Supersymmetry solution for finitely extensible dumbbell model

P. Ilg *, I. V. Karlin

Department of Materials, Institute of Polymers, ETH Zürich, CH–8092 Zürich, Switzerland

S. Succi

Institute Applied Computing, CNR, Viale Policlinico 137, 00161 Rome, Italy

Exact relaxation times and eigenfunctions for a simple mechanical model of polymer dynamics are obtained using supersymmetry methods of quantum mechanics. The model includes the finite extensibility of the molecule and does not make use of the self-consistently averaging approximation. The finite extensibility reduces the relaxation times when compared to a linear force. The linear viscoelastic behaviour is obtained in the form of the “generalized Maxwell model”. Using these results, a numerical integration scheme is proposed in the presence of a given flow kinematics.

I. INTRODUCTION

Simple mechanical models are helpful for understanding the complex dynamical behaviour of polymer molecules. The so-called elastic dumbbell constitutes the simplest model that captures the effects of stretching and orientation of the polymer. In this model the polymer is represented by two beads which are connected by a spring. The classical Hookean dumbbell model is characterised by a linear spring force. Its relaxation times decrease like the inverse of the mode number and the relaxation modulus is of a single exponential form. As noted by many authors, the finite extensibility of the molecules has to be included in order to avoid unphysical behaviour such as infinite viscosities predicted by the Hookean model. It is even argued “that taking into account the nonlinear stretching of the polymer molecules is the most important correction that should be made to the Hookean model in order to describe real systems” (Ref. 1, Chap. 13, p. 81). Molecular arguments suggest the finitely extensible spring force law to be given by the inverse Langevin function. Very often, rational or Padé approximations to the inverse Langevin function are used since they are analytically more tractable. All these approximations show the desired physical characteristics: a linear regime for small extensions of the spring and a divergence at a finite extension. These forces therefore prohibit the molecule to stretch beyond a certain value which is related to the total length of the chain.

In general, the finite extensibility of the molecules prohibits analytical expressions for the spectrum of relaxation times and the relaxation modulus. The shear relaxation modulus for the Warner spring force (so-called FENE model) has been determined numerically. The results are very close to those obtained for the Peterlin approximation to the Warner force (FENE-P model). The effect of the finite extensibility on the spectrum of relaxation times remains less studied. One might speculate that the finite extensibility decreases the slowest relaxation time as described by the Peterlin approximation. However, knowledge of the whole spectrum of relaxation times would be very desirable for understanding the dynamics of dumbbell models. It would allow, for example, to identify the number of relevant slow modes that contribute to the polymer contribution to the stress. Work in this direction was performed where the universal constitutive equation of dilute polymeric solutions was found. There, it was assumed that in the limit of low Deborah and Weissenberg number the modes corresponding to the two lowest eigenvalues dominate.

Here, we compute the relaxation times, eigenfunctions and the relaxation modulus of a finitely extensible dumbbell model exactly. The model is a one-dimensional version of the finitely extensible dumbbell models that uses trigonometric functions to approximate the inverse Langevin force. It is demonstrated that this force approximates the inverse Langevin function as good or even better than the Warner force frequently

*E-mail: pilg@ifp.mat.ethz.ch
used in Brownian dynamics simulations. The present study therefore clarifies the effect of the finitely extensible spring force on the spectrum of relaxation times, eigenfunctions and the relaxation modulus.

II. MODEL DESCRIPTION

Let \( f(q,t) \) denote the distribution function of the connector vector \( q \) of the dumbbell at time \( t \). The time evolution of \( f \) is given by the well-known Fokker-Planck equation

\[
\partial_t f = D \nabla \left( \{\nabla U + \nabla f \} \equiv L_{FP} f \right) \tag{1}
\]

where we have assumed that the spring force \( F \) can be derived from the dimensionless potential \( U \) via \( F(q) = k_BT \nabla U(q) \). The diffusion constant \( D = 2k_BT/\zeta \) is assumed to be independent of \( q \) which means we neglect hydrodynamic interactions. Note that the equilibrium distribution \( f_{eq} \) is given by \( f_{eq} = N_{eq} e^{-U}/N_{eq} \) being a normalization constant.

