The influence of the extent of excluded volume interactions on the linear viscoelastic properties of dilute polymer solutions

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Abstract

The Rouse model has recently been modified to take into account the excluded volume interactions that exist between various parts of a polymer chain by incorporating a narrow Gaussian repulsive potential between pairs of beads on the Rouse chain (Prakash, 2000). The narrow Gaussian potential is characterized by two parameters: $z^*$ — which accounts for the strength of the interaction, and $d^*$ — which accounts for the extent of the interaction. In the limit of $d^*$ going to zero, the narrow Gaussian potential tends to the more commonly used $\delta$-function repulsive potential. The influence of the parameter $d^*$, in the limit of infinite chain length, on equilibrium and linear viscoelastic properties, and on universal ratios involving these properties, is examined here. A renormalization group calculation of the end-to-end vector suggests that the value chosen for the variable $d^*$ will not affect critical exponents, or universal ratios. A similar trend is also observed for results obtained with an approximate solution, which is based on the assumption that the non-equilibrium configurational distribution function is Gaussian.

Key words: Rheology, Polymer, Solutions, Modeling, Viscoelasticity, Good solvent, Excluded volume, Universal behavior

1 Introduction

The macroscopic consequences, on both equilibrium and rheological properties of dilute polymer solutions, of the microscopic fact that two parts of a polymer chain cannot occupy the same place at the same time, have been the

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subject of innumerable investigations. Analytical treatments of this excluded volume effect have, by and large, modeled the repulsive interaction between parts of the polymer chain with a Dirac delta potential. As a result, different parts of the chain interact with each other only when they are directly in contact (Yamakawa, 1971; Doi & Edwards, 1986; Öttinger, 1989; des Cloizeaux & Jannink, 1990; Zyika & Öttinger, 1991; Schäfer, 1999). The use of a δ-function potential makes it difficult to obtain exact analytical results. Consequently, progress has usually been made by using renormalization group methods to refine the results of perturbation calculations. On the other hand, numerical investigations with Monte Carlo and Brownian dynamics simulations—which lead to exact results—have been based on potentials that have a finite range of excluded volume interaction, such as the Lennard-Jones potential, because of the unsuitability of the δ-function potential for numerical simulations (Graessler, Hayward & Grest, 1999; Hernandez Cifre & Garcia de la Torre, 1999). The quality of the approximate analytical results are usually assessed—at least in the case of static properties, which have been much more extensively studied than properties away from equilibrium—by comparison with the exact Monte Carlo simulations. The comparison is made, in spite of the fact that the analytical and numerical approaches are based on different potentials, because it is generally accepted that the choice of the excluded volume potential does not influence the scaling of observables in the limit of long chains. Such comparisons have established that the results of static theories agree well with both Monte Carlo simulations and with experimental observations (Schäfer, 1999).

Prakash and Öttinger have recently examined the influence of excluded volume effects on the rheological properties of dilute polymer solutions by representing the polymer molecule with a Hookean dumbbell model, and using a narrow Gaussian repulsive potential to describe the excluded volume interactions between the beads of the dumbbell (Prakash & Öttinger, 1999). The same potential has subsequently been used by Prakash (Prakash, 2000) to represent the excluded volume interactions between pairs of beads in a bead-spring chain model for the polymer molecule. If the bead position vectors \( r_\nu, \nu = 1, 2, \ldots, N, \) are used to denote the instantaneous configuration of the bead-spring chain (which consists of \( N \) beads connected together by \( (N-1) \) Hookean springs), the narrow Gaussian potential \( E(r_\nu - r_\mu) \) between any pair of beads \( \nu \) and \( \mu \) can be written as,

\[
E(r_\nu - r_\mu) = \left( \frac{z^*}{d^*} \right) k_B T \exp \left\{ -\frac{H}{2k_B T} \frac{r_{\nu \mu}^2}{d^*^2} \right\}
\]

(1)

where, \( k_B \) is Boltzmann’s constant, \( T \) is the absolute temperature, \( H \) is the spring constant, \( r_{\nu \mu} = r_\nu - r_\mu \), is the vector between beads \( \mu \) and \( \nu \), and the parameters \( z^* \) and \( d^* \) are non-dimensional quantities which characterize
the narrow Gaussian potential. While $z^*$ measures the strength of the excluded volume interaction, $d^*$ is a measure of the extent of excluded volume interaction. Note that in the limit $d^*$ tending to zero, the narrow Gaussian potential becomes a $\delta$-function potential. Compared to the $\delta$-function potential, analytical calculations are not significantly harder with the narrow Gaussian potential; often, upon setting $d^* = 0$, the predictions of a $\delta$-function potential can be obtained. Furthermore, Brownian dynamics simulations can be performed with a narrow Gaussian potential. As a result, the use of a narrow Gaussian potential makes it possible to compare approximate analytical results and numerical simulations consistently.

Two approximate solutions have been developed in order to examine the consequences of using a narrow Gaussian potential (Prakash, 2000). The first approximation is a first order perturbation expansion in the strength of excluded volume interaction, while the second approximation, which is non-perturbative in nature, is based on assuming that the configurational distribution function is a Gaussian distribution. The equilibrium swelling of the end-to-end vector and the radius of gyration, and zero shear rate properties, predicted by both the approximate solutions, were compared with the predictions of exact Brownian dynamics simulations.

The Brownian dynamics simulations revealed, rather unexpectedly, that for chains with an arbitrary but finite number of beads, the use of a $\delta$-function excluded volume potential leads to predictions that are identical to those of the Rouse model. In other words theta and good solvents were predicted to have the same equilibrium and rheological behavior. Departure from Rouse model predictions could only be obtained for non-zero values of $d^*$. As the number of beads $N$ became large, however, the simulation results seemed to suggest that the use of a $\delta$-function potential may be justified. It must be noted though that this conclusion is speculative, and is based on rather limited data. It is clearly worthwhile therefore to examine the equilibrium and rheological predictions obtained by carrying out the two limits $d^* \to 0$ and $N \to \infty$ simultaneously. However, it is difficult to obtain data for very long chains because of the computational intensity of Brownian dynamics simulations.

