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Intrinsic viscosities for linear and ring polymers using renormalisation group techniques

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Abstract. The complex intrinsic viscosity for a single simple ring polymer in the presence of both self-avoiding and hydrodynamic interactions is calculated using renormalisation group techniques. Results are compared with those for a linear chain and amplitude ratios to an order $O(\varepsilon)$ ($\varepsilon \equiv 4-d$, d being the spatial dimensionality) are given in the zero-frequency limit.

1. Introduction

The use of renormalisation group (RG) techniques has made it possible to explore many universal properties of long flexible polymer chains. Whereas static properties of both dilute and semidilute solutions have been studied in great detail [1-4], only recently have quantitative calculations for time-dependent properties been performed. Of central interest among the transport properties of dilute polymer solutions are the diffusion constant [5], time-dependent correlation functions [6], relaxational spectra [7] and most importantly the intrinsic viscosity [8, 9].

The minimal model (defined in § 2) which has been studied within the RG framework gives many universal predictions for transport properties, which can be compared with experiment. These predictions, which have mainly been derived for flexible *linear* chains, can also be investigated for flexible simple (single) ring polymers, another class of experimentally interesting systems. In particular, comparison of transport properties of linear and ring polymers will enable one to answer the question of how ring formation will affect universal (critical) properties of flexible (Gaussian) polymer chains. We have recently [10] investigated explicitly time-dependent correlations for a simple ring polymer in the presence of hydrodynamic interactions and have extracted the translational diffusion constant and the relaxational spectrum. The main purpose of this article will be the calculation of the intrinsic (complex) viscosity for a simple ring polymer in the presence of both self-avoiding and hydrodynamic interactions.

The first calculation of the intrinsic viscosity has been performed within the Kirkwood-Riseman formalism [11]. This formalism has the shortcoming that it does *not* allow the calculation of explicitly time-dependent quantities, and that it is *not* fully justified from the standard non-equilibrium statistical mechanics point of view.

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In order to proceed beyond this approximation, we have as a first step in [8] investigated the complex intrinsic viscosity starting directly from the Green-Kubo formalism for a Gaussian chain in the presence of hydrodynamic interactions only. In the zero-frequency limit ($\omega = 0$) we found the Green-Kubo formalism and the Kirkwood-Riseman formalism to give identical results in lowest order (i.e. to $O(\varepsilon)$, where $\varepsilon = 4 - d$, d being the spatial dimensionality). More recently in [9] we have presented the results for the complex intrinsic viscosity in the presence of self-avoiding interactions to $O(\varepsilon)$ and, extracting the $\omega = 0$ limit numerically, we concluded that to $O(\varepsilon)$ the Green-Kubo and Kirkwood-Riseman formalism give different results. In principle, this is not unexpected, because the self-avoiding interaction modifies not only the equilibrium state, but also the dynamics of the chain-solvent system. Whereas the equilibrium state and solvent velocity field motion can also be treated within the Kirkwood-Riseman scheme, the modification of the chain motion due to the direct monomer-monomer interaction cannot be taken into account.

However, as pointed out in [9], the $\omega = 0$ limit remained to be studied analytically. This is another purpose of the present paper. We will discuss, in parallel for rings and linear chains, all contributions to the momentum-flux autocorrelation function (see § 3) in lowest order in the self-avoiding and hydrodynamic interactions. From this, we can analytically extract both the finite- and the zero-frequency cases. Due to a peculiar cancellation of terms, we can show that the zero-frequency limit agrees (to lowest order) with the Kirkwood-Riseman formalism even in the presence of self-avoiding interactions (this corrects an error in [9]).

Our paper is organised as follows. In § 2 we discuss the minimal model describing the coupled chain-solvent dynamics and an effective Lagrangian which allows for rings and linear chains to calculate general time-dependent correlation functions in the presence of self-avoiding and hydrodynamic interactions. In § 3(4) all contributions to the intrinsic viscosity in the presence of self-avoiding (hydrodynamic) interactions are determined and final results are presented for finite frequency and zero frequency. In § 5 we consider the combined effect of both self-avoiding and hydrodynamic interactions. Section 6 contains our conclusions, and in particular we will compare some of our findings with experimental results.

2. Model and formalism for intrinsic viscosity

The starting point of our investigation is the following set of Langevin equations describing coupled chain-solvent dynamics [12]:

$$\frac{\partial \boldsymbol{c}}{\partial t} = -\frac{1}{\zeta_0}\frac{\delta H_{\mathrm{E}}}{\delta \boldsymbol{c}(\tau, t)} + g_0 \boldsymbol{u}(\boldsymbol{c}(\tau, t), t) + \boldsymbol{\Theta}(\tau, t) \qquad (2.1a)$$

$$\frac{\partial \boldsymbol{u}}{\partial t} = \eta_0 \Delta \boldsymbol{u}(\boldsymbol{x}, t) - g_0 \int_0^{N_0} \mathrm{d}\tau \frac{\delta H_{\mathrm{E}}}{\delta \boldsymbol{c}(\tau, t)} \delta(\boldsymbol{x} - \boldsymbol{c}(\tau, t)) - \nabla p + \boldsymbol{f}(\boldsymbol{x}, t) \qquad (2.1b)$$

together with the incompressibility condition $\nabla \cdot \boldsymbol{u} = 0$. In (2.1$a$) and (2.1$b$), $\{\boldsymbol{c}(\tau, t)\}_{\tau=0}^{N_0}$ describes the conformation of a polymer with bare chain length N_0 parametrised by a contour variable τ at time t. $\zeta_0 \equiv \lambda_0^{-1}$ is the bare translational friction constant per chain unit, g_0 the strength of the hydrodynamic interaction (the coupling to the solvent velocity field), $\boldsymbol{u}(\boldsymbol{x}, t)$ describes the solvent velocity field, η_0 is the bare solvent viscosity, Δ is the Laplacian and p denotes the pressure. H_{E} is the Edwards Hamiltonian [13]

$$H_E = \tfrac{1}{2}\int_0^{N_0} d\tau \left(\frac{\partial c}{\partial \tau}\right)^2 + \tfrac{1}{2}v_0 \int_0^{N_0} d\tau_1 \int_0^{N_0} d\tau_2 \delta(c(\tau_1) - c(\tau_2)) \tag{2.2}$$

with v_0 being the bare excluded volume parameter and $\boldsymbol{\Theta}, \boldsymbol{f}$ Gaussian random processes with zero mean and covariance given by

$$\langle \boldsymbol{\Theta}(\tau, t)\boldsymbol{\Theta}(\sigma, s)\rangle = 2\zeta_0^{-1}\delta(\tau - \sigma)\delta(t - s)I \tag{2.3}$$

$$\langle \boldsymbol{f}(\boldsymbol{x}, t)\boldsymbol{f}(\boldsymbol{x}', s)\rangle = -2\eta_0\Delta\delta(\boldsymbol{x} - \boldsymbol{x}')\delta(t - s)I \tag{2.4}$$

where I is the $d \times d$ unit matrix. One can show [3] that to $O(\varepsilon)$, i.e. lowest order in the couplings, and by using the Markov approximation (see below) for the solvent velocity field, the coupled equations (2.1a) and (2.1b) are equivalent to the Kirkwood diffusion model.

Calculations of dynamic correlation functions starting from (2.1a) and (2.1b) are straightforward, but for higher-order calculations it is desirable to have a field-theoretic method which allows a graphical representation of the perturbation terms, and also avoids the explicit averaging over the noise fields $\boldsymbol{\Theta}$ and $\boldsymbol{f}$ in (2.1a) and (2.1b). Such a field-theoretic description has been developed in [14] for the critical dynamics of stochastic models, including mode-coupling terms described by Langevin equations, and we essentially follow their approach. Eliminating the pressure p (which basically enforces the condition $\nabla \cdot \boldsymbol{u} = 0$) from (2.1$b$), we obtain

$$\frac{\partial}{\partial t}\boldsymbol{u}_\perp = -\eta_0(i\nabla)^2 A_\perp + \boldsymbol{f}_\perp(\boldsymbol{x}, t) \tag{2.5}$$

with

$$A_\perp = \left[\boldsymbol{u}(x, t) - g_0(\eta_0\Delta)^{-1}\int_0^{N_0} d\tau \frac{\delta H_E}{\delta \boldsymbol{c}(\tau, t)}\delta(\boldsymbol{x} - \boldsymbol{c}(\tau, t))\right]_\perp \tag{2.6}$$

where $\perp$ denotes the transverse part, and

$$\frac{\partial}{\partial t}\boldsymbol{c}(\tau, t) = -\lambda_0 B + \boldsymbol{\Theta}(\tau, t) \tag{2.7}$$

with $\lambda_0 = \zeta_0^{-1}$ and

$$B = \frac{\delta H_E}{\delta \boldsymbol{c}(\tau, t)} - g_0\lambda_0^{-1}\boldsymbol{u}_\perp(\boldsymbol{c}(\tau, t), t). \tag{2.8}$$