As is well-known the Fokker-Planck equation \( \text{II. MODEL DESCRIPTION} \) can be transformed into an equivalent imaginary time Schrödinger equation \( \text{II. MODEL DESCRIPTION} \). If \( \psi \) is a solution to

\[
-\partial_t \psi = DH\psi \tag{2}
\]

with the operator \( H = -(1/D)e^{U/2}L_{FP}e^{-U/2} \), then the function \( f(q,t) = \psi(q,t)f_{eq}^{1/2}(q) \) solves the original Fokker-Planck equation \( \text{II. MODEL DESCRIPTION} \). In particular, solving the eigenvalue problem \( H\psi_n = \lambda_n\psi_n \) leads immediately to the solution of the eigenvalue problem of the original Fokker-Planck operator \( L_{FP}f_n = -\lambda_n^{-1}f_n \) with \( \lambda_n^{-1} = D\epsilon_n \) and \( f_n = \psi_n f_{eq}^{1/2} \), where factors \( D \) are introduced for later convenience. Inserting \( \text{II. MODEL DESCRIPTION} \) for the Fokker-Planck operator \( H \) yields the form of the Schrödinger operator

\[
H = -\nabla^2 + V(q), \tag{3}
\]

where the Schrödinger potential \( V \) is given by \( V = \Phi^2 - \nabla\Phi \), with \( \Phi = \nabla U/2 \). Therefore, each solvable potential for the Schrödinger equation serves as a solvable model for the Fokker-Planck equation. In the following, we benefit from the fact that simple Schrödinger potentials \( V \) can have quite complicated counterparts \( U \) for the Fokker-Planck equation. Note also that operator \( H \) is Hermitian which is in general not the case for \( L_{FP} \).

The simplest exactly solvable potential for the Schrödinger equation related to finite extensibility is the three dimensional spherical symmetric infinite well potential. Up to a constant, the corresponding potential \( U \) of the Fokker-Planck equation is given by \( U = -2\ln \psi_{eq} \), where \( \psi_{eq} \) is the ground state of the Schrödinger problem. In the present case, the ground state is known to be \( \psi_{eq} \sim \sin(\pi q/q_0)/q \) leading to the force law

\[
F(q) = 2k_BT \frac{1-(\pi q/q_0)\cot(\pi q/q_0)q}{q} \tag{4}
\]

Since the force \( \text{II. MODEL DESCRIPTION} \) is one-parametric, the “spring constant” is no adjustable parameter but determined by the maximum extension \( q_0 \). If we define the spring constant \( h \) in the linear regime of \( \text{II. MODEL DESCRIPTION} \), the dimensionless finite extensibility parameter \( b = hq_0^2/(k_BT) \) is fixed: \( b = b_3 = 2\pi^2/3 \). Parameter \( b \) is known to denote roughly the number of monomer units represented by the dumbbell and should therefore be a large number. Thus, \( \text{II. MODEL DESCRIPTION} \) is of limited use. However, if \( b = b_3 \) is acceptable the force \( \text{II. MODEL DESCRIPTION} \) compares very well to the inverse Langevin force and Cohen’s Padé approximation, as shown in the inset of Fig. \( \text{II. MODEL DESCRIPTION} \). In this case, exact eigenfunctions of the Schrödinger operator are known to be the spherical Bessel functions and the exact eigenvalues are given by the zeros of these functions.

Let us now consider the one-dimensional case. One-dimensional nonlinear dumbbell models serve as toy models for various approximations that have been proposed to obtain closed constitutive equations for polymer solutions \( \text{II. MODEL DESCRIPTION} \). In addition, the one-dimensional models are believed to describe the elongational behaviour of the polymer molecule reasonably \( \text{II. MODEL DESCRIPTION} \). The one-dimensional version of the operators \( L_{FP} \) and \( H \) is obtained by replacing \( q \) with \( q \) and \( \nabla \) with \( dq/dq \).

