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Shi-Qing Wang†‡ and Karl F Freed§

† The James Franck Institute and Department of Physics, University of Chicago, Chicago, IL 60637, USA
§ The James Franck Institute and Department of Chemistry, University of Chicago, Chicago, IL 60637, USA

Abstract. The role of solvent velocity fluctuations on the transport properties of polymer solutions is studied using renormalisation group expansions to order ε^2 of the coupled Langevin equation model within a Fokker–Planck equation formulation. Introduction of the timescale separation approximation between polymer and solvent characteristic relaxation times leads to an additional expansion in powers of a small dimensionless parameter which may heuristically be interpreted as the ratio of characteristic polymer (Rouse–Zimm) to solvent relaxation rates. Retaining zeroth-order terms in the latter expansion reduces the order ε^2 solution of the Fokker–Planck equation identically to the corresponding expanded solution of the Kirkwood diffusion equation representation of the Rouse–Zimm model. Explicit expressions are derived for corrections to the Kirkwood diffusion equation due to solvent velocity fluctuations. The bare leading corrections for the intrinsic viscosity of preaveraged Gaussian chains are analysed and are shown to have a magnitude consistent with heuristic timescale separation arguments and to be negligibly small for typical polymer–solvent systems. It is therefore conjectured that the renormalised parameter is also sufficiently small to validate its neglect for these polymer systems.

1. Introduction

Renormalisation group methods have recently been extensively applied to study dynamical properties of dilute polymer solutions both with and without a systematic flow (Jasnow and Moore 1978, Oono and Freed 1981, Yamazaki and Ohta 1982, Shiwa and Kawasaki 1982, Lee *et al* 1984, Schaub *et al* 1985, Jagannathan *et al* 1985, 1987, Puri *et al* 1986, Wang and Freed 1986, 1987, 1988, Wang 1987). These applications can be classified into two categories according to the types of models employed. One approach is based on coupled Langevin equations for the dynamics of both the solvent velocity and the polymer conformation variables, while the other uses the well established Kirkwood diffusion equation (Kirkwood 1954), corresponding to the Rouse–Zimm model (Rouse 1953, Zimm 1956), for the polymer conformational distribution, where the effects of the solvent enter only through the conventional Oseen tensor. Both treatments introduce the perturbative and ε expansions of renormalisation group methods, but the coupled polymer–solvent dynamical model is somewhat more general because it includes the influence of solvent velocity fluctuations on the polymer dynamics, an effect which may be of significance because these solvent velocity fluctuations occur throughout the region occupied by the polymer and are then

‡ Present address: Department of Chemistry, University of California, Los Angeles, CA 90024, USA.

transmitted by hydrodynamics to the rest of the polymer chain. It is this possible long-range effect of the solvent velocity fluctuations which suggests the Langevin model, in part, by analogy with the theory of phase separation in binary fluids where the solvent velocity fluctuations alter dynamical critical exponents by a small amount.

Apart from the differences in physical content, the coupled Langevin and diffusion equation methods provide different useful perspectives on the treatment of polymer dynamics. The former approach gives a more straightforward way of calculating explicit time-dependent polymer quantities, while the latter method is often more convenient, partly because of its long history of usage in polymer science for the evaluation of polymer transport properties such as the translational diffusion coefficient and intrinsic viscosity.

Oono and Freed (1981) first noted the possible role played by solvent velocity fluctuations and used projection operator methods to show (Lee *et al* 1984) that to order ε (where $\varepsilon = 4 - d$ and d is the spatial dimensionality) the Kirkwood diffusion equation is equivalent to the coupled Langevin equations under the assumption that typical solvent relaxation times are much smaller than those of the polymers. Because formal calculations, determining differences, if any, between the solvent fluctuation and Kirkwood diffusion equation models, are not yet possible beyond order ε, it has been concluded that until such analyses have been made, it should be assumed that the Kirkwood diffusion equation is very likely incompatible in order ε^2 with the kinetic description of the Langevin equations for the coupled dynamics of the polymer-solvent system.

The possible inequivalence of the kinetic and diffusion equation models raises an important difficulty as follows. The renormalisation group theory of many dynamical polymer properties, such as the translational diffusion coefficient and the intrinsic viscosity, has these quantities proportional to the order ε hydrodynamic interaction parameter and, therefore, the order ε description is fairly trivial. Thus, treatments of dynamical properties of polymer solutions require at least order ε^2 computations in order to provide useful and non-trivial predictions, but such calculations have, to date, only been applied within the Rouse-Zimm model. One example is the preaveraging corrections that emerge only beginning in order ε^2 in the computation of the diffusion coefficient or intrinsic viscosity (Wang and Freed 1986, 1987). Consequently, the currently available order ε^2 Kirkwood diffusion equation renormalisation group calculations of polymer transport properties stand in contrast with the current unavailability of order ε^2 calculations for the more rigorous but complicated kinetic model containing solvent velocity fluctuations.

Our interest in this paper lies in the removal of the severe difficulties in solving the kinetic model to permit second-order computations of the differences between the two models. We utilise an analogue of the timescale separation approximation (Lee *et al* 1984) to show that it leads in a limit to the equivalence of the coupled polymer-solvent fluctuation and Kirkwood diffusion equation models for order ε^2 long-wavelength low-frequency polymer properties. The kinetic equation model contains the additional bare parameter $k_B T \rho / \zeta_0 \eta_0$ which is dimensionless and independent of both the chain length N_0 and of the spatial dimensionality d. This additional parameter may loosely be taken as equivalent to the ratio of characteristic solvent to small polymer relaxation times, where $k_B T$ is the thermal energy, ρ is the solvent density, η_0 is its viscosity and ζ_0 is the polymer 'bead' friction coefficient.

Our analysis of the magnitudes of terms in given orders of ε does not follow the projection operator approach (Lee *et al* 1984). Instead, we further develop the methods

(Wang and Freed 1986, 1987) used in order ε^2 calculations within the Kirkwood diffusion equation formulation of the Rouse–Zimm model, and this approach is combined with techniques introduced by Kawasaki and Gunton (1976) for treating mathematically analogous problems of critical dynamics. Our recent advance with this simpler model thus provides one of the tools for an onslaught into the physically interesting and mathematically difficult problem of the role of solvent velocity fluctuations on polymer dynamics.

The Kirkwood diffusion equation is traditionally obtained from the continuity equation describing conservation of polymer mass in which the solvent is treated separately by steady state hydrodynamics. A correct treatment of polymer dynamics, however, should also include the influence of the motion of solvent molecules on the dynamics of polymer segments. Such a detailed dynamical description of the coupled polymer–solvent motion is provided by the coupled Langevin equations for the polymer and solvent. Within some appropriate ranges of validity, the Kirkwood diffusion equation should be justifiable (i.e. derivable) from these fundamental Langevin equations. Full theoretical justifications of this nature are currently unavailable despite some considerable theoretical efforts on this problem.

We begin with the coupled Langevin model in § 2 and convert these coupled Langevin equations to a Fokker–Planck equation for the combined polymer–solvent dynamics. The Fokker–Planck equation is then transformed to a diffusion-like equation for the polymer distribution function by averaging out the fluctuating solvent velocity. This diffusion-like equation is still mathematically very intricate due to the physically interesting presence of couplings between the polymer and solvent dynamics (see § 2). It then becomes essential to evaluate the corrections arising from expansion in powers of the dimensionless parameter $k_B T \rho / \zeta_0 \eta_0$. This decoupling is introduced to formally extract the correction terms to the Rouse–Zimm model through order ε^2. A complete evaluation of the correction terms presents a technically rather formidable computation problem which is left for a future work. Section 3 uses the preaveraging approximation to provide only an order of magnitude estimate of the corrections to the Kirkwood diffusion equation due to the solvent velocity fluctuations.

2. Derivation of diffusion equation from Langevin equations

A fundamental kinetic model for the description of polymer dynamics in solution is provided by the coupled Langevin equations for the combined polymer and solvent dynamics. We employ a continuous chain model where $R(\tau, t)$ designates the position of the segment at a contour distance τ along the chain at time t. It is convenient to employ units in which the chain conformation is specified by $c(\tau, t) = (d/l)^{1/2} R(\tau, t)$, where d is the spatial dimensionality and l is the Kuhn length of a segment. Using these units the Langevin dynamics for the polymer conformation $c(\tau, t)$ merely states (Schaub *et al* 1985) that the friction force $\zeta_0 \{ \partial c(\tau, t)/\partial t - u[c(\tau, t), t] \}$ is balanced by polymer–polymer and random forces

$$\frac{\partial c(\tau, t)}{\partial t} = u[c(\tau, t), t] - (k_B T d / \zeta_0 l) \frac{\delta H\{c\}}{\delta c(\tau, t)} + \theta(\tau, t) \tag{2.1}$$

where ζ_0 is the bare friction coefficient of this segment, $u(r, t)$ is the effective fluctuating solvent velocity field at position r at time t, and $H\{c\}$ is the dimensionless Edwards

free energy (Edwards 1965) for the polymer configuration $c(\tau, t)$

$$H\{c\} = \frac{1}{2}\int_0^{N_0} d\tau\left(\frac{dc}{d\tau}\right)^2 + (v_2^0/2)\int_0^{N_0} d\tau\int_0^{N_0} d\tau'\,\delta[c(\tau, t) - c(\tau', t)] \tag{2.2}$$

with N_0 being the contour length of the polymer and v_2^0 the bare excluded volume parameter. The force $\theta(\tau, t)$ in (2.1) designates a random force which has a Gaussian white noise spectrum with zero mean and with variance

$$\langle\theta(\tau, t)\theta(\tau', t')\rangle = 2(k_B T d/\zeta_0)\delta(\tau - \tau')\delta(t - t')\mathbf{1} \tag{2.3}$$

where $\mathbf{1}$ is the unit tensor in d dimensions. The units of u are defined by (2.1).

