relaxation is exponential as soon as the solution to Eq. (4) approaches the steady state. However, the time constant for this exponential relaxation $|\alpha_\infty|$ is very small. Specifically, for large κ,

$$\alpha_\infty=\lim_{t\to\infty}\alpha(t)=-\frac{1}{2b}+O(\kappa^{-1}). \tag{9}$$

Thus, the steady-state solution is unique and Gaussian but the stronger the flow, the larger is the initial runaway from the Gaussian solution, while the return to it thereafter becomes flow independent. Our observation demonstrates that, though the stability condition (8) is met, *significant deviations from the Gaussian solution persist over the times when the solution of Eq. (4) is already reasonably close to the stationary state.* If we accept the usually quoted physically reasonable minimal value of parameter b of the order 20 then the minimal relaxation time is of order 40 in the reduced time units of Fig. 1. We should also stress that the two limits, $\kappa\to\infty$ and $b\to\infty$, are not commutative; thus it is not surprising that the estimation (9) does not reduce to the abovementioned Hookean result as $b\to\infty$. Finally, peculiarities of convergence to the Gaussian solution are even furthered if we consider more complicated (in particular, oscillating) flows $\kappa(t)$. We close this paper with several comments.

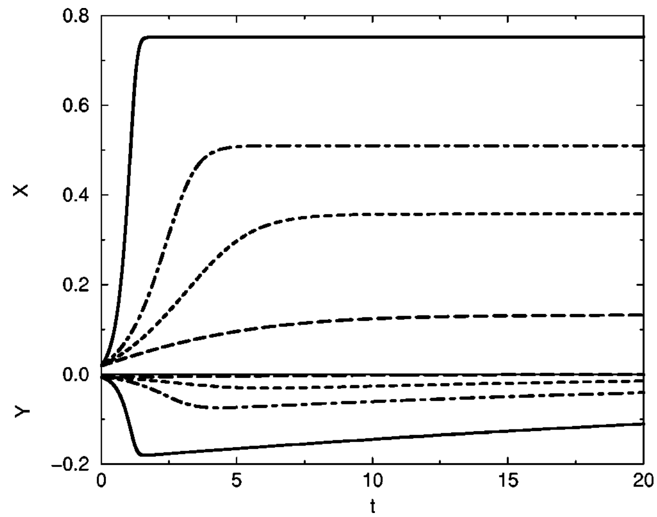

FIG. 1. Deviations of reduced moments from the Gaussian solution as a function of reduced time t in pseudoelongation flow for the FENE-P model. Upper part: reduced second moment $X=M_1/b$. Lower part: reduced deviation of fourth moment from Gaussian solution $Y=-\mu_2^{1/2}/b$. Solid: $\kappa=2$, dashed-dotted: $\kappa=1$, dashed: $\kappa=0.75$, long dashed: $\kappa=0.5$.

(i) From the standpoint of a general theory of macroscopic description [5], the set of Gaussian distributions (3) is the invariant manifold of the kinetic equation (1), while Eq.

(4) is the dynamic equation on the invariant manifold written in natural internal variables of this manifold. This macroscopic description is supplemented by Eqs. (6) and (7), which give the dynamics near the invariant manifold. Though the models we have considered here are simple, our observations demonstrate that relaxation to the invariant manifold may be very slow depending on the flow.

(ii) For more difficult models, such as the FENE model, finding invariant manifold is a difficult task. However, there exist methods to derive approximate invariant manifolds by iteration procedures [5]. It has been shown recently that the macroscopic description of any dumbbell model is a revised Oldroyd eight-constant model for low Deborah number flows [8]. For strong flows, *ad hoc* closures are frequently used and little is known about their stability and whether they respect the invariance principle. It would be interesting to find out whether good closure approximations correspond to invariant manifolds, identify them, and learn about their stability. Work in this direction is currently in preparation.

Authors gratefully acknowledge the comments of Professor H. C. Öttinger.

[1] R. B. Bird, C. F. Curtiss, R. C. Armstrong, and O. Hassager, *Dynamics of Polymeric Liquids, Vol. 2, Kinetic Theory*, 2nd ed. (Wiley, New York, 1987).

[2] R. B. Bird, P. J. Dotson, and N. L. Johnson, J. Non-Newtonian Fluid Mech. **7**, 213 (1980); **8**, 193 (1981); **15**, 225 (1984).

[3] G. Lielens, P. Halin, I. Jaumin, R. Keunings, and V. Legat, J. Non-Newtonian Fluid Mech. **76**, 249 (1998).

[4] P. Ilg, I. V. Karlin, and H. C. Öttinger, Phys. Rev. E **60**, 5783 (1999).

[5] A. N. Gorban and I. V. Karlin, Transp. Theory Stat. Phys. **23**, 559 (1994).

[6] N. Phan-Thien, C. G. Goh, and J. D. Atkinson, J. Non-Newtonian Fluid Mech. **18**, 1 (1985).

[7] M. Herrchen, and H. C. Öttinger, J. Non-Newtonian Fluid Mech. **68**, 17 (1997).

[8] V. B. Zmievski, I. V. Karlin, and M. Deville, Physica A **275**, 152 (2000).