To account for the finite extensibility we propose the following two parameter family of force laws

\[
F(q) = h q_1 \tan(q/q_1), \text{ for } -q_0 < q < q_0 \tag{5}
\]

where \( q_1 = 2q_0/\pi \) is determined by the maximum extension \( q_0 \) and \( h \) denotes the “spring constant” in the sense \( F(q) \to hq \) for \( q \to 0 \). In Fig. \( \text{II. MODEL DESCRIPTION} \) we plot the force \( F/h \) as a function of the reduced extension \( q/q_0 \). Fig.
also shows the Warner force $F(q) = hq/(1 - q^2/\tilde{q}_0^2)$, the inverse Langevin force $(h/3)L^{-1}(q/q_0)$, with $L(x) = \coth(x) - 1/x$ and Cohen’s Padé approximation $F(q) = (hq/3)(3 - q^2/\tilde{q}_0^2)/(1 - q^2/\tilde{q}_0^2)$ [4]. It is easily verified that these approximations give the correct limiting behaviour not only for small but also near the maximum extension. In addition, as can be seen from Fig. 3, the force (7) serves as an even better approximation to the inverse Langevin force as does the Warner force. Therefore we accept (7) as a reasonable force law to substitute for the inverse Langevin force in one dimension.

The potential $U$ from which the force (7) can be derived is $U(q) = -b_1 \ln \cos(q/q_1)$, where we introduced the dimensionless parameter $b_1 = hq^2/(kB_T) = (2/\pi)^2 b_1$. The equilibrium distribution function of the Fokker-Planck equation is $f_{\text{eq}}(q) = N_{\text{eq}} \cos^{b_1}(q/q_1)$, with $N_{\text{eq}}^{-1} = q_1^2 B[(b_1 + 1)/2, (b_1 + 1)/2]$, where $B[x,y]$ is the Beta function. The equilibrium distribution is very close to the one corresponding to the Warner force $f_{\text{eq}}(q) = N_{\text{eq}}(1 - q^2/\tilde{q}_0^2)^{b_1/2}$, with $N_{\text{eq}}^{-1} = q_0 B[1/2, (b + 2)/2]$.

III. SUPERSYMMETRY SOLUTION

To obtain exact eigenvalues and eigenfunctions of the Fokker-Planck equation (1) we exploit supersymmetry methods for the corresponding Schrödinger problem. Note, that the model force (7) belongs to the class of so-called Poeschl-Teller potentials which may also be solved exactly by Schrödinger’s factorization method [12]. Consider the original potential $U$ together with the inverted potential $-U$ and denote by $f$ the solution for the potential $U$ and $f^*$ for $-U$. As done before, defining $f_{\pm} = \sqrt{N_{\text{eq}}}e^{\pm U/2} \psi_{\pm}$ we arrive at $-(1/D) \partial_q \psi_{\pm} = H_{\pm} \psi_{\pm}$ with operators $H_{\pm} = \nabla^2 + V_{\pm}(q)$. The “partner potentials” are given by $V_{\pm}(q) = \Phi^2(q) \pm \Phi'(q)$ with $\Phi = U/2$, where $\Phi'$ and $U'$ denote the derivative of $\Phi$ resp. $U$ with respect to $q$. Schrödinger operators $H_{\pm}$ are very well studied in the literature since they occur in the so-called “Witten model” [3], which is the simplest model that shows all typical features of supersymmetric quantum mechanics.