The fluctuating solvent velocity field is described by the Navier–Stokes equation which incorporates friction forces due to polymers and the random thermal velocity fluctuation in the fluid

$$\rho\frac{\partial u(r, t)}{\partial t} = \eta_0\nabla^2 u(r, t) - \nabla p - (k_B T d/l^2)\int_0^{N_0} d\tau\frac{\delta H\{c\}}{\delta c(\tau, t)}\,\delta[r - R(\tau, t)] + f(r, t) \tag{2.4}$$

where ρ is the solvent density, η_0 is the solvent viscosity, p is the effective hydrostatic pressure in the fluid and f is a random force density with zero mean and with variance

$$\langle f(r, t)f(r', t')\rangle = -2(k_B T d/l)\eta_0\nabla^2\delta(r - r')\delta(t - t')\mathbf{1}. \tag{2.5}$$

Here u is assumed to satisfy the incompressibility condition $\nabla \cdot u = 0$ which suffices for computing low-frequency polymer properties. The random forces (2.3) and (2.5) are necessary to produce the correct equilibrium distribution for both polymer and solvent in the long time $(t \to \infty)$ limit. The Rouse–Zimm model can be derived by dropping the term in $\rho\partial u(r, t)/\partial t$ in (2.4), so it is clear that the kinetic model (2.1)–(2.5) introduces a new ρ-dependent parameter into the description of the polymer dynamics.

2.1. Fokker–Planck equation

The coupled Langevin equations (2.1) and (2.4) can be solved simultaneously for the polymer conformation $c(\tau, t)$ and the solvent velocity field $u(r, t)$ as functions of the noises θ and f. An alternative way of studying the polymer dynamics, as embodied in the model (2.1)–(2.5), is by means of the equivalent Fokker–Planck equation for the joint time-dependent distribution function for the polymer conformation and the solvent velocity field. The transformation of (2.1) and (2.4) into the corresponding Fokker–Planck equation is facilitated by expressing (2.4) in Fourier space with k the Fourier variable conjugate to r and with $u_k(t)$ the spatial Fourier transform of $u(r, t)$,

$$\rho\frac{\partial u_k(t)}{\partial t} = -(k^2\eta_0 d/l)u_k(t) - (k_B T d/l^2)\int_0^{N_0} d\tau\left(\frac{\delta H\{c\}}{\delta c(\tau, t)}\right)_{\perp}\exp[-ik \cdot c(\tau, t)] + f_k(t) \tag{2.6}$$

where the pressure p has been eliminated by considering only the transverse components of u_k as incompressibility implies $k \cdot u_k = 0$ and where the subscript $\perp$ on a vector designates that only the portion orthogonal to k is retained. Standard procedures (e.g. Ma and Mazenko 1975) for averaging out the Gaussian white noises θ and f enable equations (2.1) and (2.6) to be converted to the Fokker–Planck equation for the distribution $\hat{P}(\{c\}, \{u\}, t)$. This equation is written in operator form as

$$\partial\hat{P}/\partial t = (F_0 + F_1)\hat{P} \tag{2.7}$$

where the uncoupled zeroth-order operator F_0 is decomposed into polymer and solvent portions as

$$F_0 = F_{0p} + F_{0s} \tag{2.8a}$$

$$F_{0p} = (k_B T d / l^2 \zeta_0) \int_0^{N_0} d\tau \frac{\delta}{\delta c(\tau)} \cdot \left(\frac{\delta}{\delta c(\tau)} + \frac{\delta H\{c\}}{\delta c(\tau)} \right) \tag{2.8b}$$

$$F_{0s} = \int_k (k^2 \eta_0 d / l\rho) \frac{\delta}{\delta u_k} \cdot \left(u_k + [k_B T / (d/l)^{d/2} \rho] \frac{\delta}{\delta u_{-k}} \right) \tag{2.8c}$$

and where F_1 represents the coupling between the polymer $c(\tau, t)$ and solvent variables $u_k(t)$

$$F_1 = \int_0^{N_0} (d\tau / l) \int_k \left((k_B T d / \rho) \frac{\delta}{\delta u_k} \cdot (\delta H\{c\} / \delta c(\tau))_\perp \exp(-i k \cdot c(\tau)) \right.$$

$$\left. - \frac{\delta}{\delta c(\tau)} \cdot u_k \exp(i k \cdot c(\tau)) \right). \tag{2.9}$$

Equations (2.8) and (2.9) employ the shorthand notation

$$\int_k \equiv (2\pi)^{-d} \int d^d k. \tag{2.9a}$$

Below, units are used in which $\rho = k_B T = (d/l) = 1$, and at the end of the calculation natural units are reinstated.

Since we are interested in polymer properties, we seek a reduced equation for the polymer motion only. As shown below, this is accomplished by removing the fluctuations u_k from the Fokker–Planck equation (2.7) through integrations of u_k.

2.2. Diffusion equation

The probability distribution $P(\{c\}, t)$ for the polymer conformation is defined in terms of the full distribution function $\hat{P}$ of (2.7) by an integration over solvent variables

$$P(\{c\}, t) \equiv \int D\{u\} \hat{P}(\{c\}, \{u\}, t). \tag{2.10}$$

A formal equation for $P(\{c\}, t)$ is obtained by integrating the Fokker–Planck equation (2.7) for $\hat{P}$ over $\{u\}$

$$\left(\frac{\partial}{\partial t} - F_{0p} \right) P(\{c\}, t) = \int D\{u\} F_1 \hat{P}(\{c\}, \{u\}, t) \tag{2.11}$$

where F_{0p} and F_1 are defined in (2.8) and (2.9) respectively, and where use is made of the equality

$$\int D\{u\} F_{0s} \hat{P} = 0$$

which is obtained by partial integration and by invoking the boundary condition that $\hat{P}$ vanishes for $\{u\} \to \infty$.

Equation (2.11) is not a closed equation for $P(\{c\}, t)$ because $F_1 \hat{P}$ contains $\{u\}$ in combinations different from the definition (2.10) of P. To proceed further with the transformation of (2.11) into a closed equation, we begin by solving the Fokker–Planck equation (2.7) for $\hat{P}(\{c\}, \{u\}, t)$ in order that it be used in (2.11).

The polymer–solvent coupling term F_1 in (2.7) is a perturbation of order $\varepsilon^{1/2}$ within the renormalisation group theory. This observation allows the Fokker–Planck equation (2.7) to be solved perturbatively as follows. Let the full distribution $\hat{P}(\{c\}, \{u\}, t)$ be expanded as

$$\hat{P} = \hat{P}_0 + \hat{P}_1 + \hat{P}_2 + \ldots \tag{2.12a}$$

where each $\hat{P}_i$ is of order $(F_1)^i$. Then the $\hat{P}_i$ satisfy the set of equations

$$\frac{\partial \hat{P}_i(t)}{\partial t} = F_0 \hat{P}_i(t) + F_1 \hat{P}_{i-1}(t) \qquad i \geq 1 \tag{2.12b}$$

$$\frac{\partial \hat{P}_0(t)}{\partial t} = F_0 \hat{P}_0(t). \tag{2.13a}$$

Equations (2.12b) and (2.13a) only explicitly exhibit the time dependence of the $\hat{P}_i$, and the dependence on $\{u\}$ and $\{c\}$ is understood. Because of the additive structure of F_0 in (2.8a), equation (2.13a) is separable into the product of a function only of $\{u\}$ and one only of $\{c\}$. Thus, we write this zeroth-order solution as

$$\hat{P}_0(t) = \tilde{P}(\{u\}, t)\tilde{P}(\{c\}, t) \tag{2.13b}$$

where both $\tilde{P}$ depend on the initial conditions, and where the derivation of (2.13b) assumes (see below) that the initial $\hat{P}_0(0)$ is likewise separable into a product form. A determination of $\hat{P}_0(t)$ is presented below after we complete the description of the solution of (2.12b).

Equation (2.12b) can be readily integrated to give the formal operator solution

$$\hat{P}_i(t) = \int_0^t d\sigma \, \exp(F_0\sigma) F_1 \hat{P}_{i-1}(t - \sigma). \tag{2.14a}$$

We are interested only in $\hat{P}(t)$ at times t comparable to long-wavelength polymer mode relaxation timescales t_p (the times of experimental relevance for polymer properties). These t_p are much greater than the relaxation times t_s characteristic of the solvent system on the scale of the polymer size. Since the F_0 in $\exp(F_0\sigma)$ of (2.14a) is negative definite with eigenvalues of the form $-(t_s^{-1} + t_p^{-1})$, the contributing values of σ to the integral (2.14a) reside in the range of $0 \leq \sigma \leq t_s \ll t_p \approx t$, so that $\hat{P}_{i-1}(t - \sigma)$ in (2.14a) can be replaced by $\hat{P}_{i-1}(t)$. Likewise $\exp(F_0\sigma)$ is negligible at the upper integration limit of $t \approx O(t_p)$, converting the integral to one involving $\int_0^\infty d\sigma$. These replacements reduce (2.14a) to

$$\hat{P}_i(t) = -F_0^{-1} F_1 \hat{P}_{i-1}(t) \tag{2.14b}$$

and enable (2.12a) to be rewritten in terms of the zeroth-order distribution $\hat{P}_0(t)$ as

$$\hat{P}(t) = [1 - F_0^{-1}F_1 + (F_0^{-1}F_1)^2 - \ldots]\hat{P}_0(t). \tag{2.15}$$

An analysis is given in appendix 2 of the non-Markovian corrections arising from the use of (2.14a) instead of (2.14b).