In contrast to Brownian dynamics simulations, both the first order perturbation expansion and the Gaussian approximation predict a spurious non-trivial effect due to the presence of $\delta$-function excluded volume interactions, i.e. when $d^* = 0$. In the case of a dumbbell model it was shown rigorously that the source of the problem was the incorrect term-by-term integration of a series that was not uniformly convergent (Prakash & Öttinger, 1999). On the other hand, for fixed values of $N$ and $z^*$, the Gaussian approximation becomes increasingly accurate as $d^*$ increases. Furthermore, for fixed values of the re-scaled variables $d = d^* / \sqrt{N}$, and $z = z^* \sqrt{N}$, the accuracy of the Gaussian approximation increases as $N$ increases (Prakash, 2000). Since the Gaussian approximation
is not as computationally intensive as Brownian dynamics simulations, it is possible to obtain predictions in the long chain limit by accumulating data for chains of finite length and extrapolating to \( N \to \infty \). The Gaussian approximation provides a means therefore of exploring the role of the extent of excluded volume interaction in the limit of long chains. The purpose of this paper is to use the equilibrium and zero shear rate predictions of the Gaussian approximation to gain insight into the influence of the parameter \( d^* \) as \( N \to \infty \).

As a preliminary motivation to examining the Gaussian approximation in the limit of long chains, an elementary renormalization group calculation of the equilibrium end-to-end vector is also carried out in this paper. The renormalization group method is a systematic way of examining the macroscopic relevance of a microscopic parameter, i.e., if it has macroscopic consequences. It is therefore an ideal, albeit technically involved, tool to examine the role of the parameter \( d^* \).

The plan of the paper is as follows. The theoretical background for the Gaussian approximation, and the principal results obtained on making the Gaussian approximation are summarized in the next section. The renormalization of the equilibrium end-to-end vector is taken up in section 3. The results of extrapolating finite chain Gaussian approximation results to infinite chain length are discussed in section 4, and the main conclusions of the present work are summarized in section 5.

\section{The Gaussian approximation}

Two fundamental equations, (i) the diffusion equation for the configurational distribution function of the polymer chain, and (ii) the Kramers expression for the polymer contribution to the stress tensor, are the basic ingredients of a kinetic theory of dilute polymer solutions. In the presence of excluded volume interactions, one can show that the diffusion equation for a bead-spring chain with \( N \) beads, suspended in a Newtonian solvent, has the form (Prakash, 2000),

\[
\frac{\partial \psi}{\partial t} = - \sum_{j=1}^{N-1} \frac{\partial}{\partial Q_j} \cdot \left( \kappa \cdot Q_j - \frac{H}{\zeta} \sum_{k=1}^{N-1} A_{jk} Q_k + \frac{1}{\zeta} \sum_{\nu=1}^{N} B_{j\nu} F^{(E)}_\nu \right) \psi \\
+ \frac{k_B T}{\zeta} \sum_{j,k=1}^{N-1} A_{jk} \frac{\partial}{\partial Q_j} \cdot \frac{\partial \psi}{\partial Q_k}
\]

\( \text{(2)} \)
where, $Q_i = r_{i+1} - r_i$, is the bead connector vector between the beads $i$ and $i + 1$, $\psi(Q_1, \ldots, Q_{N-1}, t)$ is the configurational distribution function, $\kappa(t)$ is the traceless transpose of the velocity-gradient tensor, $\zeta$ is the bead friction coefficient, $B_{k\nu}$ is an $(N-1) \times N$ matrix defined by, $B_{k\nu} = \delta_{k+1, \nu} - \delta_{k\nu}$, with $\delta_{k\nu}$ denoting the Kronecker delta, and $A_{jk}$ is the Rouse matrix,

$$A_{jk} = \sum_{\nu=1}^{N} B_{j\nu} B_{k\nu} = \begin{cases} 2 & \text{for } |j - k| = 0, \\ -1 & \text{for } |j - k| = 1, \\ 0 & \text{otherwise} \end{cases}$$ (3)

The vector $F^{(E)}_\nu$ is the total excluded volume force on bead $\nu$. It is given, in terms of the excluded volume potential between the beads of the chain, by the expression,

$$F^{(E)}_\nu = -\sum_{\nu\neq\mu=1}^{N} \frac{\partial}{\partial r_\nu} E (r_\nu - r_\mu)$$ (4)

The Kramers expression for the polymer contribution to the stress tensor, for a bead-spring chain model with Hookean springs and an arbitrary excluded volume potential force, is given by (Bird, Curtiss, Armstrong & Hassager 1987),

$$\tau^p = -n_p H \sum_{k=1}^{N-1} \langle Q_k Q_k \rangle + Z + (N - 1) n_p k_B T \mathbf{1}$$ (5)

where, angular brackets denote an average performed with the configurational distribution function $\psi$ (obtained by solving the diffusion equation), $n_p$ is the number density of polymers, $\mathbf{1}$ is the unit tensor, and the tensor $Z$, which represents the direct contribution due to excluded volume effects (Prakash 2000), is given by,

$$Z = n_p \sum_{\nu=1}^{N} \sum_{k=1}^{N-1} B_{\nu k} \langle Q_k F^{(E)}_\nu \rangle$$ (6)

The quantity $B_{\nu k}$ is a $N \times (N - 1)$ matrix defined by, $B_{\nu k} = k/N - \Theta (k - \nu)$, with $\Theta (k - \nu)$ denoting a Heaviside step function.

The diffusion equation, Eq. (2), becomes analytically intractable when excluded volume interactions are described in terms of the narrow Gaussian potential, Eq. (1). As mentioned in the introduction, there are several different solution schemes, involving either (i) an exact numerical approach, or (ii) approximate analytical approaches, that can be developed to overcome
this problem. These have been discussed in detail in Prakash (2000). Here, we summarize one approximate non-perturbative solution procedure, called the Gaussian approximation.