Rewriting the force (7) as $F = 2kB_T \Phi$ we obtain $\Phi_{\pm}(q) = \alpha \tan(q/q_1)$, for $-q_0 < q < q_0$. We denote explicitly the dependence on the parameter $\alpha = b_1/(2q_1)$ which is proportional to the spring constant $h$. To proceed further we take advantage of the concept of “shape invariance” introduced by Gendenshtein [14]. The partner potentials $V_{\pm}(\alpha, q) = \Phi^2(\alpha, q) \pm \Phi'(\alpha, q)$ are called shape invariant if they are related by $V_{\pm}(\alpha_k, q) = V_{\pm}(\alpha_{k+1}, q) + R(q)$ where the new parameter $\alpha_{k+1}$ is a function of $\alpha_k$. In our case, $\Phi(\alpha, q) = \alpha \tan(q/q_1)$, shape invariance is easily verified for $\alpha_{k+1} = \alpha_k + 1/q_1$, $q_0 = \alpha$ and $R(\alpha_{k+1}) = \alpha_{k+1}^2 - \alpha_k^2$. For shape invariant potentials it is possible to define a series of operators that are isospectral except for the lowest eigenvalue which is $\sum_{k=1}^{\infty} R(\alpha_k)$. Going back to the original Schrödinger operator with lowest eigenvalue zero the complete spectrum is found to be $\epsilon_n = \sum_{k=1}^{\infty} R(\alpha_k)$ [12]. Inserting the special form of $R$ and multiplying by $D$, the exact (inverse) eigenvalues of the Fokker-Planck operator (1) are given by

$$\lambda_n = 2\lambda_H [n + n^2/b_1]^{-1}, \quad n = 1, 2, \ldots$$

where $\lambda_H = \zeta/(4h)$ is the time constant of the Hookean dumbbell. Note, that the eigenvalue zero corresponds to the equilibrium distribution. Corresponding eigenfunctions of operator $H$ are

$$\psi_n(q) = C_n a_n^\dagger a_{n-1}^\dagger \ldots a_0^\dagger \cos^{n+b_1/2}(q/q_1)$$

where $a_k^\dagger = -d/dq + \Phi_{\alpha_k}$ are generalized creation operators and $C_n$ denote normalization constants [13]. Remember that eigenfunctions of the original Fokker-Planck operator are obtained by $f_n = \psi_n f_{\text{eq}}^{1/2}$. The first eigenfunctions read: $f_0 = f_{\text{eq}}, f_1 = N_1 \sin(q/q_1)f_{\text{eq}}, f_2 = N_2 (b_1 + 1) \sin^2(q/q_1) - \cos^2(q/q_1)]f_{\text{eq}}$, where $N_1^2 = b_1 + 2$ and $N_2^2 = (b_1 + 4)/[2(b_1 + 1)]$. Note, that the eigenfunctions are orthonormal, $(f_n, f_m) = \delta_{nm}$, in the scalar product

$$\langle g, h \rangle = \int_{-q_0}^{q_0} f_{\text{eq}}^{-1}(q) g(q) h(q) dq.$$  

The linear viscoelastic behaviour can be obtained from linear response theory. For a given flow kinematics the perturbation of the Fokker-Planck operator is given by $L_{\text{ext}}(t) = -\partial_q \kappa(t) q$ where $\kappa(t)$ denotes the velocity gradient.

The polymer contribution to the stress, $\tau/(kB_T) = (\sigma, f) - 1, \quad \sigma = f_{\text{eq}} q U'$, is found to be
\[
\tau/(k_B T) = \int_{-\infty}^{t} G(t - t') \kappa(t') dt',
\]  

(9)

where the relaxation modulus \(G(t)\) is given by the equilibrium correlation function \(G(t) = \langle \sigma, e^{-t \lambda B} \sigma \rangle - 1\). Inserting the completeness relation of the eigenfunctions, \(\delta(q - q') = \sum_n \psi_n(q) \psi_n(q') = f_n^{-1}(q') \sum_n f_n(q) f_n(q')\), we obtain

\[
G(t) = \sum_{n=1}^{\infty} |\langle \sigma, f_{2n} \rangle|^2 e^{-t/\lambda_{2n}},
\]