Following Kawasaki and Gunton (1976), we assume that at the initial time $t = 0$ the solvent velocity fluctuations are governed by their equilibrium distribution function $P_{eq}\{u\}$ which is determined by the equation

$$F_{0s}P_{eq}\{u\} = 0 \tag{2.16a}$$

whose solution is

$$P_{eq}\{u\} = \exp\left(-\int_k \frac{1}{2}u_{-k} \cdot u_k\right). \tag{2.16b}$$

Hence, using (2.16a) the $\hat{P}_0$ of (2.13b) becomes

$$\hat{P}_0(t) = P_{eq}\{u\}\tilde{P}(\{c\}, t) \tag{2.17}$$

where $\tilde{P}(\{c\}, t)$ represents the zeroth-order polymer distribution function which is as yet unspecified and which is determined below in terms of $P(\{c\}, t)$.

In order to determine the as yet unknown $\tilde{P}(\{c\}, t)$, it is instructive to substitute (2.15) and $\hat{P}(t)$ with (2.17) into the definition for the full polymer distribution (2.10), yielding

$$P(\{c\}, t) \equiv \int D\{u\}[1 - F_0^{-1}F_1 + (F_0^{-1}F_1)^2 - \ldots]P_{eq}\{u\}\tilde{P}(\{c\}, t)$$

$$= \left(1 + \int D\{u\}(F_0^{-1}F_1)^2 P_{eq}\{u\} + O(F_1^4)\right)\tilde{P}(\{c\}, t) \tag{2.18a}$$

where the second equality in (2.18a) follows because F_1 is an odd function of $\{u\}$ and therefore the integration of its product with $P_{eq}\{u\}$ of (2.16) vanishes. Inversion of (2.18a) shows that the unspecified function $\tilde{P}(\{c\}, t)$ may be expressed in terms of $P(\{c\}, t)$ of (2.10) by

$$\tilde{P}(\{c\}, t) = \left(1 + \int D\{u\}(F_0^{-1}F_1)^2 P_{eq}\{u\} + O(F_1^4)\right)^{-1} P(\{c\}, t). \tag{2.18b}$$

Finally, we insert (2.15) for $\hat{P}$ along with (2.17) and (2.18b) into the diffusion-like equation (2.11) to obtain the closed equation for P as

$$\partial P/\partial t = \{F_{0p} - \langle[F_1 F_0^{-1}F_1 + F_1(F_0^{-1}F_1)^3]\rangle_u[1 - \langle(F_0^{-1}F_1)^2\rangle_u] + O[(F_1)^6]\}P \tag{2.19}$$

where the brackets $\langle A \rangle_u$ denotes the average over the solvent velocities by

$$\langle A \rangle_u \equiv \int D\{u\}A P_{eq}\{u\} \tag{2.20}$$

and where odd functions of $\{u\}$ are dropped in (2.19) because they produce zero averages in (2.20). For notational convenience we represent (2.19) in the compact operator form as

$$\partial P(\{c, t\})/\partial t = (F_{0p} + F_h)P(\{c\}, t) \tag{2.21}$$

where F_h is given by

$$F_h = -\langle F_1 F_0^{-1}F_1\rangle_u + \Delta F_h^{(2)} + O[(F_1)^6] \tag{2.22}$$

and where the order ε^2 contribution to (2.2) is $\Delta F_h^{(2)}$ and is defined by

$$\Delta F_h^{(2)} = \langle F_1 F_0^{-1}F_1\rangle_u\langle(F_0^{-1}F_1)^2\rangle_u - \langle F_1(F_0^{-1}F_1)^3\rangle_u. \tag{2.23}$$

Next we evaluate the $\{u\}$ integrations in (2.21)–(2.23) to obtain the explicit diffusion equation for the polymer conformation distribution function $P(\{c\}, t)$. To compute the averages $\langle \ \rangle_u$ involving F_0^{-1}, we require some elementary properties associated with the operator F_{0s}^+ that is the adjoint of F_{0s} in (2.8c) and that is given by

$$F_{0s}^+ = \int_k \left(\frac{\delta}{\delta u_{-k}} - u_k\right) \cdot \frac{\delta}{\delta u_k}(k^2\eta_0). \tag{2.24}$$

The operator F_{0s}^{+} has a structure similar to that of Hermite's equation for the Hermite polynomial $H_n(x)$. It is straightforward to obtain the first few sets of eigenvalues and eigenfunctions of F_{0s}^{+} as

$$F_{0s}^{+}1 = 0 \tag{2.25a}$$

$$F_{0s}^{+}u_q = -q^2\eta_0 u_q \tag{2.25b}$$

$$F_{0s}^{+}(u_{q_1}u_{q_2} - \delta u_{q_1}/\delta u_{-q_2}) = -(q_1^2 + q_2^2)\eta_0(u_{q_1}u_{q_2} - \delta u_{q_1}/\delta u_{q_2}). \tag{2.25c}$$

Using (2.8) and (2.9) for F_0 and F_1, respectively, along with (2.16) enables the first term in F_h of (2.22) to be represented as the integral

$$-\langle F_1 F_0^{-1} F_1 \rangle_u = -\int_0^{N_0}\int_0^{N_0} d\tau\, d\tau' \int D\{u\} \int_k \frac{\delta}{\delta c(\tau)} \cdot \exp[i\mathbf{k} \cdot \mathbf{c}(\tau)]u_k F_0^{-1}$$

$$\times \int_{k'} \left(\frac{\delta H\{c\}}{\delta c(\tau')} \cdot \exp[-i\mathbf{k}' \cdot \mathbf{c}(\tau')]u_{-k'} + \frac{\delta}{\delta c(\tau')} \cdot \exp[i\mathbf{k}' \cdot \mathbf{c}(\tau')]u_{k'} \right) P_{eq}\{u\} \tag{2.26}$$

where use is made of the fact that $P_{eq}\{u\}$ vanishes at $|u| \to \infty$ to drop terms arising from partial integration. Introducing the property (2.25b) and the equality

$$\langle u_{k'}u_k \rangle_u = \tau(k)\delta(k+k') \equiv (1 - kkk^{-2})\delta(k+k') \tag{2.27}$$

into equation (2.26) reduces the latter to

$$-\langle F_1 F_0^{-1} F_1 \rangle_u = \int\int d\tau\, d\tau' \int_k \frac{\delta}{\delta c(\tau)} \cdot \tau(k) \cdot \exp(i\mathbf{k} \cdot \mathbf{c}(\tau))(k^2\eta_0 - F_{0p})^{-1}$$

$$\times \exp(-i\mathbf{k} \cdot \mathbf{c}(\tau'))\left(\frac{\delta}{\delta c(\tau')} + \frac{\delta H\{c\}}{\delta c(\tau')} \right) \tag{2.28}$$

where F_{0p} is defined in (2.8).

2.3. Timescale separation

The coupling between the polymer and solvent dynamics is manifested in (2.28) through the combined polymer-solvent relation factor $(k^2\eta_0 - F_{0p})^{-1}$. The quantity $k^2\eta_0$ (or more precisely $k^2\eta_0 d/\rho l$) describes the relaxation rate of solvent modes at wavelength k^{-1}, and $-F_{0p}$ formally gives the polymer relaxation rate. Because F_{0p} is an operator, the diffusion-like equation (2.21) is quite complicated, and equation (2.28) is only the order ε part of the diffusion operator F_h. Lee *et al* (1984) have encountered technical difficulties of a similar nature. They simplify the problem by noting that typical solvent relaxation times are much smaller than polymer relaxation times, so that factors such as F_{0p} in the denominator of (2.28) can be neglected. In effect, the model (2.1)-(2.5) contains the additional small dimensionless parameter $k_B T\rho/\zeta_0\eta_0$ which may be taken to be the ratio of a new bare coupling constant $y_0 = k_B T\rho/\eta_0^2$ to the original bare hydrodynamic coupling parameter $g_0 = \rho_0/\eta_0$.

The bare parameter g_0 has dimensions of $L^{-\varepsilon/2}$, so bare perturbation expansions in g_0 are series in $g_0 N_0^{\varepsilon/2}$ requiring renormalisation. The bare y_0 likewise has dimensions $L^{-\varepsilon/2}$ and is thus at least an order ε quantity, making y_0/g_0 begin formally at least at order ε^0. After renormalisation the renormalised y must appear as yN^ψ with ψ a crossover exponent. Consequently, the ratio y/g emerges in perturbation expansions

multiplied by $N^{\psi-\varepsilon/2}$, making this new parameter relevant, marginal or irrelevant, depending on whether $\psi - \varepsilon/2$ is positive, zero or negative respectively. It is currently not known how to evaluate the higher-order terms necessary to renormalise y_0 and thereby to compute ψ and determine if y begins in order ε^0, $\varepsilon^1, \ldots$, or is irrelevant. Thus, we take the pragmatic view of noting below that $y_0/g_0 = k_B T\rho/\zeta_0\eta_0$ is generally quite small, so that even if this quantity is relevant, it is permissible to use an expansion in y_0/g_0 provided that the renormalised $|(y/g)N^{\psi-\varepsilon/2}| \ll 1$. It is, therefore, in this limited domain that we wish to establish the equivalence between the Langevin and diffusion equation formalism as well as to provide methods for determining and analysing these leading corrections in y_0/g_0. The expansion in y_0/g_0 is heuristically motivated in terms of the timescale separation ideas which make us optimistic that the region $|(y/g)N^{\psi-\varepsilon/2}| \ll 1$ pertains to a wide range of physical systems. Formidable technical problems, however, currently preclude a verification of this conjecture.