We have a Gaussian white noise distribution w for the random fields $\boldsymbol{f}(\boldsymbol{x}, t)$ and $\boldsymbol{\Theta}(\tau, t)$:

$$w(\{\boldsymbol{f}\}, \{\boldsymbol{\Theta}\} \mid t_0 \leqslant t \leqslant t_1) \sim \exp\left(-\tfrac{1}{4}\int_{t_0}^{t_1} dt \int d^d x \boldsymbol{f}_\perp(\boldsymbol{x}, t)[\eta_0^{-1}(i\nabla)^{-2}]\boldsymbol{f}_\perp(\boldsymbol{x}, t)\right)$$
$$\times \exp\left(-\tfrac{1}{4}\int_{t_0}^{t_1} dt \int_0^{N_0} d\tau\, \boldsymbol{\Theta}(\tau, t)\lambda_0^{-1}\boldsymbol{\Theta}(\tau, t)\right) \tag{2.9}$$

where (t_0, t_1) is some time interval. In order to calculate correlation functions from (2.1a) and (2.1b) we can, instead of solving for $\boldsymbol{c}(\tau, t)$ and $\boldsymbol{u}(\boldsymbol{x}, t)$ (in terms of $\boldsymbol{\Theta}(\tau, t)$ and $\boldsymbol{f}_\perp(\boldsymbol{x}, t)$) and then averaging over $\boldsymbol{\Theta}, \boldsymbol{f}_\perp$, alternatively introduce a path probability density $W\{\boldsymbol{u}, \boldsymbol{c}\}$ for the stochastic variables $\boldsymbol{u}, \boldsymbol{c}$ via

$$w(\{\boldsymbol{\Theta}\}, \{\boldsymbol{f}\} \mid t_0 \leqslant t \leqslant t_1)\, d\{\boldsymbol{\Theta}\}\, d\{\boldsymbol{f}\} = W(\{\boldsymbol{c}(t)\}, \{\boldsymbol{u}(t)\} \mid t_0 \leqslant t \leqslant t_1)\, d\{\boldsymbol{c}\}\, d\{\boldsymbol{u}\}. \tag{2.10}$$

Substituting $\mathbf{\Theta}$ and f from (2.5) and (2.7) we obtain

$$W(\{c\},\{u\}\,|\,t_0\leq t\leq t_1)\sim\exp J(\{c\},\{u\}\,|\,t_0\leq t\leq t_1) \tag{2.11}$$

with

$$J=-\tfrac{1}{4}\int \mathrm{d}^d x\int_{t_0}^{t_1}\mathrm{d}t[\partial_t \boldsymbol{u}+\eta_0(\mathrm{i}\nabla)^2 A_\perp]\eta_0^{-1}[(\mathrm{i}\nabla)^2]^{-1}[\partial_t\boldsymbol{u}+\eta_0(\mathrm{i}\nabla)^2 A_\perp]$$
$$-\tfrac{1}{4}\int_0^{N_0}\mathrm{d}\tau\int_{t_0}^{t_1}\mathrm{d}t(\partial_t\boldsymbol{c}+\lambda_0 \boldsymbol{B})\lambda_0^{-1}(\partial_t\boldsymbol{c}+\lambda_0\boldsymbol{B}). \tag{2.12}$$

In (2.12) we have dropped two additional terms which arise from the functional Jacobian for the change of variables $\mathbf{\Theta}\rightarrow \boldsymbol{c}$ and $f_\perp\rightarrow \boldsymbol{u}_\perp$. These terms, which have to be added to (2.12), are proportional to the step function $\theta(t)$ for $t=0$. As is discussed in [15], the value which $\theta(t)$ takes at $t=0$ depends on how the functional integral is discretised. If we choose $\theta(0)\neq 0$, then additional terms would subtract various contributions in every order to ensure causality, which is a necessary condition in the presence of response fields. We will assume $\theta(0)=0$ in the following.

From (2.11), which can be considered in the formal limit $W(\{c\},\{u\}\,|-\infty<t<\infty)$, one can write down expressions for correlation functions in terms of path integrals. However, it is convenient to perform a Gaussian transformation in order to linearise the exponent in (2.12). This can be achieved by introducing two (imaginary) response fields, $\tilde{\boldsymbol{u}}(\boldsymbol{x},t)$ and $\tilde{\boldsymbol{c}}(\tau,t)$. Then we obtain

$$W(\{\boldsymbol{u}\},\{\boldsymbol{c}\})=\int \mathrm{d}\{\mathrm{i}\tilde{\boldsymbol{c}}\}\,\mathrm{d}\{\mathrm{i}\tilde{\boldsymbol{u}}\}\,W(\{\tilde{\boldsymbol{c}}\},\{\tilde{\boldsymbol{u}}\},\{\boldsymbol{c}\},\{\boldsymbol{u}\}) \tag{2.13}$$

with

$$W(\{\tilde{\boldsymbol{c}}\},\{\tilde{\boldsymbol{u}}\},\{\boldsymbol{c}\},\{\boldsymbol{u}\})=\exp(J\{\tilde{\boldsymbol{c}},\tilde{\boldsymbol{u}},\boldsymbol{c},\boldsymbol{u}\}) \tag{2.14}$$

where $J=J_0+J_1$ can be considered as a Lagrangian and can be decomposed into a free and an interaction part. We have $J_0=J_0^{(1)}+J_0^{(2)}$ with

$$J_0^{(1)}=\int_0^{N_0}\mathrm{d}\tau\int\mathrm{d}t[\tilde{\boldsymbol{c}}(\tau,t)\lambda_0\tilde{\boldsymbol{c}}(\tau,t)-\tilde{\boldsymbol{c}}(\tau,t)\partial_t\boldsymbol{c}(\tau,t)+\tilde{\boldsymbol{c}}(\tau,t)\lambda_0\partial_\tau^2\boldsymbol{c}(\tau,t)] \tag{2.15}$$

describing the conformation field and

$$J_0^{(2)}=\int\mathrm{d}^d x\int\mathrm{d}t[\tilde{\boldsymbol{u}}(\boldsymbol{x},t)\eta_0(\mathrm{i}\nabla)^2\tilde{\boldsymbol{u}}(\boldsymbol{x},t)-\tilde{\boldsymbol{u}}(\boldsymbol{x},t)\partial_t\boldsymbol{u}_\perp(\boldsymbol{x},t)-\tilde{\boldsymbol{u}}(\boldsymbol{x},t)\eta_0(\mathrm{i}\nabla)^2\boldsymbol{u}_\perp(\boldsymbol{x},t)] \tag{2.16}$$

describing the solvent velocity field. The interaction terms containing the self-avoiding interactions can be written

$$J_1^{(1)}=\tfrac{1}{2}v_0\lambda_0\int_0^{N_0}\mathrm{d}\tau_1\int_0^{N_0}\mathrm{d}\tau_2\int_0^{N_0}\mathrm{d}\tau\int\mathrm{d}s\int\mathrm{d}t\,\tilde{\boldsymbol{c}}(\tau,t)\frac{\delta}{\delta\boldsymbol{c}(\tau,t)}\delta(\boldsymbol{c}(\tau_1,s)-\boldsymbol{c}(\tau_2,s)) \tag{2.17}$$

and the hydrodynamic interaction terms cann be written

$$J_1^{(2)}=-g_0\int_0^{N_0}\mathrm{d}\tau\int\mathrm{d}t\,\boldsymbol{c}(\tau,t)\boldsymbol{u}_\perp(\boldsymbol{c}(\tau,t),t)-g_0\int_0^{N_0}\mathrm{d}\tau\int\mathrm{d}t\,\tilde{\boldsymbol{u}}_\perp(\boldsymbol{c}(\tau,t),t)\frac{\delta H_{\mathrm{E}}}{\delta\boldsymbol{c}(\tau,t)}. \tag{2.18}$$

We can now determine the free response propagator $\langle \tilde{c}(\tau, t) c(\sigma, t')\rangle_0^{\mathrm{R}}$ for the conformation field of a simple polymer ring (R). Introducing normal coordinates into (2.15), which, in order to account for the periodic boundary conditions of a ring, are chosen in the form

$$c(\tau, t) = \sum_{k=0}^{\infty} Q_{\tau k}^{(1)} \boldsymbol{\xi}_k^{(1)} + \sum_{k=0}^{\infty} Q_{\tau k}^{(2)} \boldsymbol{\xi}_k^{(2)} \tag{2.19a}$$

$$\tilde{c}(\tau, t) = \sum_{k=0}^{\infty} Q_{\tau k}^{(1)} \tilde{\boldsymbol{\xi}}_k^{(1)} + \sum_{k=0}^{\infty} Q_{\tau k}^{(2)} \tilde{\boldsymbol{\xi}}_k^{(2)} \tag{2.19b}$$

with

$$Q_{\tau k}^{(1)} = \left(\frac{2}{N_0}\right)^{1/2} \cos\left(\frac{2\pi k \tau}{N_0}\right) \qquad k = 1, 2, \ldots \tag{2.20a}$$

$$Q_{\tau k}^{(2)} = \left(\frac{2}{N_0}\right)^{1/2} \sin\left(\frac{2\pi k \tau}{N_0}\right) \qquad k = 1, 2, \ldots \tag{2.20b}$$

$$Q_{\tau k}^{(1)} = Q_{\tau k}^{(2)} = \left(\frac{1}{N_0}\right)^{1/2} \qquad k = 0 \tag{2.20c}$$