The Gaussian approximation is based on reducing the complex higher order moments in Kramers expression, Eq. (5), to functions of only second order moments, by assuming that the non-equilibrium configurational distribution function $\psi$, is a Gaussian distribution. The Kramers expression can then be shown to assume the form,

$$\tau^p = -n_p H \sum_{k=1}^{N-1} \sigma_{kk} + Z + (N - 1) n_p k_B T \mathbf{1}$$  \hspace{1cm} (7)$$

where, the $(N - 1) \times (N - 1)$ matrix of tensor components, $\sigma_{jk} = \langle Q_j Q_k \rangle$, is the covariance matrix which uniquely characterizes the Gaussian distribution, and the tensor $Z$ is now given by the expression,

$$Z = \frac{1}{2} z^* n_p k_B T \sum_{\nu, \mu=1}^{N} \hat{\sigma}_{\nu\mu} \cdot \Pi(\hat{\sigma}_{\nu\mu})$$  \hspace{1cm} (8)$$

Here, the function $\Pi(\hat{\sigma}_{\nu\mu})$ is given by,

$$\Pi(\hat{\sigma}_{\nu\mu}) = \frac{[d_s^2 \mathbf{1} + \hat{\sigma}_{\nu\mu}]^{-1}}{\sqrt{\det ([d_s^2 \mathbf{1} + \hat{\sigma}_{\nu\mu}])}}$$  \hspace{1cm} (9)$$

with the tensors $\hat{\sigma}_{\nu\mu}$ defined by,

$$\hat{\sigma}_{\nu\mu} = \hat{\sigma}_{\nu\mu}^T = \hat{\sigma}_{\mu\nu} = \frac{H}{k_B T} \sum_{j,k=\min(\mu,\nu)}^{\max(\mu,\nu)-1} \sigma_{jk}$$  \hspace{1cm} (10)$$

The Gaussian approximation is complete when a scheme for calculating the covariance matrix $\sigma_{jk}$ is specified. A time evolution equation for $\sigma_{jk}$ can be derived by multiplying the diffusion equation, Eq. (2), by $Q_j Q_k$ and integrating over all configurations. The higher order moments that appear on the right hand side of the evolution equation are reduced to second order moments by consistently using the ansatz of the Gaussian approximation. The following evolution equation for $\sigma_{jk}$ is then obtained,

$$\frac{d}{dt} \sigma_{jk} = \kappa \cdot \sigma_{jk} + \sigma_{jk} \cdot \kappa^T - \frac{H}{\zeta} \sum_{m=1}^{N-1} [\sigma_{jm} A_{mk} + A_{jm} \sigma_{mk}]$$
\[ + \frac{2k_B T}{\zeta} A_{jk} \mathbf{1} + \mathbf{Y}_{jk} \]  \hspace{1cm} (11)

where,

\[ \mathbf{Y}_{jk} = z^* \left( \frac{H}{\zeta} \right) \sum_{m=1}^{N-1} [\mathbf{\sigma}_{jm} \cdot \mathbf{\Delta}_{km} + \mathbf{\Delta}_{jm} \cdot \mathbf{\sigma}_{mk}] \]  \hspace{1cm} (12)

In Eq. (12), the \((N-1) \times (N-1)\) matrix of tensor components \(\mathbf{\Delta}_{jm}\) is defined by,

\[ \mathbf{\Delta}_{jm} = \sum_{\mu=1}^{N} \left\{ (B_{j+1,m} - B_{\mu m}) \Pi(\mathbf{\sigma}_{j+1,\mu}) - (B_{jm} - B_{\mu m}) \Pi(\mathbf{\sigma}_{j\mu}) \right\} \]  \hspace{1cm} (13)

The system of \(9 \times (N-1)^2\) coupled ordinary differential equations for \(\mathbf{\sigma}_{jk}\), Eq. (11), can be solved analytically (correct to first order in velocity gradient), by expanding \(\mathbf{\sigma}_{jk}\) up to first order in velocity gradient about its isotropic equilibrium value. On subsequently making use of Kramers expression, Eq. (7), the following first order codeformational memory-integral expansion for the polymer contribution to the stress tensor can be derived,

\[ \tau_p = -\int_{-\infty}^{t} ds G(t-s) \mathbf{\gamma}_{[1]}(t,s) \]  \hspace{1cm} (14)

where, \(\mathbf{\gamma}_{[1]}\) is the codeformational rate-of-strain tensor \cite{Bird, Armstrong & Hassager, 1987}, and \(G(t)\) is the memory function whose explicit form is given in appendix B of \cite{Prakash, 2000}.

Exact expressions for the zero shear rate viscosity, \(\eta_{p,0}\), and the zero shear rate first normal stress difference, \(\Psi_{1,0}\), predicted by the Gaussian approximation, can be obtained from Eq. (14). These expressions, which are lengthy, are given in \cite{Prakash, 2000}. It suffices here to note that their evaluation requires the inversion of an \((N-1)^2 \times (N-1)^2\) matrix. As a result, the CPU time required for their evaluation scales as \(N^6\). Generating data for large values of \(N\) becomes extremely computationally intensive. Predictions of zero shear rate properties have been obtained for chains up to a maximum of \(N = 40\) beads, since, for this value of \(N\), a single run on an SGI Origin2000 computer with a 195 MHz processor required approximately 54 hours of CPU time.

It is appropriate now to summarize the most significant results obtained on making the Gaussian approximation. When the equilibrium swelling and the zero shear rate properties, at a constant value of \(z^*\), are plotted versus \(d^*\) for
various values of \( N \), and compared with Brownian dynamics simulations, it is found that, for each value of \( N \), the Gaussian approximation becomes accurate beyond a threshold value of \( d^* \). However, this threshold value increases as \( N \) increases, implying that the accuracy of the Gaussian approximation decreases with increasing \( N \). The picture changes considerably, however, when the same data is viewed in terms of the re-scaled extent of excluded volume interaction \( d = d^*/\sqrt{N} \), and re-scaled strength of the interaction \( z = z^*\sqrt{N} \).

The Gaussian approximation appears in much better light in the context of the re-scaled variables since, at a fixed value of \( z \), it becomes accurate over an increasingly larger range of values of \( d \) as \( N \) increases. Furthermore, as clarified below, asymptotic behavior in the limit of large \( N \) is observed.