At first sight the above assumption regarding timescales looks somewhat *ad hoc* because equation (2.28) and other operators in F_h of (2.22) have an integration over k such that, in principle, there are contributions from $(k^2\eta_0 d/\rho l) < \|F_{0p}\| \sim t_p^{-1}$. Therefore, we verify the plausibility of this assumption by first making two rough order of magnitude estimates of the two terms $k^2\eta_0 d/\rho l$ and F_{0p} in (2.28), and below we reinvestigate the problem for the preaveraged intrinsic viscosity. The basic physical point involved arises from the fact that the diffusion-like equation (2.19) is derived for evaluating polymer properties, so the length scales of the polymer are expected to be relevant. First, consider the shortest polymer length scale comparable to the Kuhn length l of the polymer chain. The solvent relaxation rate $k^2\eta_0 d/\rho l$ on this minimum length is on the order of $(\eta_0/\rho l^2)$, while on this length scale the polymer possesses the highest relaxation rate, the largest eigenvalue of $(-F_{0p})$ which is of order $(k_B T/\zeta_0 l^2)$. The ratio of the solvent relaxation time to that of the polymer for the short-wavelength modes is thus given by

$$t_s/t_p \sim (k_B T\rho/\zeta_0\eta_0) = k_B T\rho/6\pi l\eta_0^2 \qquad (2.29a)$$

where the Stokes relation $\zeta_0 = 6\pi l\eta_0$ is employed to replace ζ_0 by $\eta_0 l$. Typical values of T, η_0, ρ and l for an ordinary polymer solution are given by $T \sim$ room temperature, $\rho \sim 1.0 \text{ g cm}^{-3}$, $\eta_0 \sim 10^{-2} \text{ g cm}^{-1}\text{s}^{-1}$ and $l \sim 1.0 - 10.0 \text{ Å}$. These values lead to the first rough estimate

$$t_s/t_p \sim 10^{-4} - 10^{-3}. \qquad (2.29b)$$

On the other hand, at the longest polymer wavelength of the radius of gyration $\langle S^2\rangle_0^{1/2} \sim n_0^{1/2} l$ the solvent relaxation rate $k^2\eta_0/\rho l$ becomes $(\eta_0/n_0\rho l^2)$, while the polymer has the lowest relaxation rate $-F_{0p}$ of order $(2\pi^2 k_B T/\zeta_0 n_0^2 l^2)$. Consequently, at the maximum length scale of the polymer-solvent system, the ratio is

$$t_s/t_p \sim (2\pi^2/n_0)^{1/2}(k_B T\rho/\zeta_0\eta_0) \qquad (2.30)$$

which is very much smaller than the estimate in (2.29) for large n_0.

In a more formal sense the transformation to dimensionless $k'^2 = k^2 N_0 l$ converts the dimensionless expansion parameter into an expansion in $(\rho k_B T/\eta_0\zeta_0 n_0^{0,1})(k^2 N_0 l)^{-1}$, where the powers 0 and 1 on n_0 indicate the ranges of dependence of the smallest and longest wavelength modes. This expansion in inverse powers of k^2 can be shown to produce no new ultraviolet divergences, so renormalisation of the additional bare parameter $\rho k_B T/\eta_0^2$ is expected to proceed by direct analogy with that used for the polymer surface (Nemirovsky and Freed 1985) or surface critical phenomena problems

(Diehl 1986) which employ expansions in c_0. The double expansion in $\rho k_B T / \eta_0 \zeta_0$ and in ε is meaningful for the small values of $\rho k_B T / \eta_0 \zeta_0$ estimated in (2.29b), and there must exist some range of the renormalised parameter for which the expansion is likewise meaningful.

Therefore, for most polymer systems it is legitimate to drop F_{0p} with respect to $k^2 \eta_0 / \rho l$, and this approximation converts (2.28) into

$$-\langle F_1 F_0^{-1} F_1 \rangle_u = F_H$$

$$\equiv \int_0^{N_0} \int_0^{N_0} d\tau \, d\tau' \frac{\delta}{\delta c(\tau)} \cdot \mathsf{T}[c(\tau), c(\tau')] \cdot \left(\frac{\delta}{\delta c(\tau')} + \frac{\delta H\{c\}}{\delta c(\tau')} \right) \qquad (2.31a)$$

where $\mathsf{T}[c(\tau), c(\tau')]$ is the conventional Oseen tensor which in d-dimensional space is

$$\mathsf{T}[c(\tau), c(\tau')] = \int_k \tau(k) \exp\{ik[c(\tau) - c(\tau')]\}(k^2 \eta_0)^{-1} \qquad (2.31b)$$

with the projection tensor τ defined in (2.27). Lee *et al* (1984) have derived (2.31) from the Langevin equations (2.1) and (2.4) using projection operator methods. On the other hand, our treatment leading to (2.31) may readily be applied in higher orders, and it produces explicit expressions for the neglected terms.

The next section presents a more reliable computation of the correction to (2.31) from (2.28) by use of an expansion in powers of the small bare parameter $k_B T \rho / \zeta_0 \eta_0$ for the preaveraged intrinsic viscosity using (2.21). We find that indeed the correction is very small as indicated by the rough estimates (2.29) and (2.30). The separation of timescales approximation, as described heuristically in (2.29) and (2.30), is also used in appendix 1 to show that the order ε^2 correction $\Delta F_h^{(2)}$ in (2.22) and (2.23) is negligible.

3. Corrections from solvent velocity fluctuations

In order to investigate the difference between the exact expression (2.28) and the zeroth-order expansion (2.31) in the small bare parameter $k_B T \rho / \zeta_0 \eta_0$, it is useful to consider the computation of some particular dynamical polymer properties from (2.21). We illustrate this procedure for the steady state intrinsic viscosity $[\eta]$ which is given by the correlation function (Felderhof *et al* 1975)

$$[\eta] = (N_A / M \eta_0 k_B T) \int_0^\infty dt \, \langle J_{12}(0) J_{12}(t) \rangle_{eq} \qquad (3.1)$$

with $\langle \ \rangle_{eq}$ denoting the average over the equilibrium distribution

$$P_{eq}\{c\} = \exp[-H\{c\}] \left(\int D\{c\} \exp[-H\{c\}] \right)^{-1} \qquad (3.2)$$

N_A is Avogadro's number and M is the molecular weight. The quantity $J_{12}(0)$ is the momentum flux

$$J_{12}(0) = (k_B T / l) \int_0^{N_0} d\tau \frac{\delta H\{c\}}{\delta c_1(\tau)} c_2(\tau) \qquad (3.3)$$

with 1 and 2 designating the first two Cartesian directions. Use of the diffusion-like equation (2.21) converts (3.1) into

$$[\eta] = -(N_A / M \eta_0 k_B T) \langle J_{12} | (L_0 + L_h)^{-1} | J_{12} \rangle_{eq} \qquad (3.4)$$

where $L_0(L_h)$ is the adjoint of $F_{0p}(F_h)$. The renormalisation group assigns L_h as being at least of order ε, so that equation (3.4) can be expanded in L_h to yield

$$[\eta] = -(N_A/M\eta_0 k_B T)\langle J_{12}|(L_0^{-1} - L_0^{-1}L_h L_0^{-1} + L_0^{-1}L_h L_0^{-1}L_h L_0^{-1} + \ldots)|J_{12}\rangle_{eq}$$

$$= -(N_A/M\eta_0 k_B T)\langle J_{12}|[L_0^{-1} + L_0^{-1}\langle F_1 F_0^{-1}F_1\rangle_u^\dagger L_0^{-1}$$

$$+ L_0^{-1}\langle F_1 F_0^{-1}F_1\rangle_u^\dagger L_0^{-1}\langle F_1 F_0^{-1}F_1\rangle_u^\dagger L_0^{-1} - L_0^{-1}\Delta L_h^{(2)}L_0^{-1} + O(\varepsilon^3)]|J_{12}\rangle_{eq} \quad (3.5)$$

where $\langle F_1 F_0^{-1}F_1\rangle_u^\dagger$ is the adjoint of (2.28) and $\Delta L_h^{(2)}$ is the adjoint of (2.23) for $\Delta F_h^{(2)}$.