we obtain

$$J_0^{(1)\mathrm{R}} = \int \mathrm{d}t \sum_{k=0}^{\infty} \{\lambda_0[\tilde{\boldsymbol{\xi}}_k^{(1)}(t)\tilde{\boldsymbol{\xi}}_k^{(1)}(t) + \tilde{\boldsymbol{\xi}}_k^{(2)}(t)\tilde{\boldsymbol{\xi}}_k^{(2)}(t)] - \tilde{\boldsymbol{\xi}}_k^{(1)}(t)\partial_t \boldsymbol{\xi}_k^{(1)} - \tilde{\boldsymbol{\xi}}_k^{(2)}(t)\partial_t \boldsymbol{\xi}_k^{(2)}(t)$$
$$- \lambda_k^{\mathrm{R}}[\tilde{\boldsymbol{\xi}}_k^{(1)}(t)\boldsymbol{\xi}_k^{(1)}(t) + \tilde{\boldsymbol{\xi}}_k^{(2)}(t)\boldsymbol{\xi}_k^{(2)}(t)]\} \tag{2.21}$$

where $\lambda_k^{\mathrm{R}} = \lambda_0(2\pi k/N_0)^2$. From (2.21) we find [10]

$$\langle \tilde{\xi}_{k\alpha}^{(i)}(t)\xi_{k'\beta}^{(i')}(t')\rangle_0 = \Theta(t'-t)\delta^{(ii')}\delta_{kk'}\delta_{\alpha\beta} \exp[-\lambda_k^{\mathrm{R}}(t'-t)] \tag{2.22}$$

and

$$\langle c(\tau, t)c(\sigma, t')\rangle_0^{\mathrm{R}} = \sum_{k,k'=0}^{\infty} Q_{\tau k}^{(1)} Q_{\sigma k'}^{(1)} \langle \tilde{\boldsymbol{\xi}}_k^{(1)}(t)\boldsymbol{\xi}_{k'}^{(1)}(t')\rangle_0 + \sum_{k,k'=0}^{\infty} Q_{\tau k}^{(2)} Q_{\sigma k'}^{(2)} \langle \tilde{\boldsymbol{\xi}}_k^{(2)}(t)\boldsymbol{\xi}_{k'}^{(2)}(t')\rangle_0$$
$$= \Theta(t'-t) G_0^{\mathrm{R}}(\tau, \sigma \mid t'-t) \tag{2.23}$$

where

$$G_0^{\mathrm{R}}(\tau, \sigma \mid t) = \frac{1}{N_0}\left(1 + 2\sum_{k=1}^{\infty} \cos 2\hat{k}_0(\tau - \sigma) \exp(-\lambda_k^{\mathrm{R}} t)\right) \tag{2.24}$$

is the Green function matrix and $\hat{k}_0 = \pi k/N_0$. From (2.23) we determine the static Green function $G_0^{*\mathrm{R}}(\tau, \sigma)$ for a polymer ring in the centre of mass system, using

$$G_0^{*\mathrm{R}}(\tau, \sigma) = \lambda_0 \int_0^{\infty} \mathrm{d}t\, G_0^{*\mathrm{R}}(\tau, \sigma \mid t) \tag{2.25}$$

where we have excluded the $k=0$ mode in $G_0^{\mathrm{R}}(\tau, \sigma \mid t)$ by putting $\xi_{k=0}^{(1)} = \xi_{k=0}^{(2)} = 0$. Performing the sum over k we find the static correlation function in the centre of mass system

$$\langle c^*(\tau) \cdot c^*(\tau')\rangle_0^{\mathrm{R}} = \tfrac{1}{12} d N_0 - \tfrac{1}{2} d |\tau - \tau'| + \frac{d}{2N_0}(\tau - \tau')^2 \tag{2.26}$$

where $\langle c^*(\tau)c^*(\tau')\rangle^{\mathrm{R}} \equiv G_0^{*\mathrm{R}}(\tau, \sigma)$. The correlation function $\langle c(\tau)\cdot c(\tau')\rangle_0^{\mathrm{R}}$ in the relative system (including the centre of mass motion) can be determined from (2.26) using $\langle [c^*(\tau)-c^*(\tau')]^2\rangle_0^{\mathrm{R}} = \langle [c(\tau)-c(\tau')]^2\rangle_0^{\mathrm{R}}$

$$\langle c(\tau)\cdot c(\tau')\rangle_0^{\mathrm{R}} = d\ \min(\tau, \tau') - \frac{d}{N_0}\tau\tau'. \tag{2.27}$$

In order to determine the free response propagator for the conformation field of a linear chain (L), we introduce into (2.15) normal coordinates defined by

$$c(\tau, t) = \sum_{k=0}^{\infty} Q_{\tau k}\xi_k(t) \tag{2.28a}$$

$$c(\tau, t) = \sum_{k=0}^{\infty} Q_{\tau k}\tilde{\xi}_k(t) \tag{2.28b}$$

with

$$Q_{\tau k} = \left(\frac{2}{N_0}\right)^{1/2} \cos\left(\frac{\pi k \tau}{N_0}\right) \qquad k = 1, 2, \ldots \tag{2.29a}$$

$$Q_{\tau k} = \left(\frac{1}{N_0}\right)^{1/2} \qquad k = 0. \tag{2.29b}$$

We then obtain

$$J_0^{(1)\mathrm{L}} = \int \mathrm{d}t \sum_{k=0}^{\infty} [\lambda_0 \tilde{\xi}_k(t)\tilde{\xi}_k(t) - \tilde{\xi}_k(t)\partial_t \xi_k(t) + \lambda_k^{\mathrm{L}} \tilde{\xi}_k(t)\xi_k(t)] \tag{2.30}$$

where $\lambda_k^{\mathrm{L}} = \lambda_0(\pi k/N_0)^2$. It follows that

$$\langle \tilde{\xi}_{k\alpha}(t)\xi_{k'\beta}(t')\rangle_0 = \theta(t'-t)\delta_{kk'}\delta_{\alpha\beta}\exp[-\lambda_k^{\mathrm{L}}(t'-t)] \tag{2.31}$$

and therefore

$$\langle c(\tau, t)c(\sigma, t')\rangle_0^{\mathrm{L}} = \sum_{k=0}^{\infty} Q_{\tau k}Q_{\sigma k}\langle \tilde{\xi}_k(t)\xi_k(t')\rangle_0 = \theta(t'-t)G_0^{\mathrm{L}}(\tau, \sigma\,|\,t'-t) \tag{2.32}$$

with

$$G_0^{\mathrm{L}}(\tau, \sigma\,|\,t) = \frac{1}{N_0}\left(1 + 2\sum_{k=1}^{\infty} \cos \hat{k}_0\tau \cos \hat{k}_0\sigma \exp(-\lambda_k^{\mathrm{L}} t)\right). \tag{2.33}$$

For the linear chain we find in the same way as above for the ring the static correlation function in the centre of mass system:

$$\langle c^*(\tau)\cdot c^*(\tau')\rangle_0^{\mathrm{L}} = \tfrac{1}{3}dN_0 + \frac{d}{2N_0}(\tau^2 + \tau'^2) - d\ \max(\tau, \tau') \tag{2.34}$$

and

$$\langle c(\tau)\cdot c(\tau')\rangle_0^{\mathrm{L}} = d\ \min(\tau, \tau'). \tag{2.35}$$

We will need in the following sections various free time-dependent two-point correlation functions of the form $\langle c(\tau, t)\cdot c(\sigma, s)\rangle_0$. For the ring (R) we have $(t > s)$

$$\begin{aligned}\langle c(\tau, t)\cdot c(\sigma, s)\rangle_0^{\mathrm{R}}/d &= \frac{2\lambda_0 s}{N_0} + \frac{N_0}{2}\sum_{p=1}^{\infty}\frac{1}{(\pi p)^2}\{1 + \cos 2\hat{p}_0(\tau-\sigma)\exp[-\lambda_p^{\mathrm{R}}(t-s)] \\ &\quad - \cos 2\hat{p}_0\tau \exp(-\lambda_p^{\mathrm{R}} t) - \cos 2\hat{p}\sigma \exp(-\lambda_p^{\mathrm{R}} s)\}\end{aligned} \tag{2.36}$$

and for the linear chain (L)

$$\langle c(\tau, t)\cdot c(\sigma, s)\rangle_0^{\mathrm{L}}/d$$

$$=\frac{2\lambda_0 s}{N_0}+2N_0\sum_{p=1}^{\infty}\frac{1}{(\pi p)^2}\{1+\cos\hat{p}_0\tau\cos\hat{p}_0\sigma\exp[-\lambda_p^{\mathrm{L}}(t-s)]$$
$$-\cos\hat{p}_0\tau\exp(-\lambda_p^{\mathrm{L}}t)-\cos\hat{p}_0\sigma\exp(-\lambda_p^{\mathrm{L}}s)\}. \quad (2.37)$$

In particular we have for the ring (R)

$$\langle[c(\alpha, s)-c(\beta, s)]^2\rangle_0^{\mathrm{R}}=d[|\alpha-\beta|-(1/N_0)(\alpha-\beta)^2] \quad (2.38)$$

and for the linear chain (L)

$$\langle[c(\sigma, s)-c(\beta, s)]^2\rangle_0^{\mathrm{L}}=d|\alpha-\beta|. \quad (2.39)$$