In the limit of large \( N \), curves for various values of \( N \) begin to collapse onto a single curve, indicating that all the equilibrium and linear viscoelastic properties are independent of the value of \( N \), and are in fact, only functions of \( z \) and \( d \). This implies that, if some knowledge about the leading order corrections to the infinite chain length limit can be obtained, data accumulated for finite chains for large enough values of \( N \) can be efficiently extrapolated to the limit \( N \to \infty \). As will be seen in the section below, in addition to elucidating the role of \( d^* \) in the theory, a renormalization group calculation of the equilibrium end-to-end vector also provides insight into the leading order correction. Discussion of the extrapolation procedure, and the results obtained on extrapolating the Gaussian approximation data to infinite chains, will be taken up in section 4.

### 3 Renormalization of the equilibrium end-to-end vector

The second moment of the end-to-end vector \( \mathbf{r} \) at equilibrium is given by the expression,

\[
\langle \mathbf{rr} \rangle_{\text{eq}} = \sum_{j,k=1}^{N-1} \langle Q_j Q_k \rangle_{\text{eq}}
\]

(15)

where, the suffix “eq” indicates that the average is carried out with the equilibrium distribution function, \( \psi_{\text{eq}} \), given by,

\[
\psi_{\text{eq}}(Q_1, \ldots, Q_{N-1}) = N_{\text{eq}} e^{-\phi/k_BT}
\]

(16)

The quantity \( \phi \) denotes the potential energy of the bead-spring chain, and \( N_{\text{eq}} \) denotes the normalization constant. In the present model, the potential energy \( \phi \) is the sum of the potential energies of all the springs in the chain, and the
excluded volume interaction energies between all pairs of beads \( \mu \) and \( \nu \),

\[
\phi = \frac{1}{2} H \sum_{i=1}^{N-1} \mathbf{Q}_i \cdot \mathbf{Q}_i + \frac{1}{2} \sum_{\mu, \nu=1 \atop \mu \neq \nu}^{N} E (\mathbf{r}_\nu - \mathbf{r}_\mu) \tag{17}
\]

In order to perform a renormalization group calculation of the end-to-end vector, it is first necessary to expand the equilibrium configurational distribution function in a perturbation expansion up to first order in the strength of the excluded volume interaction. As will be clear shortly, the expansion must be made in a space of arbitrary dimensions \( D \).

Upon expanding both the potential energy \( \phi \) (Eq. (17), with \( E (\mathbf{r}_\nu - \mathbf{r}_\mu) \) given by the narrow Gaussian potential, Eq. (1), extended to \( D \) dimensions), and the normalization constant \( N_{eq} \), to first order in the strength of the excluded volume interaction, one can show that,

\[
\langle \mathbf{Q}_j \mathbf{Q}_k \rangle_{eq} = \left[ 1 + \frac{1}{2} z^*_D \sum_{\mu, \nu=1 \atop \mu \neq \nu}^{N} \frac{1}{\sqrt{\det \left[ d^2 1 + (H/k_B T) \langle \mathbf{r}_{\nu\mu} \mathbf{r}_{\nu\mu} \rangle_{eq}^R \right]}} \right] \sigma^R_{eq, jk}
\]

\[- \frac{1}{2 k_B T} \sum_{\mu, \nu=1 \atop \mu \neq \nu}^{N} \langle \mathbf{Q}_j \mathbf{Q}_k E (\mathbf{r}_\nu - \mathbf{r}_\mu) \rangle_{eq}^R \tag{18}
\]

where, \( z^*_D \) is an extension of the definition of the \( z^* \) parameter to \( D \) dimensions, and angular brackets with superfix “\( R \)” and suffix “eq” represent averages carried out with the equilibrium distribution function, \( \psi^R_{eq} \), of the Rouse model, extended to \( D \) dimensions. As is well known, \( \psi^R_{eq} \) is a Gaussian distribution function,

\[
\psi^R_{eq} (\mathbf{Q}_1, \ldots, \mathbf{Q}_{N-1}) = \left( \frac{H}{2 \pi k_B T} \right)^{(N-1)/2} \exp \left[ -\frac{1}{2} \sum_{j, k} \mathbf{Q}_j \cdot (\sigma^{-1})^R_{eq, jk} \cdot \mathbf{Q}_k \right] \tag{19}
\]

with a covariance matrix, \( \sigma^R_{eq, jk} = \langle \mathbf{Q}_j \mathbf{Q}_k \rangle_{eq}^R = (k_B T/H) \delta_{jk} \mathbf{1} \). Note that \( \psi^R_{eq} \) reduces to \( \psi^R_{eq} \) in the absence of excluded volume interactions.

The Gaussian nature of the configurational distribution function in the Rouse model has two consequences, (i) the vector \( \mathbf{r}_{\nu\mu} \) between beads \( \mu \) and \( \nu \) is also a Gaussian distributed random variable because it is a sum of Gaussian variables, and (ii) the complex higher order moment in the second term on the right hand side of Eq. (18) can be reduced to second order moments by using general decomposition rules for the moments of a Gaussian distribution (Prakash, 2000). On exploiting these consequences, the expression for the
covariance matrix $\langle Q_j Q_k \rangle_{eq}$, correct to first order in $z^*_D$, has the following simple form,

$$
\langle Q_j Q_k \rangle_{eq} = \frac{k_B T}{H} \left[ \delta_{jk} + \frac{1}{2} z^*_D \sum_{\mu,\nu=1}^{N} \frac{\theta(\mu, j, k, \nu)}{(d^* + |\mu - \nu|)^{1+\frac{\epsilon}{2}}} \right]
$$

The function $\theta(\mu, m, n, \nu)$ has been introduced previously in the treatment of hydrodynamic interaction (Ôttinger, 1989). It is unity if $m$ and $n$ lie between $\mu$ and $\nu$, and zero otherwise,

$$
\theta(\mu, m, n, \nu) = \begin{cases} 
1 & \text{if } \mu \leq m, n < \nu \text{ or } \nu \leq m, n < \mu \\
0 & \text{otherwise}
\end{cases}
$$

Substituting Eq. (20) into Eq. (15), and carrying out the sum over the indices $j$ and $k$, one can show that the mean square end-to-end vector at equilibrium, in a space of arbitrary dimensions $D$, correct to first order in $z^*_D$, is given by,

$$
\langle r^2 \rangle_{eq} = \frac{D k_B T}{H} \left[ (N-1) + \frac{1}{2} z^*_D \sum_{\mu,\nu=1}^{N} \frac{|\mu - \nu|^2}{(d^* + |\mu - \nu|)^{1+\frac{\epsilon}{2}}} \right]
$$