The adjoint of F_H in (2.31a) is written as L_H and is used to define the difference operator

$$\Delta L_h^{(1)} \equiv [-\langle F_1 F_0^{-1}F_1\rangle_u^\dagger] - L_H \quad (3.6)$$

and to rewrite (3.5) as

$$[\eta]^{FP} = -(N_A/M\eta_0 k_B T)\langle J_{12}|[L_0^{-1} - L_0^{-1}L_H L_0 + L_0^{-1}(L_H L_0^{-1})^2 - L_0^{-1}\Delta L_h^{(1)}L_0^{-1}$$

$$+ L_0^{-1}\Delta L_h^{(1)}L_0^{-1}L_H L_0^{-1} + L_0^{-1}L_H L_0^{-1}\Delta L_h^{(1)}L_0^{-1}$$

$$+ L_0^{-1}\Delta L_h^{(1)}L_0^{-1}\Delta L_h^{(1)}L_0^{-1} - L_0^{-1}\Delta L_h^{(2)}L_0^{-1} + O(\varepsilon^3)]|J_{12}\rangle_{eq}$$

$$= [\eta]^{RZ} + \Delta[\eta]_1 + \Delta[\eta]_2 + O(\varepsilon^3) \quad (3.7)$$

where the second equality holds because the expression for $[\eta]^{RZ}$ (zeroth order in $\Delta L_h^{(1)}$) is identical to that for the intrinsic viscosity in the Rouse-Zimm model using the conventional Kirkwood diffusion equation. Wang and Freed (1987) represent $[\eta]^{RZ}$ in the ε expansion

$$[\eta]^{RZ} = -(N_A/M\eta_0 k_B T)\langle J_{12}|[L_0^{-1} - L_0^{-1}L_H L_0^{-1} + L_0^{-1}L_H L_0^{-1}L_H L_0^{-1} + O(\varepsilon^3)]|J_{12}\rangle_{eq}. \quad (3.8)$$

The quantities $\Delta[\eta]_1$ and $\Delta[\eta]_2$ in (3.7) are, respectively, the terms in $\Delta L_h^{(1)}$ and $\Delta L_h^{(2)}$ of order ε and order ε^2 which are corrections to $[\eta]^{RZ}$, arising from the inclusion of the solvent velocity fluctuations that originate from the Fokker-Planck equation (2.11). These correction terms are more explicitly represented in operator form as

$$\Delta[\eta]_1 = (N_A/M\eta_0 k_B T)\langle J_{12}|L_0^{-1}\Delta L_h^{(1)}L_0^{-1}|J_{12}\rangle_{eq} \quad (3.9)$$

$$\Delta[\eta]_2 = -(N_A/M\eta_0 k_B T)\langle J_{12}|[L_0^{-1}\Delta L_h^{(1)}L_0^{-1}L_H L_0^{-1} + L_0^{-1}L_H L_0^{-1}\Delta L_h^{(1)}L_0^{-1}$$

$$+ L_0^{-1}\Delta L_h^{(1)}L_0^{-1}\Delta L_h^{(1)}L_0^{-1} - L_0^{-1}\Delta L_h^{(2)}L_0^{-1}]|J_{12}\rangle_{eq} \quad (3.10)$$

where the superscripts 1 and 2 indicate order ε and ε^2 quantities, respectively.

The bare corrections $\Delta[\eta]_1$ and $\Delta[\eta]_2$ are now both shown to be negligible, in comparison with the corresponding order bare quantities in $[\eta]^{RZ}$, and consequently both the full kinetic and diffusion equation models lead to the same intrinsic viscosity to order ε^2 within the range for which the renormalised $(y/g)N^{\psi-\varepsilon/2}$ is sufficiently small. We begin this analysis by quoting (Wang and Freed 1986) some properties of the operator L_0:

$$L_0 \equiv F_{0p}^\dagger = \sum_{a=1}^{n_0-1} (\delta/\delta\xi^a - \lambda_a^2\xi^a)\delta/\delta\xi^a \quad (3.11)$$

where ξ^a are the Rouse normal coordinates related to $\{c\}$ by the transformation

$$\xi_\alpha^a = \sum_{(\tau/l)=0}^{n_0-1} Q_a(\tau)c_\alpha(\tau) \qquad (3.12a)$$

$$Q_a(\tau) = [(2-\delta_{0a})/n_0]^{1/2}\cos[\pi a(\tau+l/2)N_0]. \qquad (3.12b)$$

The eigenvalue equation for L_0 is written in terms of the normal coordinates $\{\xi\}$ as

$$L_0\psi_{n_a^\alpha}(X_\alpha^a) = -(n_a^\alpha\lambda_a^2/\zeta_0)\psi_{n_a^\alpha}(X_\alpha^a) \qquad (3.13a)$$

with the variables and eigenfunctions

$$X_\alpha^a = \lambda_a\xi_\alpha^a/2^{1/2} \qquad \lambda_a = 2\sin(\pi a/2n_0) \qquad (3.13b)$$

$$\psi_n(X) = (2^n n!)^{-1/2}H_n(X) \qquad (3.13c)$$

where $H_n(X)$ is the nth-order Hermite polynomial. The label α in (3.12) and (3.13) denotes the αth cartesian component. Given (3.12) and (3.13) it is straightforward to expand J_{12} in (3.1) as a series expansion in the $\{\psi_n\}$ by (Wang and Freed 1986, 1987)

$$L_0^{-1}J_{12} = k_B T \sum_{p=1}^{n_0-1} (\zeta_0/2\lambda_p^2)\psi_1(X_1^p)\psi_1(X_2^p). \qquad (3.14)$$

Since the evaluation of the correction $\Delta[\eta]_1$ involves the operator $\Delta L_h^{(1)}$, we first substitute (2.28) and (2.31) into (3.6) to write $\Delta L_h^{(1)}$ in the form

$$\Delta L_h^{(1)} = \int_0^{N_0}\int_0^{N_0} d\tau\, d\tau' \int_k \left(\frac{\delta}{\delta c(\tau)} - \frac{\delta H\{c\}}{\delta c(\tau)}\right)\cdot\tau(k)\cdot\exp(ik\cdot c(\tau))$$

$$\times (k^2\eta_0 - L_0)^{-1}L_0(k^2\eta_0)^{-1}\exp(-ik\cdot c(\tau'))\frac{\delta}{\delta c(\tau')} \qquad (3.15)$$

where L_0 is defined in (3.11) and satisfies (3.13a). We obtain a leading order of magnitude estimate for $\Delta[\eta]_1$, by replacing the factor $(k^2\eta_0 - L_0)^{-1}$ in (3.15) by $(k^2\eta_0)^{-1}$, thereby rendering the computation of $\Delta[\eta]_1$ tractable. This approximation is again in the spirit of an expansion in powers of the ratio of polymer to solvent relaxation times. More formally, it neglects terms of one higher order in the small additional bare parameter $k_B T\rho/\eta_0\zeta_0$. Introducing this approximation and substituting (3.15) into (3.9) we find after some algebra that

$$\Delta[\eta]_1^p = (N_A k_B T/M\eta_0)\sum_{a,b=1}^{n_0-1}\int_0^{N_0}\int_0^{N_0} d\tau\, d\tau'\, (\zeta_0/2\lambda_a^2)(\zeta_0/2\lambda_b^2)\int D\{\xi\}P_{eq}\{\xi\}\lambda_a^2\xi_1^a\xi_2^a$$

$$\times\sum_{p=1}^{n_0-1}\int_k \left(\frac{\delta}{\delta\xi^p} - \lambda_p^2\xi^p\right)\cdot\tau(k)\cdot(\xi_2^b\rho_1 + \xi_1^b\rho_2)Q_b(\tau')Q_p(\tau)$$

$$\times (k^2\eta_0)^{-2}\exp(-k^2|\tau-\tau'|/2)(\lambda_b^2/\zeta_0)\left(\sum_{p'=0}^{n_0-1} k^2Q_{p'}^2(\tau') - \lambda_b^2\right) \qquad (3.16)$$

where the preaveraging approximation is used to replace $\exp\{ik\cdot[c(\tau)-c(\tau)]\}$ by its equilibrium average $\langle\exp[ik\cdot(c-c')]\rangle_{eq}$, and where ρ_1 and ρ_2 are unit vectors in the first two cartesian directions, respectively. Performing the integrations over the normal

coordinates $\{\xi\}$ reduces (3.16) to

$$\Delta[\eta]_1^p = -(N_A k_B T / M \eta_0) \sum_{a=1}^{n_0-1} (\zeta_0/2\lambda_a^2)^2 \int_0^{N_0} \int_0^{N_0} d\tau \, d\tau' \int_k (k^2 \eta_0)^{-2} \exp(-k^2|\tau-\tau'|/2)$$

$$\times Q_a(\tau) Q_a(\tau')(\lambda_a^2/\zeta_0)(k^2 - \lambda_a^2)(1 - 1/d). \tag{3.17}$$

The k integral in (3.17) can be easily evaluated to produce

$$\Delta[\eta]_1^p = -(N_A k_B T / M \eta_0) \sum_{a=1}^{n_0-1} (\zeta_0/2\lambda_a^2)^2 \int_0^{N_0} \int_0^{N_0} d\tau \, d\tau' \, Q_a(\tau) Q_a(\tau')(\lambda_a^2/\zeta_0 \eta_0^2)$$

$$\times [(1-1/d)/(d-2)](2\pi)^{d/2}[|\tau-\tau'|^{\varepsilon/2-1} + \lambda_a^2|\tau-\tau'|^{\varepsilon/2}(1/\varepsilon)]$$

$$\approx -(N_A k_B T / M \eta_0) \sum_{a=1}^{n_0-1} (\zeta_0/2\lambda_a^2)^2 \int_0^{N_0} \int_0^{N_0} d\tau \, d\tau' \, Q_a(\tau) Q_a(\tau')$$

$$\times |\tau-\tau'|^{\varepsilon/2-1}[(1-1/d)/(d-2)](\lambda_a^2/\eta_0)(k_B T \rho/\zeta_0 \eta_0) \tag{3.18}$$

where the factor of $k_B T \rho$ is introduced to restore natural units and where the contribution from the second term in the square brackets of the middle expression in (3.18) is neglected because it is much smaller than that due to the first term by a factor of $(1/n_0)$. The latter result follows because in the summation over a the $\lambda_a^2 \sim n_0^{-2}$ while $\tau \sim n_0$. Note that the retained term in $|\tau - \tau'|^{\varepsilon/2-1}$ represents the correction at wavelength l and has a magnitude corresponding to (2.29a), while the neglected term in $\lambda_a^2|\tau - \tau'|^{\varepsilon/2}$ is the correction at wavelength $\langle S^2 \rangle_0^{1/2}$ and has a magnitude corresponding to (2.29b). (Both contributions contain singular ε^{-1} portions as well as non-singular contributions.)