Introducing Fourier transforms for the solvent velocity and the solvent velocity response field

$$u(x, t)=\int_k \exp(\mathrm{i}k\cdot x)u(k, t) \quad (2.40a)$$

$$\tilde{u}(x, t)=\int_k \exp(\mathrm{i}k\cdot x)\tilde{u}(k, t) \quad (2.40b)$$

where $\int_k\equiv\int \mathrm{d}^d k/(2\pi)^d$, we obtain for $J_0^{(2)}$

$$J_0^{(2)}=\int_k\int \mathrm{d}t[\tilde{u}(-k, t)\eta_0 k^2\tilde{u}(k, t)-\tilde{u}(-k, t)\partial_t u_\perp(k, t)-\eta_0 k^2\tilde{u}(-k, t)u_\perp(k, t)] \quad (2.41)$$

from which we determine the free solvent velocity field response function

$$\langle\tilde{u}(k, t)u_\perp(k', t')\rangle_0=\Theta(t'-t)\delta(k+k')P\exp[-\eta_0 k^2(t'-t)] \quad (2.42)$$

and the free solvent velocity field autocorrelation function

$$\langle u_\perp(k, t)u_\perp(k', t')\rangle_0=\delta(k+k')P\exp(-\eta_0 k^2|t'-t|) \quad (2.43)$$

with $P=(I-kk/k^2)$. In the presence of hydrodynamic interactions we will use to lowest order, i.e. to $O(g_0^2)$, the Markov (static) approximation for the solvent velocity field, which means we replace

$$\exp(-\eta_0 k^2|t'-t|)\rightarrow\frac{2}{\eta_0 k^2}\delta(t'-t). \quad (2.44)$$

This replacement amounts to assuming that the relaxation of the solvent velocity field is much faster than that of the chain conformation. This approximation is equivalent to using the Oseen tensor. Using the effective Lagrangian given above, we can now calculate general correlation functions for linear chains and simple ring polymers in the presence of both self-avoiding and hydrodynamic interactions.

In the following we will calculate the correlation function

$$C(t)=\langle J_{\mathrm{p}}(t)J_{\mathrm{p}}(0)\rangle \quad (2.45)$$

where $J_{\mathrm{p}}(t)$ is the xy component of the momentum flux tensor for the polymer chain and $\langle\ \rangle$ is the average over the initial equilibrium ensemble and over the Gaussian noise. From (2.45) we obtain the intrinsic viscosity according to the Green–Kubo formula [16] as

$$[\eta]=\frac{N_{\mathrm{A}}}{MkT}\eta_0^{-1}\int_0^{\infty}\mathrm{d}t\langle J_{\mathrm{p}}(t)J_{\mathrm{p}}(0)\rangle \quad (2.46)$$

where N_A is Avogadro's constant and M is the molecular weight of the chain. We should note that the expression (2.45) is reliable only to the lowest non-trivial order ($O(\varepsilon)$) of the renormalised perturbation theory. In general (as has been pointed out already in [8]) we have to consider the correlation function [17]

$$C(t)=\langle J(t)J(0)\rangle \tag{2.47}$$

where $J(t)$ consists of the contribution from the solute polymer J_p and the solvent J_s. Only if we can ignore the correlation between J_p and J_s can we use equation (2.45). This is possible when the respective timescales are sufficiently different. To lowest order we can assume this to be the case, as we assume the Markov approximation (see above) to this order. To higher orders in g_0 however, we cannot make this assumption *a priori*.

In the next section we will outline the calculation of the momentum flux autocorrelation function (2.45) in the presence of self-avoiding interactions.

3. Self-avoiding interactiions

We will now outline the calculation of $C(t)$ in the presence of self-avoiding interactions (i.e. a Gaussian chain in the vacuum) for both ring (R) and linear (L) chains to $O(v_0)$. $J_p(t)$ in (2.46) can be written as

$$J_p(t)=-\int_0^{N_0} d\tau\, c_y(\tau,t)\frac{\delta H_E}{\delta c_x(\tau,t)}. \tag{3.1}$$

$C(t)$ is the sum of the following contributions:

$$C(t)=C_0(t)+\sum_{j=1}^{4} C_{ja}(t)+\sum_{j=1}^{4} C_{jb}(t) \tag{3.2}$$

where

$$C_0(t)=\int_0^{N_0} d\sigma\int_0^{N_0} d\tau \frac{\partial^2}{\partial\delta^2}\bigg|_{\delta=\tau}\frac{\partial^2}{\partial\gamma^2}\bigg|_{\gamma=\sigma}\langle c_y(\tau,t)c_x(\delta,t)c_y(\sigma,0)c_x(\gamma,0)\rangle_{O(v_0)}. \tag{3.3}$$

Introducing a generating functional, we can decompose $C_0(t)$ in a sum of four terms

$$C_0(t)=\sum_{j=1}^{4} C_{0j} \tag{3.4}$$

where $C_{00}(t)$ is the free contribution and $C_{01}(t),\ldots,C_{03}(t)$ are $O(v_0)$ contributions. For the ring (R) we have

$$C_{00}^{R}(t)=2\sum_{p=1}^{\infty}\exp(-2\lambda_p^{R}t) \tag{3.5}$$

and for the linear chain (L)

$$C_{00}^{L}(t)=\sum_{p=1}^{\infty}\exp(-2\lambda_p^{L}t). \tag{3.6}$$

The other terms can be expressed in terms of products of free correlations. Introducing a Fourier transform for the δ-function interaction we obtain for $C_{01}(t)$:

$$C_{01}(t)=-\tfrac{1}{2}v_0\int_0^{N_0} d\sigma\int_0^{N_0} d\tau\frac{\partial^2}{\partial\delta^2}\bigg|_{\delta=\tau}\frac{\partial^2}{\partial\gamma^2}\bigg|_{\gamma=\sigma}\int_0^{N_0} d\alpha\int_0^{N_0} d\beta\int_k k_x^2k_y^2$$
$$\times\exp(-\tfrac{1}{2}k^2\langle A^2\rangle_0/d)\langle A_xc_x(\gamma)\rangle_0\langle A_yc_y(\sigma)\rangle_0\langle A_xc_x(\delta,t)\rangle_0\langle A_yc_y(\tau,t)\rangle_0 \tag{3.7}$$

where $A = c(\beta, 0) - c(\alpha, 0)$. Using the free correlation functions given in (2.36) and (2.37) and integrating over σ and τ we obtain for the ring (R)

$$C_{01}^{\mathrm{R}}(t) = -\tfrac{1}{2}v_0 N_0^2 \int_0^{N_0} \mathrm{d}\alpha \int_0^{N_0} \mathrm{d}\beta \int_k k_x^2 k_y^2 \exp\{-\tfrac{1}{2}k^2[|\alpha-\beta| - (1/N_0)(\alpha-\beta)^2]\}$$
$$\times \sum_{p'=1}^{\infty} \frac{1}{(\pi p')^2}[1 - \cos 2\hat{p}_0'(\alpha - \beta)] \exp(-2\lambda_{p'}^{\mathrm{R}} t)$$
$$\times \sum_{p=1}^{\infty} \frac{1}{(\pi p)^2}[1 - \cos 2\hat{p}_0(\beta - \alpha)] \tag{3.8}$$

and for the linear chain (L)

$$C_{01}^{\mathrm{L}}(t) = -2v_0 N_0^2 \int_0^{N_0} \mathrm{d}\alpha \int_0^{N_0} \mathrm{d}\beta \int k_x^2 k_y^2 \exp(-\tfrac{1}{2}k^2|\alpha-\beta|)$$
$$\times \sum_{p=1}^{\infty} \frac{1}{(\pi p)^2} (\cos \hat{p}_0 \beta - \cos \hat{p}_0 \alpha)^2$$
$$\times \sum_{p'=1}^{\infty} \frac{1}{(\pi p')^2} (\cos \hat{p}_0' \beta - \cos \hat{p}_0' \alpha)^2 \exp(-2\lambda_{p'}^{\mathrm{L}} t). \tag{3.9}$$

The contribution $C_{02}(t)$ is given by

$$C_{02}(t) = \tfrac{1}{2}v_0 \int_0^{N_0} \mathrm{d}\sigma \int_0^{N_0} \mathrm{d}\tau \frac{\partial^2}{\partial \delta^2}\bigg|_{\delta=\tau} \frac{\partial^2}{\partial \gamma^2}\bigg|_{\gamma=\sigma} \int_0^{N_0} \mathrm{d}\alpha \int_0^{N_0} \mathrm{d}\beta \int_k k_x^2$$
$$\times \exp(-\tfrac{1}{2}k^2\langle A^2\rangle_0/d)\langle A_x c_x(\gamma)\rangle_0 \langle A_x c_x(\delta, t)\rangle_0 \langle c_y(\tau, t) c_y(\sigma)\rangle_0 \tag{3.10}$$

with A given as before. We obtain for the ring (R)

$$C_{02}^{\mathrm{R}}(t) = \tfrac{1}{2}v_0 N_0 \int_0^{N_0} \mathrm{d}\alpha \int_0^{N_0} \mathrm{d}\beta \int_k k_x^2 \exp\{-\tfrac{1}{2}k^2[|\alpha-\beta| - (1/N_0)(\alpha-\beta)^2]\}$$
$$\times \sum_{p=1}^{\infty} \frac{1}{(\pi p)^2}[1 - \cos 2\hat{p}_0(\alpha - \beta)] \exp(-2\lambda_p^{\mathrm{R}} t) \tag{3.11}$$

and for the linear chain (L)

$$C_{02}^{\mathrm{L}}(t) = v_0 N_0 \int_0^{N_0} \mathrm{d}\alpha \int_0^{N_0} \mathrm{d}\beta \int_k k_x^2 \exp(-\tfrac{1}{2}k^2|\alpha - \beta|)$$
$$\times \sum_{p=1}^{\infty} \frac{1}{(\pi p)^2} (\cos \hat{p}_0 \beta - \cos \hat{p}_0 \alpha)^2 \exp(-2\lambda_p^{\mathrm{L}} t). \tag{3.12}$$