We now consider the limit of a large number of beads, $N$. In this limit, the sums in Eq. (22) can be replaced by integrals. Introducing the following variables,

$$
x = \frac{\mu}{N}; \quad y = \frac{\nu}{N}
$$

and exploiting the symmetry in $x$ and $y$, we obtain,

$$
\langle r^2 \rangle_{eq} = \frac{D k_B T}{H} \int_0^{\frac{1}{N}} \int_0^{\frac{1}{N}} dx \int_0^{\frac{1}{N}} dy \int_{y+c}^{\frac{1}{N}} (x-y)^2 \frac{1}{(d^2 + x-y)^{3-\epsilon/2}}
$$

where, $\epsilon = 4 - D$, $c$ is a cutoff parameter of order $1/N$ which accounts for the fact that $\mu, \nu$, and the parameter $d = d^*/\sqrt{N}$, has already been introduced earlier. It is worth noting that the leading correction to the integrals in Eq. (24) is of order $N^{-1+\epsilon/2}$ (Schäfer, 1999)—a fact of particular relevance to the extrapolation procedure to be adopted in the next section.

From Eq. (24), it is clear that the excluded volume corrections to the Rouse end-to-end vector are proportional to $z^*_D N^{c/2}$. Therefore, the proper perturbation parameter to choose is $z_D = z^*_D N^{c/2}$, and not $z^*_D$. This well known
result of the theory of polymer solutions (Doi & Edwards, 1986; des Cloizeaux & Jannink, 1990; Schäfer, 1999), indicates that (i) for $D = 3$ a perturbation expansion in $z_D^*$ is rendered useless for long chains, and (ii) useful results can be obtained only when $D$ is close to 4 dimensions.

The integrals in Eq. (24) can be performed analytically, and the resultant expression can be expanded as a power series in $\epsilon$. For the purposes of renormalization, the expansion is required only up to order $\epsilon^0$. Carrying out the expansion in $\epsilon$, retaining terms up to this order, and neglecting the cutoff $c$, one obtains,

$$\langle r^2 \rangle_{eq} = \frac{D k_B T}{H} N \left\{ 1 + z_D^* N^{\epsilon/2} J(d, \epsilon) \left[ \frac{2}{\epsilon} - K(d, \epsilon) \right] \right\}$$

(25)

where,

$$J(d, \epsilon) = (1 + 3 d^2) \left[ (1 + d^2)^{\epsilon/2} - d^\epsilon \right]$$

(26)

and,

$$K(d, \epsilon) = \frac{1}{J(d, \epsilon)} \left[ \frac{3}{2} d^\epsilon (1 + d^2) + (1 - \frac{3}{2} d^4) (1 + d^2)^{-1+\epsilon/2} \right]$$

(27)

If we keep $\epsilon$ finite and set $d = 0$ in Eq. (25), we get the expression for a $\delta$-function excluded volume potential. This expression has a $(1/\epsilon)$ singularity which arises because of the neglect of the cutoff. As has been pointed out by Öttinger (Öttinger, 1989), a renormalization group analysis can be performed to get rid of the $(1/\epsilon)$ singularity, or, if the cutoff is retained, renormalization group analysis can be used to get rid of the cutoff dependence. Curiously, when $d \neq 0$, the parameter $d$ plays a role similar to the cutoff parameter $c$. This follows from the fact that Eq. (25) is free of any singularities as $\epsilon \rightarrow 0$.

In order to perform the renormalization of the end-to-end vector, we follow standard practice (Öttinger & Rabin, 1989, Öttinger, 1989), and introduce the concept of a polymer segment. The polymer segment is used to represent a unit of molecular weight, free of any mechanical interpretation. The polymer chain is thus assumed to consist of $N_s$ segments, each consisting of $L_s$ beads, so that $N = N_s L_s$. The segments are introduced in order to remove the ambiguities associated with the arbitrariness in the choice of the number of beads in a polymer chain. The size of a polymer segment, $L_s$, is assumed to be related to the number of beads in a segment $L_s$, through the relation $L = Z_N L_s$. Introducing a non-dimensional excluded volume parameter,

$$u_s = (2\pi)^{\frac{D}{2}} z_D^* L^{\epsilon/2} J(d, \epsilon)$$

(28)
Eq. (25) can be rewritten in terms of \( N_s, u_s, \) and \( L \) as,

\[
\langle r^2 \rangle_{eq} = \frac{D k_B T}{H} L N_s Z_N^{-1} \left\{ 1 + \frac{u_s}{4 \pi^2} (2 \pi N_s)^{\epsilon/2} Z_N^{-\epsilon/2} \left[ \frac{2}{\epsilon} - K(d, \epsilon) \right] \right\}
\]  

(29)

The next step in the renormalization procedure consists of introducing a segment excluded volume parameter \( u \), which, by renormalizing the bare excluded volume parameter \( u_s \), takes into account all the excluded volume interactions between the many monomers within a segment,

\[
u = Z_u u_s
\]

(30)

The parameters \( u_s \) and \( L_s \) are then expected to be functions of \( u \), and expanded in a Taylor’s series,

\[
u_s = u(1 + Au + \ldots); \quad L_s = L(1 + Bu + \ldots)
\]

so that, for small \( u \),

\[
Z_u = 1 - Au + \cdots; \quad Z_N = 1 - Bu + \cdots
\]

(31)

Substituting Eqs. (31) into Eq. (29), keeping only first order terms in \( u \), and expanding \( (2 \pi N_s)^{\epsilon/2} \) to first order in \( \epsilon \), we have,

\[
\langle r^2 \rangle_{eq} = \frac{D k_B T}{H} L N_s \left\{ 1 + \frac{u}{2 \pi^2} \left( \frac{1}{\epsilon} + \frac{1}{2} \ln(2 \pi N_s) - \frac{K(d, \epsilon)}{2} + 2 \pi^2 B \right) \right\}
\]

(32)