(10)

which is of the form of the “generalized Maxwell model”. Note, that only even terms are included in (10) since they correspond to symmetric eigenfunctions whereas odd terms, corresponding to antisymmetric eigenfunctions, vanish by symmetry. Analytical expressions for \(G(t)\) resulting from dumbbell models are known for linear springs (Hookean dumbbell) where \(G(t) = e^{-t/\lambda_H}\). For the Warner spring force no such expression is available. The Peterlin approximation [4] leads also to a single-exponential form with relaxation time \(\lambda_H [1 + 1/b]^2\). The relaxation modulus (13) in our model shows a spectrum of relaxation times \(\lambda_n\), the lowest one being \(\lambda_2 = \lambda_H [1 + 2/b_1]^2\). The finite extensibility of the dumbbell therefore reduces the longest relaxation time when compared to the Hookean dumbbell. Only in the limit \(b \to \infty\) the result for the Hookean dumbbell is recovered. As can be seen from Fig. 2, \(G(t)\) is dominated by the lowest relaxation time since the relative weight of the higher modes decreases rapidly. For \(b = 20\), the relative weight of the first two modes is 99%, for \(b = 50\) the first mode carries 99% and for \(b \to \infty\) all weights except for the first vanish, reflecting the single-exponential form of the Hookean dumbbell.

The relaxation modulus determines the zero-elongational viscosity \(\dot{\eta}_0 = \int_0^\infty G(t) dt\). As shown in [4], \(\dot{\eta}_0\) can be expressed in terms of second moments of the equilibrium distribution function for arbitrary dumbbell models. In our model, the resulting integral cannot be done analytically.

Knowledge of the exact relaxation times and eigenfunctions (1) and (3) can further be used to integrate the kinetic equation (1) in the presence of a given flow field. Expanding the distribution function into eigenfunctions, \(f(q; t) = \sum_n c_n(t) f_n(q)\), leads to

\[
\dot{c}_n = -\lambda_n^{-1} c_n - \kappa(t) \sum_k A_{nk} c_k,
\]

(11)

with \(A_{nk} = \langle f_n, \partial_q q f_k \rangle\) a constant matrix independent of the flow. Coefficients \(c_n(t)\) are defined by \(c_n(t) = \langle f_n, f(q; t) \rangle\). Eqs. (11) are an equivalent formulation of the kinetic equation (1). Conservation of total probability is guaranteed by \(c_0 = 0\), which is easily verified from (11). The stress \(\tau\) is determined by the coefficients \(c_n\) via \(\tau/(k_B T) = \sum_{n=1}^{\infty} \langle \sigma, f_{2n} \rangle c_{2n}\). Because of symmetry, only even terms contribute to \(\tau\). Moreover, Eqs. (11) for even coefficients decouple from those for odd coefficients since \(A_{nk}\) is nonzero only if \(n\) and \(k\) are both even or both odd. Therefore, if we are interested only in the polymer contribution to the stress, only even coefficients have to be included in (11). Given \(A_{nk}\), Eqs. (11) can be integrated for a finite set of eigenfunctions quite efficiently using standard integrators for ordinary differential equations. How many eigenfunctions have to be included in order to obtain a desired accuracy is a delicate question. A simple estimation is the following. To a first approximation, coefficients \(c_n\) are still of exponential form but with a different time constant \(\lambda_n^{-1} + \kappa A_{nn}\). Modes that decrease quadratically with number \(n\) will then be negligible. This leads to a minimal number of modes \(n_c\) that satisfies \(n_c^2/b_1 = n_c + 2\lambda_H |\kappa(t) A_{nn}|\). If this number is not too large, method (11) is much more efficient than Brownian dynamics simulation.