Finally, the contribution $C_{03}(t)$ is given by

$$C_{03}(t) = \tfrac{1}{2}v_0 \int_0^{N_0} \mathrm{d}\sigma \int_0^{N_0} \mathrm{d}\tau \frac{\partial^2}{\partial \delta^2}\bigg|_{\delta=\tau} \frac{\partial^2}{\partial \gamma^2}\bigg|_{\gamma=\sigma} \int_0^{N_0} \mathrm{d}\alpha \int_0^{N_0} \mathrm{d}\beta \int_k k_y^2 \exp(-\tfrac{1}{2}k^2\langle A^2\rangle_0/d)$$
$$\times \langle A_y c_y(\sigma)\rangle_0 \langle A_y c_y(\tau, t)\rangle_0 \langle c_x(\delta, t) c_x(\gamma)\rangle_0. \tag{3.13}$$

We find $C_{03}(t) = C_{02}(t)$ and therefore

$$C_0(t) = C_{00}(t) + C_{01}(t) + 2C_{02}(t) \tag{3.14}$$

for both rings (R) and linear chains (L). Now we consider the contributions $\Sigma_{j=1}^{4} C_{ja}$. We find

$$C_{1a}(t)=v_0\lambda_0\int_0^{N_0}\mathrm{d}\tau\int_0^{N_0}\mathrm{d}\sigma\int_0^{N_0}\mathrm{d}\alpha\int_0^{N_0}\mathrm{d}\beta\int_k k_x^2\exp(-\tfrac{1}{2}k^2\langle A^2\rangle_0/d)$$
$$\times\int_0^t \mathrm{d}s'\frac{\partial^2}{\partial\tau^2}G_0(\tau,\beta\,|\,t-s')\frac{\partial^2}{\partial\gamma^2}\bigg|_{\gamma=\sigma}\langle c_y(\tau,t)c_y(\sigma)\rangle_0\langle A_xc_x(\gamma)\rangle_0 \tag{3.15}$$

where now $A\equiv \boldsymbol{c}(\beta,s')-\boldsymbol{c}(\alpha,s')$. We obtain, performing the τ and σ integrations, for the ring (R)

$$C_{1a}^{R}(t)=2v_0\lambda_0N_0^{-1}t\int_0^{N_0}\mathrm{d}\alpha\int_0^{N_0}\mathrm{d}\beta\int_k k_x^2\exp\{-\tfrac{1}{2}k^2[|\alpha-\beta|-(1/N_0)(\alpha-\beta)^2]\}$$
$$\times\sum_{p=1}^{\infty}[1-\cos 2\hat{p}_0(\alpha-\beta)]\exp(-2\lambda_p^{\mathrm{R}}t) \tag{3.16}$$

and for the linear chain (L)

$$C_{1a}^{\mathrm{L}}(t)=2v_0\lambda_0N_0^{-1}t\int_0^{N_0}\mathrm{d}\alpha\int_0^{N_0}\mathrm{d}\beta\int_k k_x^2\exp(-\tfrac{1}{2}k^2|\alpha-\beta|)$$
$$\times\sum_{p=1}^{\infty}\cos\hat{p}_0\beta(\cos\hat{p}_0\beta-\cos\hat{p}_0\alpha)\exp(-2\lambda_p^{\mathrm{L}}t). \tag{3.17}$$

Next we consider the contribution $C_{4a}(t)$,

$$C_{4a}(t)=\int_0^{N_0}\mathrm{d}\sigma\int_0^{N_0}\mathrm{d}\tau\int_0^{N_0}\mathrm{d}\alpha\int_0^{N_0}\mathrm{d}\beta\int_k k_y^2\exp(-\tfrac{1}{2}k^2\langle A^2\rangle_0/d)\int_0^t\mathrm{d}s'G_0(\tau,\beta\,|\,t-s')$$
$$\times\langle A_yc_y(\sigma,0)\rangle_0\frac{\partial^2}{\partial\gamma^2}\bigg|_{\gamma=\tau}\frac{\partial^2}{\partial\delta^2}\bigg|_{\delta=\sigma}\langle c_x(\gamma,t)c_x(\delta)\rangle_0 \tag{3.18}$$

where $A\equiv \boldsymbol{c}(\beta,s')-\boldsymbol{c}(\alpha,s')$. We find $C_{4a}(t)=C_{1a}(t)$ for both ring (R) and linear chain (L). The contribution $C_{2a}(t)$ is given by

$$C_{2a}(t)=v_0\int_0^{N_0}\mathrm{d}\sigma\int_0^{N_0}\mathrm{d}\alpha\int_0^{N_0}\mathrm{d}\beta\int_k k_x^2\exp(-\tfrac{1}{2}k^2\langle A^2\rangle_0/d)$$
$$\times\langle c_y(\beta,t)c_y(\sigma)\rangle_0\frac{\partial^2}{\partial\delta^2}\bigg|_{\delta=\sigma}\langle A_xc_x(\delta)\rangle_0 \tag{3.19}$$

where $A\equiv \boldsymbol{c}(\beta,t)-\boldsymbol{c}(\alpha,t)$. We obtain for the ring (R)

$$C_{2a}^{\mathrm{R}}(t)=-\tfrac{1}{2}v_0N_0\int_0^{N_0}\mathrm{d}\alpha\int_0^{N_0}\mathrm{d}\beta\int_k k_x^2\exp\{-\tfrac{1}{2}k^2[|\alpha-\beta|-(1/N_0)(\alpha-\beta)^2]\}$$
$$\times\sum_{p=1}^{\infty}\frac{1}{(\pi p)^2}[1-\cos 2\hat{p}_0(\beta-\alpha)]\exp(-2\lambda_p^{\mathrm{R}}t) \tag{3.20}$$

and for the linear chain (L)

$$C_{2a}^{\mathrm{L}}(t)=-2v_0N_0\int_0^{N_0}\mathrm{d}\alpha\int_0^{N_0}\mathrm{d}\beta\int_k k_x^2\exp(-\tfrac{1}{2}k^2|\alpha-\beta|)$$
$$\times\sum_{p=1}^{\infty}\frac{1}{(\pi p)^2}(\cos\hat{p}_0\beta-\cos\hat{p}_0\alpha)\cos\hat{p}_0\beta\exp(-2\lambda_p^{\mathrm{L}}t). \tag{3.21}$$

For $C_{3a}(t)$ we find

$$C_{3a}(t)=v_0\int_0^{N_0}\mathrm{d}\tau\int_0^{N_0}\mathrm{d}\alpha\int_0^{N_0}\mathrm{d}\beta\int_k k_x^2\exp(-\tfrac{1}{2}k^2\langle A^2\rangle_0/d)\left.\frac{\partial^2}{\partial\delta^2}\right|_{\delta=\tau}$$
$$\times\langle c_y(\tau,t)c_y(\beta)\rangle_0\langle A_xc_x(\delta,t)\rangle_0 \tag{3.22}$$

where $A\equiv \boldsymbol{c}(\beta,0)-\boldsymbol{c}(\sigma,0)$. We have for both ring (R) and linear chains (L)

$$C_{3a}(t)=C_{2a}(t) \tag{3.23}$$

and therefore $\Sigma_{j=1}^4 C_{ja}(t)=2C_{1a}(t)+2C_{2a}(t)$.