Making the choice,

\[
B = -\frac{1}{2 \pi^2 \epsilon} + \frac{K(d, \epsilon)}{4 \pi^2}
\]

gets rid of all the \textit{micro-structure} dependent terms in Eq. (32), and leads to

\[
\langle r^2 \rangle_{eq} = \frac{D k_B T}{H} L N_s \left\{ 1 + u \frac{1}{4 \pi^2} \ln(2 \pi N_s) \right\}
\]

(33)

The form of Eq. (33) is not consistent with the expectation of a power law dependence of \( \langle r^2 \rangle_{eq} \) on \( N_s \). Renormalization group analysis resolves this prob-

\footnote{In the limit \( d \to 0 \), since \( K(d, \epsilon) \) is a constant equal to one, the quantity \( B \) is usually chosen to be equal to \((-1/2 \pi^2 \epsilon)\). As a result, an additional term equal to \((-u/4 \pi^2)\), appears within the braces on the right hand side of Eq. (33).}
lem by exponentiating the first order perturbation expansion result, giving rise to the expression,

$$\langle r^2 \rangle_{eq} = \frac{D k_B T}{H} L \left(2\pi\right)^\frac{u}{2} N_s^{2\nu}$$

(34)

where, $\nu = \frac{1}{2} + \frac{u}{8\pi^2}$. The exponent $\nu$ is then obtained by substituting the fixed point value, $u = u^*$, for $u$ (Ottinger, 1989). The fixed point denotes the regime where the properties of the infinitely long polymer chain have a power law dependence on $N_s$, and the fixed point value is found by setting $Z_u = 0$. For instance, in the case of a $\delta$-function excluded volume potential, the fixed point value is known to be $u^* = (\pi^2 \epsilon/2)$, which leads to an exponent, $\nu = \frac{1}{2} + \frac{1}{16} \epsilon$. In the present instance, the fixed point can be expected to be a function of $\epsilon$ and $d$.

It is not possible to find the fixed point value $u^*$ in the present model by only considering the renormalization of $\langle r^2 \rangle_{eq}$, since the quantity $A$ does not appear in Eq. (32), which is correct only to first order in $u$. However, we do not require the fixed point value in order to make the following argument. The form of Eq. (34) suggests that, in the limit $N \to \infty$ (which is a consequence of $Z_u = 0$), the parameter $d^*$, which always appears as the combination $d^*/\sqrt{N}$, will not in any way alter the $N_s$ dependence of the mean square end-to-end vector. Indeed, for any finite value of $d^*$, the value of $\nu$ will always tend, as $N$ increases, to the value for a $\delta$-function potential. The validity of the above renormalization procedure can only be confirmed by ensuring that the same definition of $u_s$ and choice of parameter $B$ made here, cancels the microstructure dependence of all the other observable quantities in the theory, such as $n_p$, $\Psi_1$, etc. This has not been pursued here as it is considered outside the scope of the present work. However, the expected independence of the results from the choice of $d^*$ is in line with the accepted wisdom in static theories of polymer solutions that the choice of the excluded volume potential does not influence the scaling of observables with molecular weight. Furthermore, dimensionless ratios constructed from observable quantities are also expected to be free of micro-structure dependence. In our case, this implies that universal ratios can be expected to be independent of the choice of the value of $d^*$.

We shall make use of the insight gained in this section in our analysis of the results of the Gaussian approximation below. This is justified since the Gaussian approximation and renormalization group analysis are similar in a certain sense; both are exact to first order in the strength of excluded volume interaction (the Gaussian approximation was shown to be exact to first order in $z^*$ in Prakash (2000)), and both account for an infinite number of higher order contributions.
Fig. 1. Swelling of the radius of gyration versus $1/\sqrt{N}$, at various values of $d^*$. The symbols ($\square : d^* = 0$, $\triangle : d^* = 0.1$, $\Diamond : d^* = 0.2$, $\bigcirc : d^* = 0.3$, $+: d^* = 0.4$, $\nabla : d^* = 0.5$), are the predictions of the Gaussian approximation, while the dashed lines are drawn to guide the eye. The filled circle on the $y$-axis represents the common extrapolated value, to $N = \infty$, of all the curves.

We now examine the asymptotic predictions of the Gaussian approximation, in order to examine the role of the parameter $d^*$. The renormalization group arguments of the previous section indicate that, for large values of the number of beads $N$, one would expect the scaling with $N$, of various observable quantities, to become independent of $d^*$. A similar behavior is expected of non-dimensional ratios constructed with these quantities.

Figures 1 and 2 examine the dependence of two quantities, predicted by the Gaussian approximation, on $1/\sqrt{N}$, for various values of $d^*$, at $z = 1$. The first quantity, $\alpha_g^2$, is both an equilibrium property and a linear viscoelastic property, since (as was shown in Prakash (2000)), it describes the equilibrium
swelling of the radius of gyration, and the ratio of the zero shear rate viscosity in the presence of excluded volume interactions to the zero shear rate viscosity in the Rouse model,

$$\alpha^2_g = \frac{\langle R^2_g \rangle_{eq}}{\langle R^2_g \rangle_R} = \frac{\eta_{p,0}}{\eta_{R,0}}$$  \hspace{1cm} (35)$$

Here, $\langle R^2_g \rangle_{eq}$ is the radius of gyration, and a superfix “$R$” on a quantity indicates the Rouse model value of the quantity. The second quantity is a
Table 1
Asymptotic values of ratios of equilibrium and zero shear rate properties, at \( z = 1 \). Numbers in parentheses indicate the uncertainty in the last figure.

| \( \alpha^2 \) | \( \alpha_g^2 \) | \( (\Psi_{1,0}/\Psi_{1,0}^R) \) | \( U_{\Psi\eta} \) | \( U_R \) |
|----------------|----------------|-------------------|----------------|--------|
| 1.960 (3)      | 1.905 (4)      | 3.32 (1)          | 0.7324 (4)     | 0.9723 (3) |

non-dimensional ratio, \( U_{\Psi\eta} \), defined by,

\[
U_{\Psi\eta} = \frac{n_p k_B T \Psi_{1,0}}{\eta_{\nu,0}}
\]  

(36)

The dependence of these quantities on \( 1/\sqrt{N} \) was examined for two reasons, (i) the leading order correction, in 3 dimensions, to the integrals in Eq. (24) is of order \( 1/\sqrt{N} \), and (ii) the renormalisation group calculation of the previous section, and asymptotic results obtained earlier with the Gaussian approximation (Prakash, 2000), suggest that the parameter \( d^* \) always appears in the theory as the re-scaled variable \( d = d^*/\sqrt{N} \). As a result, the leading order corrections to the infinite chain length limit, of all material properties, are expected to be functions of \( 1/\sqrt{N} \). In the limit \( N \to \infty \), therefore, all material properties should become independent of \( d^* \), and depend only on the variable \( z \).