The expression (3.18) for $\Delta[\eta]_1^p$ contains a pole in ε just as the leading term $[\eta]_1^p$ in $[\eta]^{FP}$ does (see (3.19) below), producing a dependence of the dynamical polymer exponent z on the solvent viscosity. Such a bare contribution, however, is shown below to be negligibly small compared to that in $[\eta]_1^p$ (see (3.20)). For the purpose of assessing the magnitude of the correction $\Delta[\eta]_1$, it is convenient to quote the corresponding leading part in the intrinsic viscosity $[\eta]^{FP}$ of (3.7), which is given in the preaveraging approximation by (Wang and Freed 1987)

$$[\eta]_1^p = (N_A / M \eta_0 k_B T)\langle J_{12}|L_0^{-1} L_H L_0^{-1}|J_{12}\rangle_{eq}$$

$$= -(N_A k_B T / M \eta_0) \sum_{a=1}^{n_0-1} (\zeta_0/2\lambda_a^2)^2 \int_0^{N_0} \int_0^{N_0} d\tau \, d\tau' \, (\lambda_a^2/\eta_0) Q_a(\tau) Q_a(\tau')$$

$$\times |\tau-\tau'|^{\varepsilon/2-1}(1-1/d)/(d-2). \tag{3.19}$$

It is not surprising to see that the ratio $\Delta[\eta]_1/[\eta]_1$ (dropping the superscript p) is simply the ratio of the two timescales given in (2.29b), namely

$$\Delta[\eta]_1/[\eta]_1 = (k_B T \rho/\zeta_0 \eta_s) \sim 10^{-4} - 10^{-3} \tag{3.20}$$

where the numerical estimate in (3.20) uses values quoted between (2.29a) and (2.29b). Therefore, as we predicted by the rough argument in § 2, the bare first correction $\Delta[\eta]_1$, due to the thermal fluctuations of the solvent, is indeed extremely small for practically all polymer-solvent systems. Equations (3.9) and (3.19) enable us formally to say that the value of $\Delta L_h^{(1)}$ is smaller than L_H by at least a factor of 10^{-3} because of (3.20), namely $\|\Delta L_h^{(1)}\| \ll \|L_H\|$. Since the solvent fluctuations relax much faster than the polymer does, in effect they do not enter into the dynamical process of the polymer

motion, and they therefore contribute little to the dynamical observables of the polymer. Thus, it is adequate to neglect $\Delta[\eta]_1$ in (3.7).

The order ε^2 correction $\Delta[\eta]_2$ contains four terms. Using either the physical arguments of (2.29) and (2.30) or the type of estimate illustrated above, it can be shown (see appendix 1) that again each of the four terms in $\Delta[\eta]_2$ is much smaller than the leading-order ε^2 term in $[\eta]^{FP}$ of (3.7). This illustrative calculation of the intrinsic viscosity makes it clear through order ε^2 that the bare solvent velocity fluctuations play a negligible role in affecting the polymer dynamics and its associated dynamical exponent and that the bare $[\eta]^{FP}$ calculated from the Fokker–Planck equation is identical to the bare $[\eta]^{RZ}$ from the full Kirkwood diffusion equation. This conclusion may be demonstrated to likewise apply for other long-wavelength low-frequency polymer dynamical properties as well. Consequently, we have justified the use of the Kirkwood diffusion equation for order ε^2 evaluations of dynamical polymer properties within a range of small $(k_B T \rho / \zeta_0 \eta_0)(N/l)^{\psi - \varepsilon / 2}$ which we conjecture to apply to most polymer systems. Unfortunately, it is currently not possible to evaluate the terms in ρ^2 that are required for renormalising $k_B T \rho / \eta_0^2$ and for calculating ψ.

The example of the intrinsic viscosity indicates, in effect, that the term in $-\langle F_1 F_0^{-1} F_1 \rangle_u$ of (2.22) for F_h can be replaced by F_H and that $\Delta F_h^{(2)}$ in (2.22) contributes negligibly to F_h or to the averaged Fokker–Planck equation (2.21). Therefore, these results reduce equation (2.21) to

$$\frac{\partial P(\{c\}, t)}{\partial t} = (F_{0p} + F_H) P(\{c\}, t) \tag{3.21}$$

with F_{0p} and F_H given by (2.28b) and (2.31), respectively. Equation (3.21) is simply the Kirkwood diffusion equation for polymer dynamics. Thus, we demonstrate through order ε^2 (note that F_1^4 is of order ε^2) the conditions under which the kinetic equations (2.1) and (2.4) are equivalent to the frequently used Rouse–Zimm model of polymer dynamics in the diffusion equation formulation. As remarked by Oono, the investigation here necessarily relies on the use of renormalisation group theory, namely, our demonstration of the validity of the Kirkwood diffusion equation approach to $O(\varepsilon^2)$ applies only within a renormalisation group framework and with our heuristically motivated arguments concerning the smallness of $k_B T \rho / \zeta_0 \eta_0$.

4. Discussion

We have performed a double perturbation expansion in the hydrodynamic interactions g_0 and a bare expansion in the parameter $y_0 = k_B T \rho / \eta_0^2$. The ratio of these two parameters appears in the bare perturbation expansion and is loosely interpreted as the ratio of characteristic solvent and polymer timescales. The former expansion is a standard renormalisation expansion, while the latter is an expansion in an additional bare parameter which has the same critical dimensionality as the hydrodynamic interactions. This new parameter y_0 is thus of order ε, and may even begin in higher order in ε. Expansions in the ratio y_0/g_0 are heuristically argued to be justified on the basis of the smallness of the bare $k_B T \rho / \eta_0 \zeta_0$ for most polymer-solvent systems. This double expansion shows that the classical Kirkwood diffusion equation can be derived within the renormalisation group formalism through order ε^2 from the kinetic Langevin equations that include contributions from the solvent velocity fluctuations, provided

the renormalised $(y/g)(N/l)^{\psi-\epsilon/2}$ is sufficiently small. Then, the solvent velocity fluctuations contribute negligibly to low-frequency long-wavelength polymer dynamics provided the solvent possesses a much smaller characteristic relaxation timescale than that of the polymer modes of interest.

The general theory is illustrate by calculation for Gaussian chains of the corrections to the Rouse-Zimm model for the polymer intrinsic viscosity $[\eta]$ arising from the solvent velocity fluctuations. The correction terms do affect the power law exponents for the dependence of $[\eta]$ on molecular weight, but the bare contributions are found to be negligible as they are of the order of $\rho k_B T/\zeta_0\eta_0$, the ratio of polymer and solvent relaxation timescales where that for the solvent is measured at length scales comparable to a Kuhn length l. Only the leading-order correction in the ratio of polymer to solvent relaxation times has been studied within the preaveraging approximation as the higher-order terms and preaveraging corrections are not yet analytically tractable. However, the present calculations do indicate the appropriate length scales for the viscous relaxation modes of the solvent to identify the relevant dimensionless expansion parameter for the corrections due to solvent velocity fluctuations. The negligible magnitude of the bare corrections supports the use of the Rouse-Zimm model through order ϵ^2, an order to which we have previously performed several dynamical renormalisation group calculations (Wang and Freed 1986, 1987), in part, to study preaveraging corrections and effects of partial draining on polymer dynamics.

The presence of a systematic flow makes it a much more complicated matter to investigate the correction to the ordinary Kirkwood diffusion equation due to solvent velocity fluctuations. These difficulties arise because the zeroth-order equilibrium distribution for the solvent velocity field (analogous to $P_{eq}\{u\}$ here) becomes very complicated, and the distribution $P(\{c\})$ for the polymer conformation even without hydrodynamic interactions is no longer spatially isotropic. Nevertheless, it is still quite interesting to study these problems under flow to order ϵ. It currently appears to us that the treatment of the polymer-flow problems is more conveniently made directly from the coupled kinetic (Langevin) equations.

Acknowledgment

Appendix 1. Evaluation of the correction $\Delta[\eta]_2$

Section 3 shows that $\|\Delta L_h^{(1)}\| \ll \|L_H\|$, and consequently the first three terms of (3.10) are all much smaller than the leading-order ϵ^2 contribution of $\langle J_{12}|L_0^{-1}L_H L_0^{-1}L_H L_0^{-1}|J_{12}\rangle$ to the renormalisation group Rouse-Zimm model $[\eta]^{RZ}$. The last term in (3.10), containing $\Delta L_h^{(2)}$, is of a new type and we now analyse it to verify that it is likewise very small compared to the leading-order ϵ^2 contribution to $[\eta]^{RZ}$.