Now we consider the terms $\Sigma_{j=1}^4 C_{jb}(t)$.

$$C_{1b}(t)=-v_0\lambda_0\int_0^{N_0}\mathrm{d}\sigma\int_0^{N_0}\mathrm{d}\tau\int_0^{0}\mathrm{d}\alpha\int_0^{N_0}\mathrm{d}\beta\int_k k_x^2k_y^2$$
$$\times\exp(-\tfrac{1}{2}k^2\langle A^2\rangle_0/d)\int_0^t\mathrm{d}s\frac{\partial^2}{\partial\tau^2}G_0(\tau,\beta\,|\,t-s)\left.\frac{\partial^2}{\partial\gamma^2}\right|_{\gamma=\sigma}$$
$$\times\langle A_xc_x(\gamma)\rangle_0\langle A_yc_y(\sigma)\rangle_0\langle A_yc_y(\tau,t)\rangle_0 \tag{3.24}$$

with $A\equiv\boldsymbol{c}(\beta,s)-\boldsymbol{c}(\alpha,s)$. This gives for the ring (R)

$$C_{1b}^{\mathrm{R}}(t)=-2v_0\lambda_0\int_0^{N_0}\mathrm{d}\alpha\int_0^{N_0}\mathrm{d}\beta\int_k k_x^2k_y^2\exp\{-\tfrac{1}{2}k^2[|\alpha-\beta|-(1/N_0)(\alpha-\beta)^2]\int_0^t\mathrm{d}s$$
$$\times\sum_{p=1}^{\infty}[\cos 2\hat{p}_0(\alpha-\beta)-1]\exp(-2\lambda_p^{\mathrm{R}}t)\exp(2\lambda_p^{\mathrm{R}}s)$$
$$\times\sum_{p'=1}^{\infty}\frac{1}{(\pi p')^2}[\cos 2\hat{p}_0'(\alpha-\beta)-1]\exp(-2\lambda_{p'}^{\mathrm{R}}s) \tag{3.25}$$

and for the linear chain (L)

$$C_{1b}^{\mathrm{L}}(t)=-4v_0\lambda_0\int_0^{N_0}\mathrm{d}\alpha\int_0^{N_0}\mathrm{d}\beta\int_k k_x^2k_y^2\exp(-\tfrac{1}{2}k^2|\alpha-\beta|)\int_0^t\mathrm{d}s$$
$$\times\sum_{p=1}^{\infty}\cos\hat{p}_0\beta(\cos\hat{p}_0\beta-\cos\hat{p}_0\alpha)\exp(-2\lambda_p^{\mathrm{L}}t)\exp(2\lambda_p^{\mathrm{L}}s)$$
$$\times\sum_{p'=1}^{\infty}\frac{1}{(\pi p')^2}(\cos\hat{p}_0'\beta-\cos\hat{p}_0'\alpha)^2\exp(-2\lambda_{p'}^{\mathrm{L}}s). \tag{3.26}$$

Next we consider $C_{4b}(t)$,

$$C_{4b}(t)=-v_0\lambda_0\int_0^{N_0}\mathrm{d}\sigma\int_0^{N_0}\mathrm{d}\tau\int_0^{N_0}\mathrm{d}\alpha$$
$$\times\int_0^{N_0}\mathrm{d}\beta\int_k k_x^2k_y^2\exp(-\tfrac{1}{2}k^2\langle A^2\rangle_0/d)\int_0^t\mathrm{d}sG_0(\tau,\beta\,|\,t-s)$$
$$\times\left.\frac{\partial^2}{\partial\gamma^2}\right|_{\gamma=\tau}\left.\frac{\partial^2}{\partial\delta^2}\right|_{\delta=\sigma}\langle A_xc_x(\delta)\rangle_0\langle A_yc_y(\sigma)\rangle_0\langle A_xc_x(\gamma,t)\rangle_0 \tag{3.27}$$

with A as before. We find $C_{4b}(t) = C_{1b}(t)$ for both ring (R) and linear chains (L). Now we determine $C_{2b}(t)$:

$$C_{2b}(t) = -v_0 \int_0^{N_0} \mathrm{d}\sigma \int_0^{N_0} \mathrm{d}\alpha \int_0^{N_0} \mathrm{d}\beta \int_k k_x^2 k_y^2 \exp(-\tfrac{1}{2}k^2 \langle A^2 \rangle_0 / d)$$
$$\times \frac{\partial^2}{\partial \delta^2}\bigg|_{\delta=\sigma} \langle A_x c_x(\delta)\rangle_0 \langle A_y c_y(\sigma)\rangle_0 \langle A_y c_y(\beta, t)\rangle_0 \tag{3.28}$$

where $A \equiv c(\beta, t) - c(\alpha, t)$. Evaluation of this contribution gives for the ring (R)

$$C_{2b}^{\mathrm{R}}(t) = \tfrac{1}{2} v_0 N_0^2 \int_0^{N_0} \mathrm{d}\alpha \int_0^{N_0} \mathrm{d}\beta \int_k k_x^2 k_y^2 \exp\{-\tfrac{1}{2}k^2[|\alpha-\beta| - (1/N_0)(\alpha-\beta)^2]\}$$
$$\times \sum_{p=1}^{\infty} \frac{1}{(\pi p)^2} [\cos 2\hat{p}_0(\alpha-\beta) - 1]$$
$$\times \sum_{p'=1}^{\infty} \frac{1}{(\pi p')^2} [\cos 2\hat{p}_0'(\alpha-\beta) - 1] \exp(-2\lambda_{p'}^{\mathrm{R}} t) \tag{3.29}$$

and for the linear chain (L)

$$C_{2b}^{\mathrm{L}}(t) = 4 v_0 N_0^2 \int_0^{N_0} \mathrm{d}\alpha \int_0^{N_0} \mathrm{d}\beta \int_k k_x^2 k_y^2 \exp(-\tfrac{1}{2}k^2 |\alpha-\beta|)$$
$$\times \sum_{p=1}^{\infty} \frac{1}{(\pi p)^2} \cos \hat{p}_0 \beta (\cos \hat{p}_0 \beta - \cos \hat{p}_0 \alpha)$$
$$\times \sum_{p'=1}^{\infty} \frac{1}{(\pi p')^2} (\cos \hat{p}_0' \beta - \cos \hat{p}_0' \alpha)^2 \exp(-2\lambda_{p'}^{\mathrm{L}} t). \tag{3.30}$$

Finally, we consider $C_{3b}(t)$:

$$C_{3b}(t) = -v_0 \int_0^{N_0} \mathrm{d}\tau \int_0^{N_0} \mathrm{d}\alpha \int_0^{N_0} \mathrm{d}\beta \int_k k_x^2 k_y^2 \exp(-\tfrac{1}{2}k^2 \langle A^2 \rangle_0 / d)$$
$$\times \frac{\partial^2}{\partial \delta^2}\bigg|_{\delta=\tau} \langle A_x c_x(\delta, t)\rangle_0 \langle A_y c_y(\beta)\rangle_0 \langle A_y c_y(\tau, t)\rangle_0 \tag{3.31}$$

where $A \equiv c(\beta, 0) - c(\alpha, 0)$. We find for both the ring (R) and the linear chain (L) $C_{3b}(t) = C_{2b}(t)$. Therefore $\Sigma_{j=1}^4 C_{jb}(t) = 2C_{1b}(t) + 2C_{2b}(t)$. Collecting all terms, we find to $\mathrm{O}(v_0)$:

$$C(t) = C_{00}(t) + C_{01}(t) + 2(C_{02}(t) + C_{1a}(t) + C_{2a}(t) + C_{1b}(t) + C_{2b}(t)). \tag{3.32}$$

Observing a cancellation between $C_{02}(t)$ and a part of $C_{1a}(t) + C_{2a}(t)$ and a partial cancellation between $C_{01}(t)$ and $2C_{1b}(t) + 2C_{2b}(t)$, we secure for the ring (R):

$$C^{\mathrm{R}}(t) = 2\sum_{p=1}^{\infty} \exp(-2\lambda_p^{\mathrm{R}} t) + 4 v_0 N_0^{-1} \lambda_0 t \int_0^{N_0} \mathrm{d}\alpha \int_0^{N_0} \mathrm{d}\beta \int_k k_x^2$$
$$\times \exp\{-\tfrac{1}{2}k^2[|\alpha-\beta| - (1/N_0)(\alpha-\beta)^2]\}$$
$$\times \sum_{p=1}^{\infty} [1 - \cos 2\hat{p}_0(\beta-\alpha)] \exp(-2\lambda_p^{\mathrm{R}} t)$$
$$+ v_0 \int_0^{N_0} \mathrm{d}\alpha \int_0^{N_0} \mathrm{d}\beta \int_k k_x^2 k_y^2 \exp\{-\tfrac{1}{2}k^2[|\alpha-\beta| - (1/N_0)(\alpha-\beta)^2]\}$$
$$\times \sum_{p=1}^{\infty} \sum_{p'=1}^{\infty} \frac{1}{(\pi p')^2} [\cos 2\hat{p}_0(\beta-\alpha) - 1][\cos 2\hat{p}_0'(\beta-\alpha) - 1]$$

$$\times\left(\frac{1}{2}\frac{N_0^2}{(\pi p)^2}\exp(-2\lambda_{p'}^{R}t)-4\lambda_0\int_0^t \mathrm{d}s\,\exp(-2\lambda_p^{R}t)\exp(-2\lambda_{p'}^{R}s)\exp(2\lambda_p^{R}s)\right) \tag{3.33}$$

and for the linear chain (L):

$$C^{L}(t)=\sum_{p=1}^{\infty}\exp(-2\lambda_p^{L}t)+2v_0N_0^{-1}\lambda_0 t\int_0^{N_0}\mathrm{d}\alpha\int_0^{N_0}\mathrm{d}\beta\int_k k_x^2\exp(-\tfrac{1}{2}k^2|\alpha-\beta|)$$

$$\times\sum_{p=1}^{\infty}(\cos\hat{p}_0\beta-\cos\hat{p}_0\alpha)^2\exp(-2\lambda_p^{L}t)$$

$$+4v_0\int_0^{N_0}\mathrm{d}\alpha\int_0^{N_0}d\beta\int_k k_x^2k_y^2\exp(-\tfrac{1}{2}k^2|\alpha-\beta|)$$

$$\times\sum_{p=1}^{\infty}\sum_{p'=1}^{\infty}\frac{1}{(\pi p')^2}(\cos\hat{p}_0\beta-\cos\hat{p}_0\alpha)^2$$

$$\times(\cos\hat{p}'_0\beta-\cos\hat{p}'_0\alpha)^2\left(\frac{1}{2}\frac{N_0^2}{(\pi p)^2}\exp(-2\lambda_p^{L}t)\right.$$

$$\left.-\lambda_0\int_0^t \mathrm{d}s\,\exp(-2\lambda_p^{L}t)\exp(-2\lambda_{p'}^{L}s)\exp(2\lambda_p^{L}s)\right). \tag{3.34}$$