The filled circles on the y-axis in Figs. 1 and 2, represent the common extrapolated value, to \( N = \infty \), of each of the curves for the various values of \( d^* \). The values for different \( N \), for each value \( d^* \), were extrapolated to the limit \( N \to \infty \), using a rational function extrapolation algorithm (Press, Teukolsky, Vetterling & Flannery, 1992). Clearly, both \( \alpha_g^2 \) and \( U_{\Psi\eta} \) become independent of \( d^* \) in the limit \( N \to \infty \).

The variables, (i) \( \alpha^2 = \langle r^2 \rangle_{eq}/\langle r^2 \rangle_{eq}^R \), which is the swelling of the end-to-end vector at equilibrium, (ii) \( (\Psi_{1,0}/\Psi_{1,0}^R) \), which is the ratio of the zero shear rate first normal stress difference in the presence of excluded volume interactions to the zero shear rate first normal stress difference in the Rouse model, and (iii) \( U_R \), which is a non-dimensional ratio of the radius of gyration to the
end-to-end vector at equilibrium, defined by,

\[ U_R = 6 \frac{\langle R_g^2 \rangle_{eq}}{\langle r^2 \rangle_{eq}} \]  

(37)

exhibit the same behavior (as that displayed in Figs. 1 and 2), in the limit \( N \to \infty \). The asymptotic values, for \( z = 1 \), of each of these variables is given in Table 1.\(^3\)

Fig. 3. Asymptotic swelling of the radius of gyration versus \( z \). The symbols are the results of the Gaussian approximation, while the line is a curve fit using an equation of the form given in Eq. (38). The curve fit parameters are given in Table 2.

Figures 3 and 4 describe the asymptotic \( z \) dependence of \( \alpha_g^2 \) and \( (\Psi_{1,0}/\Psi_{1,0}^R) \). The behavior of \( \alpha^2 \) has not been displayed as it is very similar to that of \( \alpha_g^2 \).

\(^3\) The non-dimensional ratio, \( U_R = \left[ \eta_p/\eta_s (4\pi/3) \langle R_g^2 \rangle_{eq}^{3/2} \right] \), is not a universal ratio in the present model since it scales with \( N \) as \( N^{1-\nu} \). It becomes a universal ratio only when hydrodynamic interaction effects are included in the model.
Fig. 4. Asymptotic ratio of the zero shear rate first normal stress difference coefficient in the presence of excluded volume interactions to the zero shear rate first normal stress difference coefficient in the Rouse model versus $z$. The symbols are the results of the Gaussian approximation, while the line is a curve fit using an equation of the form given in Eq. (38). The curve fit parameters are given in Table 2.

The symbols in Figs. 3 and 4 are the asymptotic predictions of the Gaussian approximation. These predictions were obtained, at each value of $z$, by using the extrapolation procedure described above for $z = 1$.

The lines through the symbols are curve fits, using an equation which has a form commonly used to fit results of renormalization group analysis (Schafer, 1993),

$$y = \left(1 + a z + b z^2\right)^m$$

(38)

where, $y$ represents the fitted variable. The parameters $a$, $b$ and $m$, for $\alpha^2$, $\alpha_g^2$ and $(\Psi_{1,0}/\Psi_{1,0}^R)$, are given in Table 2. The maximum difference between
Table 2
Parameters appearing in Eq. (38), used to fit the asymptotic predictions of the
Gaussian approximation, displayed in Figs. 3 and 4.

|    | $\alpha^2$ | $\alpha_g^2$ | $(\Psi_{1,0}/\Psi_{1,0}^R)$ |
|----|------------|--------------|-----------------------------|
| $a$ | 4.352      | 4.178        | 4.058                       |
| $b$ | 2.715      | 2.453        | 1.755                       |
| $m$ | 0.323      | 0.318        | 0.630                       |

the computed data and the curve fit for all the three properties was less than
0.5%.

The $N$ dependence of the equilibrium properties $\langle r^2 \rangle_{eq}$ and $\langle R_g^2 \rangle_{eq}$, for large
values of $N$, can be obtained from Eq. (38), and the definitions of the quantities
$\alpha^2$ and $\alpha_g^2$. Both the properties scale identically with molecular weight, namely, as $N^{2\nu}$. Experimental results suggest a value of $\nu = 0.592 \pm 0.003$ (Hayward &
Graessley, 1999), while renormalization group calculations and Monte Carlo
simulations suggest a value of $\nu = 0.588$ (Schäfer, 1999; Graessley et al.,
1999). Since $z$ scales as $N^{1/2}$, it is clear from Eq. (38) that for large values
of $N$, $\nu = (1 + m)/2$. From Table 2, one can see that the values of $m$ for $\alpha^2$
and $\alpha_g^2$, imply a Gaussian approximation prediction of $\nu$ between 0.659 and
0.662. We expect the value of $m$ for $(\Psi_{1,0}/\Psi_{1,0}^R)$ to be twice the value of $m$
for $\alpha_g^2$. This follows from Eq. (35), since $\Psi_{1,0}$ scales as $\eta_{p,0}$ and $\Psi_{1,0}^R$
and $\Psi_{1,0}^R$ scale with $N$ as $N^2$ and $N^4$, respectively. As can be seen from Table 2, this
expectation is reasonably fulfilled.