We begin by computing $\Delta F_h^{(2)}$, the adjoint of $\Delta L_h^{(2)}$ in (2.23). Partial integration of the second term of (2.23) over $\{u\}$ produces the integral

$$J_1 = \langle F_1(F_0^{-1}F_1)^3\rangle_u = -\int_k \int d\tau \frac{\delta}{\delta c} \cdot \exp(i\boldsymbol{k}\cdot\boldsymbol{c}) \int D\{u\}(k^2\eta_0 - F_{0p})^{-1}\boldsymbol{u}_k$$

$$\times \int_{k'} \int d\tau \left(\frac{\delta}{\delta c'} \cdot u_{k'} \exp(ik' \cdot c') - \frac{\delta}{\delta u_{k'}} \cdot \frac{\delta H}{\delta c'} \exp(-ik' \cdot c') \right)$$

$$\times (F_0^{-1} F_1)^2 P_{eq}\{u\} \tag{A1.1}$$

where c and c' are shorthand notation for $c(\tau, t)$ and $c(\tau', t)$ and where equations (2.8), (2.9) and (2.25b) have been used along with the fact that $P_{eq}\{u\}$ of (2.16b) vanishes at infinity $|u| \to \infty$. After another partial integration over $\{u\}$, equation (A1.1) can be manipulated to give

$$J_1 = -\left[\left[\int_0^{N_0} \int_0^{N_0} d\tau \, d\tau' \int_k \frac{\delta}{\delta c} \cdot \tau(k) \cdot \exp(ik \cdot c)(k^2 \eta_0 - F_{0p})^{-1} \right. \right.$$

$$\times \int_{k'} \left(\frac{\delta u_k}{\delta u_{-k'}} \cdot \frac{\delta}{\delta c'} \exp(ik' \cdot c') + \frac{\delta u_k}{\delta u_{k'}} \cdot \frac{\delta H}{\delta c'} \exp(-ik' \cdot c') \right) \Big] \langle (F_0^{-1} F_1)^2 \rangle_u$$

$$- \int_0^{N_0} \int_0^{N_0} d\tau \, d\tau' \int_k \int_{k'} \frac{\delta}{\delta c} \cdot \exp(ik \cdot c)(k^2 \eta_0 - F_{0p})^{-1}$$

$$\times \int D\{u\} \left(u_k u_{k'} - \frac{\delta u_k}{\delta u_{-k'}} \right) \cdot \frac{\delta}{\delta c'} \exp(ik' \cdot c')(F_0^{-1} F_1)^2 P_{eq}\{u\} \tag{A1.2}$$

where use is made of the equality

$$\frac{\delta u_k}{\delta u_{k'}} = \tau(k)\delta(k - k'). \tag{A1.3}$$

Comparing (A1.2) with (2.28) shows that the factor in large square brackets of (A1.2) is identical to (2.28). Consequently, the first term in (A1.2) is $-\langle F_1 F_0^{-1} F_1 \rangle_u \langle (F_0^{-1} F_1)^2 \rangle_u$ and cancels the first term on the right-hand side of (2.23), reducing (2.23) to a form involving the second term on the right-hand side of (A1.2),

$$\Delta F_h^{(2)} = \int_0^{N_0} \int_0^{N_0} d\tau \, d\tau' \int_k \int_{k'} \frac{\delta}{\delta c} \cdot \exp(ik \cdot c)(k^2 \eta_0 - F_{0p})^{-1}$$

$$\times \int D\{u\} \left(u_k u_{k'} - \frac{\delta u_k}{\delta u_{-k'}} \right) \cdot \frac{\delta}{\delta c'} \exp(ik' \cdot c')(F_0^{-1} F_1)^2 P_{eq}\{u\}. \tag{A1.4}$$

The presence of the second-order Hermite function $(u_k u_{k'} - \delta u_k / \delta u_{k'})$ in (A1.4) prevents contributions from the 'ground state' (2.25a) entering to convert the left-hand factor of F_0^{-1} into an F_{0p}^{-1}, and thereby this feature keeps $\Delta F_h^{(2)}$ small as we describe below.

Following the arguments presented in § 3, factors such as $(k^2 \eta_0 - F_{0p})^{-1}$ in (A1.4) are replaced to lowest order in the ratio of polymer to solvent relaxation rates by $(k^2 \eta_0)^{-1}$. This is equivalent to the replacement of F_0 in (A1.5) below by F_{0s} of (2.8c). Consequently, using (2.25b) converts (A1.4) to

$$\Delta F_h^{(2)} = -\int_0^{N_0} \int_0^{N_0} d\tau \, d\tau' \int_k \int_{k'} \frac{\delta}{\delta c} \cdot \exp(ik \cdot c)(k^2 \eta_0)^{-1}[(k^2 + k'^2)\eta_0]^{-1}$$

$$\times \int D\{u\}(u_k u_{k'} - \delta u_k / \delta u_{-k'}) \cdot \frac{\delta}{\delta c'} \exp(-ik' \cdot c') F_1 F_{0s}^{-1} F_1 P_{eq}\{u\}. \tag{A1.5}$$

Insertion of (2.9) in (A1.9) for the left F_1 factor in $F_1 F_{0s}^{-1} F_1$ of (A1.5) produces

$$\Delta F_h^{(2)} \equiv I_1 + I_2 \equiv -\int_0^{N_0} \int_0^{N_0} \mathrm{d}\tau \, \mathrm{d}\tau' \int_k \int_{k'} \frac{\delta}{\delta c} \cdot \exp(\mathrm{i}k \cdot c)(k^2 \eta_0)^{-1}[(k^2 + k'^2)\eta_0]^{-1}$$

$$\times \int_{k_1} \int D\{u\}[u_{k'}\delta(k - k_1) + u_k \delta(k' - k_1)] \cdot \tau(k_1) \cdot \frac{\delta}{\delta c'} \cdot \exp(-\mathrm{i}k' \cdot c')$$

$$\times \int_0^{N_0} \mathrm{d}\tau_1 \frac{\delta H}{\delta c_1} \exp(-\mathrm{i}k_1 \cdot c_1) F_{0s}^{-1} F_1 P_{\mathrm{eq}}\{u\}$$

$$+ \int_0^{N_0} \int_0^{N_0} \mathrm{d}\tau \, \mathrm{d}\tau' \int_k \int_{k'} \frac{\delta}{\delta c} \cdot \exp(\mathrm{i}k \cdot c)(k^2 \eta_0)^{-1}[(k^2 + k'^2)\eta_0]^{-1}$$

$$\times \int D\{u\}(u_k u_{k'} - \delta u_k / \delta u_{-k'}) \cdot \frac{\delta}{\delta c'} \cdot \exp(-\mathrm{i}k' \cdot c')$$

$$\times \int_0^{N_0} \mathrm{d}\tau_1 \int_{k_1} \frac{\delta}{\delta c_1} \cdot \exp(\mathrm{i}k_1 \cdot c_1) u_{k_1} F_{0s}^{-1} F_1 P_{\mathrm{eq}}\{u\} \tag{A1.6}$$

where the term in $u_{k'}\delta(k - k_1) + u_k \delta(k' - k_1)$ appears because of partial integration of the $\delta/\delta u_{k_1}$ part of F_1.

We proceed with the first term I_1 on the right-hand side of (A1.6) by again substituting (2.9) for the remaining F_1, using (2.25b) and (2.27) and performing the u integration to reduce I_1 to

$$I_1 = \int_0^{N_0} \int_0^{N_0} \mathrm{d}\tau \, \mathrm{d}\tau' \int_k \int_{k'} \frac{\delta}{\delta c} \cdot \tau(k) \cdot \frac{\delta}{\delta c'} \cdot \exp(\mathrm{i}k \cdot c - \mathrm{i}k' \cdot c')(k^2 \eta_0)^{-1}[(k^2 + k'^2)\eta_0]^{-1}$$

$$\times \int_0^{N_0} \int_0^{N_0} \mathrm{d}\tau_1 \, \mathrm{d}\tau_2 \frac{\delta H}{\delta c_1} \cdot \tau(k') \cdot \left(\frac{\delta}{\delta c_2} + \frac{\delta H}{\delta c_2}\right)$$

$$\times [(k'^2 \eta_0)^{-1} \exp(-\mathrm{i}k \cdot c_1 + \mathrm{i}k' \cdot c_2) + (k^2 \eta_0)^{-1} \exp(-\mathrm{i}k' \cdot c_1 + \mathrm{i}k \cdot c_2)]. \tag{A1.7}$$

Now we compare $I_1^\dagger$, the adjoint of I_1, with the leading-order ε^2 contribution $L_H L_0^{-1} L_H$ to $[\eta]^{\mathrm{RZ}}$ by explicitly writing the latter as the integral

$$L_H L_0^{-1} L_H = \int_0^{N_0} \int_0^{N_0} \mathrm{d}\tau \, \mathrm{d}\tau' \left(\frac{\delta}{\delta c} - \frac{\delta H}{\delta c}\right) \cdot \int_k \tau(k)(k^2 \eta_0)^{-1} \exp[\mathrm{i}k \cdot (c - c')] \cdot \frac{\delta}{\delta c'}$$

$$\times L_0^{-1} \int_0^{N_0} \int_0^{N_0} \mathrm{d}\tau_1 \, \mathrm{d}\tau_2 \cdot \left(\frac{\delta}{\delta c_1} - \frac{\delta H}{\delta c_1}\right) \cdot \int_{k'} \tau(k') \cdot (k'^2 \eta_0)^{-1}$$

$$\times \exp[\mathrm{i}k' \cdot (c_1 - c_2)] \cdot \frac{\delta}{\delta c_2}. \tag{A1.8}$$