Now we can study the zero-frequency ($\omega=0$) limit. We find for the ring (R)

$$\int_0^{\infty}\mathrm{d}t\,C^{R}(t)=\tfrac{1}{24}\zeta_0N_0^2+\tfrac{1}{16}v_0\zeta_0N_0^3\int_0^{N_0}\mathrm{d}\alpha\int_0^{N_0}\mathrm{d}\beta\int_k k_x^2$$

$$\times\exp\{-\tfrac{1}{2}k^2[|\alpha-\beta|-(1/N_0)(\alpha-\beta)^2]\}$$

$$\times\sum_{p=1}^{\infty}\frac{1}{(\pi p)^4}[1-\cos 2\hat{p}_0(\beta-\alpha)]. \tag{3.35}$$

Note the complete disappearance of the double sum in (3.33) for this limit. This is the reason why, although unexpected on physical grounds, we find the $\omega=0$ limit to agree with the Kirkwood–Riseman formalism. Performing the momentum integration and summing up, with

$$\sum_{p=1}^{\infty}\frac{1}{(\pi p)^4}[1-\cos 2\hat{p}_0(\beta-\alpha)]=\frac{1}{3N_0^2}(\beta-\alpha)^2\left(1-\frac{2}{N_0}|\alpha-\beta|+\frac{(\beta-\alpha)^2}{N_0^2}\right) \tag{3.36}$$

we obtain in $d=4-\varepsilon$ dimensions

$$\int_0^{\infty}\mathrm{d}t\,C^{R}(t)=\tfrac{1}{24}\zeta_0N_0^2+v_0\zeta_0N_0\frac{(2\pi)^{-d/2}}{48}\int_0^{N_0}\mathrm{d}\alpha\int_0^{N_0}\mathrm{d}\beta$$

$$\times[|\alpha-\beta|-(1/N_0)(\alpha-\beta)^2]^{-3+\varepsilon/2}$$

$$\times(\beta-\alpha)^2[1-(2/N_0)|\alpha-\beta|+(1/N_0)(\beta-\alpha)^2]. \tag{3.37}$$

Performing the remaining contour integrations, we find, using

$$\int_0^1\mathrm{d}x\,x^a(1-x)^b=\frac{\Gamma(a+1)\Gamma(b+1)}{\Gamma(a+b+2)} \tag{3.38}$$

$$\int_0^{\infty}\mathrm{d}t\,C^{R}(t)=\tfrac{1}{24}\zeta_0N_0^2\left[1+\frac{v_0}{(2\pi)^{2-\varepsilon/2}}\left(\frac{2}{\varepsilon}+\ln N_0\right)\right]. \tag{3.39}$$

Renormalisation is performed with

$$N = Z_N N_0 \tag{3.40a}$$

$$\zeta = Z_\zeta \zeta_0 \tag{3.40b}$$

$$\xi = \zeta L^{\varepsilon/2} \tag{3.40c}$$

$$v_0 = u_0 L^{-\varepsilon/2} \tag{3.40d}$$

where L is a length scale. In lowest order we use $Z_\xi = 1-(2/\varepsilon)[u/(2\pi)^2]$, $Z_N = 1+(2/\varepsilon)[u/(2\pi)^2]$ and we find at the fixed point $u^*/(2\pi)^2 = \frac{1}{8}\varepsilon$ (free-draining self-avoiding limit), putting $\eta_0 = 1$,

$$[\eta]^{\mathrm{R}} \frac{MkT}{N_{\mathrm{A}}} = \frac{1}{24} \frac{\xi}{(2\pi)^2} L^{d/2} \left(\frac{2\pi N}{L}\right)^{\nu z} \exp(0\varepsilon) \tag{3.41}$$

where ν is the Flory exponent $\nu = \frac{1}{2} + \frac{1}{16}\varepsilon$ and z is the dynamical critical exponent $z = 2 + 1/\nu$. (To lowest order the exponent ν is the same for a ring and a linear chain [18].)

For the linear chain (L) we obtain

$$\int_0^\infty \mathrm{d}t\, C^{\mathrm{L}}(t) = \tfrac{1}{12}\zeta_0 N_0^2 + \tfrac{1}{2}\zeta_0 v_0 N_0^3 (2\pi)^{-d/2} \int_0^{N_0} \mathrm{d}\alpha \int_0^{N_0} \mathrm{d}\beta |\alpha - \beta|^{-3+\varepsilon/2} \times \sum_{p=1}^{\infty} \frac{(\cos\hat{p}_0\beta - \cos\hat{p}_0\alpha)^2}{(\pi p)^4}. \tag{3.42}$$

Using

$$\sum_{p=1}^{\infty} \frac{(\cos\hat{p}_0\beta - \cos\hat{p}_0\alpha)^2}{(\pi p)^4} = -\frac{1}{8N_0^4}(\alpha^2 - \beta^2)^2 + \frac{1}{12N_0^3}(\alpha - \beta)^2[3(\alpha+\beta) - |\alpha - \beta|] \tag{3.43}$$

and performing the remaining contour integrations, we obtain

$$\int_0^\infty \mathrm{d}t\, C^{\mathrm{L}}(t) = \frac{\zeta_0 N_0^2}{12}\left[1 - \frac{v_0}{(2\pi)^{d/2}}\left(-\frac{2}{\varepsilon} N_0^{\varepsilon/2} + \frac{13}{12}\right)\right]. \tag{3.44}$$

Renormalisation and exponentiation of the result at the fixed point $u^*/(2\pi)^2 = \frac{1}{8}\varepsilon$ gives

$$[\eta]^{\mathrm{L}} \frac{MkT}{N_{\mathrm{A}}} = \frac{1}{12} \frac{\xi}{(2\pi)^2} L^{d/2} \left(\frac{2\pi N}{L}\right)^{\nu z} \exp(-\tfrac{13}{96}\varepsilon). \tag{3.45}$$

This result has been derived in [11] employing the Kirkwood–Riseman formalism. We should note that due to a computational mistake we concluded in [9] that the Green–Kubo and KR formalisms give different results to lowest order.

Let us now consider $C(t)$ for t finite. In order to obtain a result which is valid in the large-t limit we cannot (after performing the renormalisation and inserting the fixed-point values) naively exponentiate the results to $O(\varepsilon)$. Rather we have to use the idea of singular perturbation theory [19] and exploit the asymptotic behaviour of the relaxation times as dictated by the renormalisation group equation [3]. This procedure (see [8] for a discussion) amounts to introducing an effective eigenvalue for the relaxation spectrum by exponentiating single sum terms which have prefactors linear in the time t. To $O(\varepsilon)$ we find the relaxation spectrum for a ring (R):

$$\lambda_{pp}^{R}=2\lambda_{p}^{R}\exp\left[\tfrac{1}{8}\varepsilon\left(\frac{1}{(\pi p)^4}[\tfrac{15}{4}A^{R}(4p)-15A^{R}(2p)]\right.\right.$$
$$\left.\left.-\frac{3\pi}{(\pi p)^3}[B^{R}(4p)-2B^{R}(2p)]-\frac{1}{(\pi p)^2}[C^{R}(2p)-C^{R}(4p)]\right)\right] \tag{3.46}$$

where λ_{pp}^{R} is the reciprocal of the relaxation time of the doubly excited p mode. $\lambda_{pp}^{R}/2\lambda_{p}^{R}$ describes the interference effect of two p modes in the presence of self-avoiding interactions. λ_{p}^{R} is the eigenvalue which appears in the calculation of, for example, the correlation function $\langle c(\tau,t)\cdot c(\tau,t)\rangle$ to $O(v_0)$. We find

$$\lambda_{p}^{R}=\frac{1}{\zeta}\left(\frac{2\pi p}{N}\right)^2\left(\frac{Lp}{N}\right)^{\varepsilon/8}\exp\left[\tfrac{1}{8}\varepsilon\left(\hat{\gamma}-\mathrm{ci}(2\pi p)-\frac{3}{2}+\frac{3}{2}\frac{1}{(\pi p)^2}A^{R}(2p)\right)\right]. \tag{3.47}$$