**IV. CONCLUSIONS**

We have obtained the spectrum of relaxation times, the eigenfunctions and the relaxation modulus for a one-dimensional finitely extensible dumbbell model exactly. It is observed that the relaxation times are reduced when compared to the Hookean dumbbell model. Moreover, the decrease of the relaxation times with mode number \(n\) shows a crossover from \(n^{-1}\) to \(n^{-2}\) at the value of the finite extensibility parameter \(b\). The relaxation modulus is obtained in the form of the “generalized Maxwell model”. For rather large values of the finite extensibility parameter \(b\), which are commonly believed to be physically meaningful (see, e.g., (5)), the linear viscoelastic behaviour is well described by a single relaxation time. This is because the relative weight of the higher modes is decreasing rapidly with increasing \(b\). Therefore, it is not surprising that the linear viscoelastic regime is well described by the Peterlin ap-
proximation as found in [5]. To calculate the non-linear dynamical response to a given flow kinematics we propose a numerical integration scheme using the expansion of the distribution function into the exact eigenfunctions in the absence of flow.

All these results are limited to the one-dimensional case. In three dimensions the class of solvable potentials is much more restricted. In particular we did not find any relevant two parameter potential that can be solved exactly. However, there is some evidence, that “a simple one-dimensional version of the FENE theory captures qualitatively and quantitatively the elongational behaviour of the actual three-dimensional theory” (Ref. [10], Introduction).

ACKNOWLEDGMENT

The authors gratefully acknowledge valuable discussions with H. C. Ottinger.

[1] R. B. Bird, C. F. Curtiss, R. C. Armstrong, O. Hassager, Dynamics of Polymeric Liquids, Vol. 2, Kinetic Theory, Wiley, New York, 2nd Ed., 1987.
[2] L. R. G. Treloar, The Physics of Rubber Elasticity, 3rd ed., Oxford University Press, London (1975), Chapter VI.
[3] H.R. Warner, Ind. Eng. Chem. Fundam. 11, 169 (1972).
[4] A. Cohen, Rheol. Acta 30, 270 (1991).
[5] M. Herrchen, H. C. Ottinger, J. Non-Newtonian Fluid Mech. 68, 17 (1997).
[6] R. B. Bird, P. J. Dotson, N. L. Johnson, J. Non-Newton. Fluid Mech. 7, 213 (1980); 8, 193 (1981) and 15, 225 (1984) (errata).
[7] V. B. Zmievski, I. V. Karlin and M. Deville, Physica A 275, 152 (2000).
[8] C. F. Curtiss, J. Chem. Phys. 95, 1337 (1991).
[9] H. Risken, The Fokker-Planck Equation, Springer, 2nd Ed., 1996.
[10] G. Lielens, P. Halin, I. Jaumati, R. Keunings, V. Legat, J. Non-Newton. Fluid Mech. 76, 249 (1998).
[11] R. Keunings, J. Non-Newton. Fluid Mech. 68, 85 (1997).
[12] G. Junker, Supersymmetric Methods in Quantum and Statistical Physics, Springer 1996.
[13] E. Witten, Nucl. Phys. B188, 513 (1981); E. Witten, Nucl. Phys. B202, 253 (1982).
[14] G. E. Gendenshtein, JETP Lett. 38, 356 (1983).

FIG. 1. Nonlinear, finitely extensible dumbbell forces are shown as a function of the reduced extension. Long dashed: Warner force, dotted: the force ([5]) proposed here, dashed: Cohen’s Padé approximation, solid line: the inverse Langevin function and dot-dashed: the Hookean spring. As easily seen from the figure the proposition ([3]) approximates the inverse Langevin function even better than does the most frequently used Warner approximation. The inset shows these forces for the special case $b = b_3$ in three dimensions. The same symbols are used as before, but the force ([5]) is replaced by ([3]).

FIG. 2. The first ten relaxation times $\lambda_n$, $n$ even, are displayed as full circles ([6]). The histogram shows their relative weights $|\langle \sigma, f_n \rangle|^2 / G(0)$. The dimensionless parameter $b$ was chosen to be $b = 20$. With increasing $b$ the relaxation times approach $1/n$ while $\lambda_2$ accumulates the total weight.