It must be noted that the present data, which has been accumulated for rela-
tively small values of $z$, might still be describing the crossover region between
Rouse scaling and the final scaling in the ‘excluded volume limit’ of large $z$. In
that case, the curve fit parameter $m$ might be modified as data is compiled for
larger values of $z$. In calculations based on renormalization group arguments,
the convergence to a value $\nu = 0.588 \pm 0.01$ is relatively fast (roughly by
$z = 18$), but the final convergence is very slow (occuring at $z > 100$) (Schäfer,
The problem with going to larger values of $z$ with the Gaussian approximation is that, in order to maintain the accuracy of the numerical extrapolation procedure, one must have data for values of $N > 40$, which, as was mentioned earlier, requires large amounts of CPU time. In the treatment of the non-linear microscopic phenomenon of hydrodynamic interaction, the use of a normal mode approximation, simultaneously with the Gaussian approximation, led to a non-perturbive solution scheme which was as accurate as the Gaussian approximation, but significantly less computationally intensive. As a result, chains with lengths up to $N = 100$ could be examined (Prakash & Ottinger, 1997). It is worth examining if a normal mode approximation in the present situation also leads to a significant reduction in the computational intensity.
Fig. 6. Universal ratio constructed from the zero shear rate first normal stress
difference coefficient and the zero shear rate viscosity versus $z$. The symbols are the
results of the Gaussian approximation, while the line is drawn to guide the eye.

Figures 5 and 6 examine the asymptotic $z$ dependence of the two universal
ratios, $U_R$ and $U_{\Psi \eta}$, predicted by the Gaussian approximation. In the Rouse
model, $U_R = 1$. Both renormalization group calculations and Monte Carlo
simulations yield an identical value of $U_R = 0.959$ in the excluded volume
limit (Schäfer, 1999). Though the curve in Fig. 5 decreases relatively rapidly
for small values of $z$, and appears to be levelling off as $z$ increases, it still has
a non-zero slope at $z = 30$. This suggests that the asymptotic value of the
ratio, at large values of $z$, is yet to be reached, and that the present data is
still in the crossover region.

For long chains, $U_{\Psi \eta} = 0.8$ in the Rouse model. On the other hand, a renor-
malization group calculation yields a value $U_{\Psi \eta} = 0.6288$ (Ottinger, 1989).
The value of $U_{\Psi \eta}$ in Fig. 6, at $z = 30$, is quite close to the prediction of
the renormalization group calculation (which was based on a $\delta$-function po-
tential). However, the non-zero slope at $z = 30$ indicates that the excluded
volume limit is yet be reached.

5 Conclusions

Renormalisation group arguments, carried out in the context of the end-to-end vector at equilibrium, seem to suggest that the scaling with molecular weight of the equilibrium and zero shear rate properties, and the values of non-dimensional ratios of these quantities, should become independent of \( d^* \) in the limit of large \( N \). The asymptotic results of the Gaussian approximation have been examined in the light of these expectations. The data clearly indicates independence from the choice of \( d^* \). The asymptotic dependence on \( z \) presented here, of the universal ratios \( U_{\Psi \eta} \) and \( U_R \), appears to lie in the crossover region between Rouse scaling and the scaling in the excluded volume limit of large \( z \). Accumulation of more data at larger values of \( z \) is required before the scaling of the Gaussian approximation in the excluded volume limit can be described unambiguously. This task is rendered difficult because of the computational intensity of the Gaussian approximation, which scales with chain length as \( N^6 \).

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References

Bird, R. B., Armstrong, R. C., & Hassager, O. (1987). *Dynamics of Polymeric Liquids, Vol. 1, Fluid Mechanics* (2nd ed.). New York: Wiley-Interscience: New York.

Bird, R. B., Curtiss, C. F., Armstrong, R. C., & Hassager, O. (1987). *Dynamics of Polymeric Liquids, Vol. 2, Kinetic Theory* (2nd ed.). New York: Wiley-Interscience: New York.

des Cloizeaux, J., & Jannink, G. (1990). *Polymers in Solution, Their Modelling and Structure*. Oxford: Oxford University Press.
Doi, M., & Edwards, S. F. (1986). *The Theory of Polymer Dynamics*. Oxford: Oxford University Press.

Graessley, W. W., Hayward, R. C., & Grest, G.S. (1999). Excluded-volume effects in polymer solutions. 2. Comparison of experimental results with numerical simulation data. *Macromolecules, 32*(10), 3510-3517.

Hayward, R. C., & Graessley, W. W. (1999). Excluded volume effects in polymer solutions. 1. Dilute solution properties of linear chains in good and θ solvents. *Macromolecules, 32*(10), 3502-3509.

Hernandez Cifre, J. G., & Garcia de la Torre, J. (1999). Steady-state behavior of dilute polymers in elongational flow. Dependence of the critical elongational rate on chain length, hydrodynamic interaction, and excluded volume. *J. Rheol.*, 43(2), 339-358.

Öttinger, H. C. (1989). Renormalization-group calculation of excluded-volume effects on the viscometric functions for dilute polymer solutions. *Phys. Rev., A40*(5), 2664-2671.

Öttinger, H. C. (1989). Gaussian approximation for Rouse chains with hydrodynamic interaction. *J. Chem. Phys., 90*(1), 463-473.

Öttinger, H. C., & Rabin, Y. (1989). Renormalization-group calculation of viscometric functions based on conventional polymer kinetic theory. *J. Non-Newtonian Fluid Mech., 33*, 53-93.

Prakash, J. R., & Öttinger, H. C. (1997). Universal viscometric functions for dilute polymer solutions. *J. Non-Newtonian Fluid Mech., 71*, 245-272.

Prakash, J. R., & Öttinger, H. C. (1999). Viscometric functions for a dilute solution of polymers in a good solvent. *Macromolecules, 32*(6), 2028-2043.

Prakash, J. R. (2000). Rouse chains with excluded volume interactions: Linear viscoelasticity. [http://arXiv.org/abs/cond-mat/0002448](http://arXiv.org/abs/cond-mat/0002448)

Press, W. H., Teukolsky, S. A., Vetterling, W. T., & Flannery, B. P. (1992). *Numerical Recipes in FORTRAN* (2nd ed.). Cambridge: Cambridge University Press.

Schäfer, L. (1999). *Excluded Volume Effects in Polymer Solutions*. Berlin: Springer.

Yamakawa, H. (1971). *Modern Theory of Polymer Solutions*. New York: Harper and Row.

Zylka, W., & Öttinger H. C. (1991). Calculation of various universal properties for dilute polymer solutions undergoing shear flow. *Macromolecules, 24*(2), 484-494.