Sections 2 and 3 demonstrate the ratio $(\|L_0\|/k^2 \eta_0)$ in the k integral is much smaller than unity (i.e. of the order of t_s/t_p) so that we have

$$\|L_H L_0^{-1} L_H\| \gg \left\| \int_0^{N_0} \int_0^{N_0} \mathrm{d}\tau \, \mathrm{d}\tau' \left(\frac{\delta}{\delta c} - \frac{\delta H}{\delta c}\right) \cdot \int_k \tau(k) \cdot \exp[\mathrm{i}k \cdot (c - c')] \cdot \frac{\delta}{\delta c'} \right.$$

$$\times (k^2 \eta_0)^{-1}(L_0/k^2 \eta_0)L_0^{-1} \int_0^{N_0} \int_0^{N_0} \mathrm{d}\tau_1 \, \mathrm{d}\tau_2 \left(\frac{\delta}{\delta c_1} - \frac{\delta H}{\delta c_1}\right) \cdot$$

$$\times \left. \int_{k'} \tau(k') \cdot (k'^2 \eta_0)^{-1} \exp[\mathrm{i}k' \cdot (c_1 - c_2)] \frac{\delta}{\delta c_2} \right\|$$

$$= \left\| \int_0^{N_0} \int_0^{N_0} \mathrm{d}\tau \, \mathrm{d}\tau' \left(\frac{\delta}{\delta c} - \frac{\delta H}{\delta c}\right) \cdot \int_k \tau(k) \cdot \exp[\mathrm{i}k \cdot (c - c')] \cdot \frac{\delta}{\delta c'} (k^2 \eta_0)^{-2} \right.$$

$$\times \int_0^{N_0} \int_0^{N_0} d\tau_1 \, d\tau_2 \left(\frac{\delta}{\delta c_1} - \frac{\delta H}{\delta c_1} \right) \cdot \int_{k'} \tau(k') \cdot (k'^2 \eta_0)^{-1}$$

$$\times \exp[i k' \cdot (c_1 - c_2)] \cdot \frac{\delta}{\delta c_2} \Bigg\| \tag{A1.9}$$

where $A \gg B$ is understood to imply B is smaller than A by (t_s/t_p). The right-hand side of (A1.9) has a similar structure to that of the adjoint $I_1^\dagger$ of (A1.7) and up to an accuracy of the order of magnitude $I_1^\dagger$ is approximately given by

$$I_1^\dagger = \int_0^{N_0} \int_0^{N_0} d\tau \, d\tau' \left(\frac{\delta}{\delta c} - \frac{\delta H}{\delta c} \right) \cdot \int_k \tau(k) \cdot \exp[i k \cdot (c - c')] \cdot \frac{\delta}{\delta c'} (k^2 \eta_0)^{-2}$$

$$\times \int_0^{N_0} \int_0^{N_0} d\tau_1 \, d\tau_2 \left(-\frac{\delta H}{\delta c_1} \right) \cdot \int_{k'} \tau(k') \cdot (k'^2 \eta_0)^{-1}$$

$$\times \exp[i k' \cdot (c_1 - c_2)] \cdot \frac{\delta}{\delta c_2}. \tag{A1.10}$$

Equation (A1.10) shows $I^\dagger$ as having a similar analytical form to the right-hand side of (A1.9). Therefore, $I_1^\dagger$ is of the same order of magnitude as the right-hand side of (A1.9). Consequently, our order of magnitude analysis leads to

$$\| L_H L_0^{-1} L_H \| \gg \| I_1^\dagger \|. \tag{A1.11}$$

The estimation of I_2 or $I_2^\dagger$ proceeds in a similar fashion where it again follows that

$$\| L_H L_0^{-1} L_H \| \gg \| I_2^\dagger \|. \tag{A1.12}$$

The combination of (A1.11) and (A1.12) demonstrates our contention

$$\| L_H L_0^{-1} L_H \| \gg \| [\Delta F_h^{(2)}]^\dagger \| = \| \Delta L_h^{(2)} \| \tag{A1.13a}$$

which implies (see (A1.9) and thereafter)

$$\| \Delta L_h^{(2)} \| / \| L_H L_0^{-1} L_H \| \sim t_s / t_p. \tag{A1.13b}$$

While these analyses are admittedly crude, they do serve to suggest that the bare correction term involving $\Delta L_h^{(2)}$ in $\Delta[\eta]_2$ of (3.10) is negligible compared to the leading bare contribution involving $L_H L_0^{-1} L_H$ in $[\eta]^{RZ}$.

Appendix 2. Non-Markovian corrections

The reduction of (2.11) to a closed equation requires the solution $\hat{P}(\{c\}, \{u\}, t)$ to the Fokker–Planck equation (2.7). Section 2 presents the perturbative solution in terms of (2.13) and (2.14a) and then introduces a Markovian approximation to (2.14a). In this appendix we retain the full solution of (2.14a) and convert it using Laplace transforms into

$$\hat{P}_i(s) = \int_0^\infty \exp(-st) \hat{P}_i(t) \, dt = (s - F_0)^{-1} F_1 \hat{P}_{i-1}(s). \tag{A2.1}$$

Now the Laplace transform $\hat{P}(s)$ of the full solution of (2.7) becomes expressed as

$$\hat{P}(s) = \{1 + (s - F_0)^{-1} F_1 + [(s - F_0)^{-1} F_1]^2 + \ldots\} P_{eq}\{u\} \tilde{P}(s) \tag{A2.2}$$

where the Laplace transform of (2.17) is used. Equation (2.10) implies that the Laplace transform $P(\{c\}, s)$ of $P(t)$ is obtained by integrating both sides of (A2.2) over $\{u\}$ to yield

$$P(s) = \langle \{1 + (s - F_0)^{-1} F_1 + [(s - F_0)^{-1} F_1]^2 + \ldots\} \rangle_u \tilde{P}(s). \tag{A2.3}$$

Inversion of (A2.3) shows the unspecified $\tilde{P}(s)$ may be expressed in terms of $P(s)$ by

$$\tilde{P}(s) = \{1 - \langle [(s - F_0)^{-1} F_1]^2 \rangle_u + \ldots \} P(s). \tag{A2.4}$$

Insert the inverse Laplace transform

$$\hat{P}(\{c\}, \{u\}, t) = \int_{\alpha - i\infty}^{\alpha + i\infty} \frac{\mathrm{d}s}{2\pi \mathrm{i}} \exp(st) \hat{P}(s)$$

together with (A2.2) and (A2.4) into (2.11) produces

$$\left(\frac{\partial}{\partial t} - F_{0p} \right) P(\{c\}, t)$$

$$= \int_{\alpha - i\infty}^{\alpha + i\infty} \frac{\mathrm{d}s}{2\pi \mathrm{i}} \exp(st) \langle F_1 (s - F_0)^{-1} F_1 \rangle_u P(s) + \int_{\alpha - i\infty}^{\alpha + i\infty} \frac{\mathrm{d}s}{2\pi \mathrm{i}} \exp(st)$$

$$\times \{ \langle F_1 [(s - F_0)^{-1} F_1]^3 \rangle_u - \langle F_1 (s - F_0)^{-1} F_1 \rangle_u \langle [(s - F_0)^{-1} F_1]^2 \rangle_u \} P(s) \tag{A2.5}$$

where $P(s)$ is the Laplace transform of $P(\{c\}, t)$. Equation (A2.5) is derived without use of a Markovian approximation, while its Markovian approximation (2.21)–(2.23) is valid only for times $t \geq t_p$, the polymer mode relaxation times, and $t_p \gg t_s$.

The factor $(s - F_0)^{-1}$ in the first term on the right-hand side of (A2.5) may be transformed with the timescale separation $\|F_{0s}\| \gg \|F_{0p}\|$ approximation into a term containing the dynamic Oseen tensor. Qualitative arguments by Edwards and Freed (1974) and more quantitative ones by Metiu and Freed (1977) demonstrate that this dynamical Oseen tensor can safely be replaced by its static value for long-wavelength low-frequency polymer properties. On the other hand, the presence of s in the second term on the right-hand side of (A2.5) introduces no extra difficulties in showing that this term is negligible as outlined in appendix 1 for demonstrating the smallness of $\Delta F_h^{(2)}$.

References

Diehl H W 1986 *Phase Transitions and Critical Phenomena* vol 10, ed C Domb and J L Lebowitz (New York: Academic) p 75
Edwards S F 1965 *Proc. Phys. Soc.* **85** 613
Edwards S F and Freed K F 1974 *J. Chem. Phys.* **61** 1189
Felderhof B U, Deutch J M and Titulaer U M 1975 *J. Chem. Phys.* **63** 740
Jagannathan A, Oono Y and Schaub B 1985 *Phys. Lett.* **113A** 341
—— 1987 *J. Chem. Phys.* **86** 2276
Jasnow D and Moore M A 1978 *J. Physique Lett.* **38** L467
Kawasaki K and Gunton J 1976 *Phys. Rev.* B **13** 4658
Kirkwood J G 1954 *J. Polym. Sci.* **12** 1
Lee A, Baldwin P and Oono Y 1984 *Phys. Rev.* A **30** 968
Ma S K and Mazenko G F 1975 *Phys. Rev.* B **11** 4077
Metiu H and Freed K F 1977 *J. Chem. Phys.* **67** 3303
Nemirovsky A M and Freed K F 1985 *J. Chem. Phys.* **83** 4166
Oono Y and Freed K F 1981 *J. Chem. Phys.* **75** 1009
Puri S, Schaub B and Oono Y 1986 *Phys. Rev.* A **34** 541
Rouse P E Jr 1953 *J. Chem. Phys.* **21** 1272
Schaub B, Friedman B A and Oono Y 1985 *Phys. Lett.* **110A** 136
Shiwa Y and Kawasaki K 1982 *J. Phys. C: Solid State Phys.* **15** 5345

Wang S Q 1987 *Phys. Lett.* **125A** 208
Wang S Q and Freed K F 1986 *J. Chem. Phys.* **85** 6210
—— 1987 *J. Chem. Phys.* **86** 3021
—— 1988 *J. Chem. Phys.* in press
Yamazaki K and Ohta T 1982 *J. Phys. A: Math. Gen.* **15** 287
Zimm B H 1956 *J. Chem. Phys.* **24** 269