In (3.46) and (3.47) we have introduced the functions

$$A^{R}(p)=-\pi p[\mathrm{si}(\pi p)+\tfrac{1}{2}\pi]+2[\mathrm{ci}(|\pi p|)-\hat{\gamma}-\ln(|\pi p|)] \tag{3.48a}$$

$$C^{R}(p)=\pi p[\mathrm{si}(\pi p)+\tfrac{1}{2}\pi] \tag{3.48b}$$

$$B^{R}(p)=p[\mathrm{ci}(|\pi p|)-\ln(|\pi p|)] \tag{3.48c}$$

where $\hat{\gamma}$ is Euler's constant, $\mathrm{ci}(x)=-\int_x^\infty \mathrm{d}t\cos t/t$ and $\mathrm{si}(x)=-\int_x^\infty \mathrm{d}t\sin t/t$. Note that $\lambda_p\approx p^{2+\varepsilon/8}$ asymptotically as required by the renormalisation group [3, 6]. For the linear chain (L) we have

$$\lambda_{pp}^{L}=2\lambda_{p}^{L}\exp\left[\tfrac{1}{8}\varepsilon\left(8\frac{[1-(-1)^p]}{(\pi p)^4}+\frac{1}{4}\frac{\pi}{(\pi p)^3}[50B^{L}(2p)-35B^{L}(p)-27B^{L}(3p)\right.\right.$$
$$\left.\left.+4B^{L}(4p)-12pA^{L}(2p)+12pA^{L}(p)]\right)\right] \tag{3.49}$$

where

$$\lambda_{p}^{L}=\frac{1}{\zeta}\left(\frac{\pi p}{N}\right)^2\left(\frac{Lp}{2N}\right)^{\varepsilon/8}\exp\left[\frac{\varepsilon}{8}\left(\hat{\gamma}-\mathrm{ci}(\pi p)-\tfrac{3}{2}-\frac{2}{(\pi p)^2}(1-(-1)^p)\right.\right.$$
$$\left.\left.+\frac{3\mathrm{si}(\pi p)}{\pi p}-\frac{2\mathrm{si}(2\pi p)}{\pi p}+\frac{1}{2p}\right)\right] \tag{3.50}$$

and we have introduced the functions

$$A^{L}(p)=(-1)^{p+1}-\mathrm{ci}(|\pi p|)+\ln(|\pi p|)-\pi p(\mathrm{si}(\pi p)+\tfrac{1}{2}\pi) \tag{3.51a}$$

$$B^{L}(p)=p(\mathrm{ci}(|\pi p|)-\ln(|\pi p|)). \tag{3.51b}$$

Inserting λ_{pp} also in the double sums in (3.33), we obtain (at the fixed point $u^*/(2\pi)^2=\frac{1}{8}\varepsilon$) after performing a Fourier transform, the real and imaginary part of the complex intrinsic viscosity $[\bar{\eta}(\bar{\omega})]=(N_A/MkT)\bar{C}(\bar{\omega})$ valid for both the ring (R) and the linear chain (L):

$$\mathrm{Re}\,\bar{C}(\bar{\omega})=a\sum_{p=1}^{\infty}\frac{1}{\bar{\lambda}_{pp}(1+\bar{\omega}^2/\bar{\lambda}_{pp}^2)}\exp(\tfrac{1}{4}\varepsilon E(p))$$
$$+\frac{\varepsilon}{\pi^2}\sum_{p\neq p'=1}^{\infty}\left(\frac{Q_{pp'}^{(2)}}{p^2p'^2}+\frac{Q_{pp'}^{(2)}}{p'^2(p'^2-p^2)}\right)\frac{1}{\bar{\lambda}_{p'p'}(1+\bar{\omega}^2/\bar{\lambda}_{p'p'}^2)}$$
$$+\frac{\varepsilon}{\pi^2}\sum_{p\neq p'=1}^{\infty}\frac{Q_{pp'}^{(2)}}{p'^2(p^2-p'^2)}\frac{1}{\bar{\lambda}_{pp}(1+\bar{\omega}^2/\bar{\lambda}_{pp}^2)} \tag{3.52a}$$

$$\operatorname{Im} \bar{C}(\bar{\omega}) = a \sum_{p=1}^{\infty} \frac{\bar{\omega}/\bar{\lambda}_{pp}}{\lambda_{pp}(1+\bar{\omega}^2/\bar{\lambda}_{pp}^2)} \exp(\tfrac{1}{4}\varepsilon E(p))$$
$$+ \frac{\varepsilon}{\pi^2} \sum_{p \neq p=1}^{\infty} \left(\frac{Q_{pp'}^{(2)}}{p^2 p'^2} + \frac{Q_{pp'}^{(2)}}{p'^2(p'^2-p^2)} \right) \frac{\bar{\omega}/\bar{\lambda}_{p'p'}}{\bar{\lambda}_{p'p'}(1+\bar{\omega}^2/\bar{\lambda}_{p'p'}^2)}$$
$$+ \frac{\varepsilon}{\pi^2} \sum_{p \neq p'=1}^{\infty} \frac{Q_{pp'}^{(2)}}{p'^2(p^2-p'^2)} \frac{\bar{\omega}/\bar{\lambda}_{pp}}{\bar{\lambda}_{pp}(1+\bar{\omega}^2/\bar{\lambda}_{pp}^2)}. \tag{3.52b}$$

In (3.52a) and (3.52b) $a = 2$ for the ring (R) and $a = 1$ for the linear chain (L) and we have introduced new universal quantities $\bar{\lambda}_{pp} = 2\lambda_{pp}/\lambda_{pp}$ $(p = 1)$, $\bar{C}(\bar{\omega}) = C(\bar{\omega})\lambda_{pp}$ $(p = 1)$, $\bar{\omega} = \omega/\lambda_{pp}$ $(p = 1)$. Besides we have defined

$$E^{\mathrm{R}}(p) = \tfrac{1}{2} Q_{pp}^{\mathrm{R}(2)} \tag{3.53}$$

where $Q_{pp}^{\mathrm{R}(2)}$ is the $p = p'$ contribution of the double sum in (3.33),

$$Q_{pp}^{\mathrm{R}(2)} = \frac{1}{(\pi p)^4} (\tfrac{15}{4} A^{\mathrm{R}}(4p) - 15 A^{\mathrm{R}}(2p)) - \frac{3\pi}{(\pi p)^3} (B^{\mathrm{R}}(4p) - B^{\mathrm{R}}(2p))$$
$$- \frac{1}{(\pi p)^2} (C^{\mathrm{R}}(2p) - C^{\mathrm{R}}(4p)). \tag{3.54}$$

The double sum contribution $(p \neq p') Q_{pp'}^{\mathrm{R}(2)}$ is given in the appendix. For the linear chain (L) we have

$$E^{\mathrm{L}}(p) = 3 Q_{pp}^{\mathrm{L}(2)} \tag{3.55}$$

where

$$Q_{pp}^{\mathrm{L}(2)} = \frac{4}{3} \frac{(1-(-1)^p)}{(\pi p)^4} + \frac{1}{24} \frac{\pi}{(\pi p)^3} (50 B^{\mathrm{L}}(2p) - 35 B^{\mathrm{L}}(p) - 27 B^{\mathrm{L}}(3p)$$
$$+ 4 B^{\mathrm{L}}(4p) - 12 p A^{\mathrm{L}}(2p) + 12 p A^{\mathrm{L}}(p)) \tag{3.56}$$

and the double sum contribution $(p \neq p') Q_{pp'}^{\mathrm{L}(2)}$ is given in the appendix. This concludes our discussion of self-avoiding interactions.

4. Hydrodynamic interactions

Using the effective Lagrangian $J_1^{(2)}$ we obtain to $\mathrm{O}(g_0^2)$ the following contributions to $C(t)$:

$$C(t) = C_0(t) + 2C_1(t) + C_2(t) \tag{4.1}$$

where

$$C_0(t) = \int_0^{N_0} \mathrm{d}\tau \int_0^{N_0} \mathrm{d}\sigma \left\langle c_y(\tau, t) \frac{\partial^2}{\partial \tau^2} c_x(\tau, t) c_y(\sigma, 0) \frac{\partial^2}{\partial \sigma^2} c_x(\sigma, 0) \right\rangle_0 \tag{4.2}$$

$$C_1(t) = g_0^2 \int_0^{N_0} \mathrm{d}\tau \int_0^{N_0} \mathrm{d}\sigma \int_0^{N_0} \mathrm{d}\alpha \int_0^{N_0} \mathrm{d}\beta \int \mathrm{d}t' \int \mathrm{d}t''$$
$$\times \sum_\lambda \sum_\mu \left\langle \tilde{c}_\lambda(\alpha, t') u_\lambda^\perp(\boldsymbol{c}(\alpha, t'), t') \tilde{\mu}_\rho^\perp(\boldsymbol{c}(\beta, t''), t'') \frac{\partial^2}{\partial \beta^2} \right.$$
$$\left. \times c_\rho(\beta, t'') c_y(\tau, t) \frac{\partial^2}{\partial \tau^2} c_x(\tau, t) c_y(\sigma, 0) \frac{\partial^2}{\partial \sigma^2} c_x(\sigma, 0) \right\rangle_0 \tag{4.3}$$

$$C_2(t)=\tfrac{1}{2}g_0^2\int_0^{N_0}\mathrm{d}\tau\int_0^{N_0}\mathrm{d}\sigma\int_0^{N_0}\mathrm{d}\alpha\int_0^{N_0}\mathrm{d}\beta\int\mathrm{d}t'\int\mathrm{d}t''\sum_\lambda\sum_\mu\Big\langle\tilde{c}_\lambda(\alpha,t')u_\lambda^\perp(\boldsymbol{c}(\alpha,t'),t')$$
$$\times\tilde{c}_\rho(\beta,t'')u_\rho^\perp(\boldsymbol{c}(\beta,t''),t'')c_y(\tau,t)\frac{\partial^2}{\partial\tau^2}c_x(\tau,t)c_y(\sigma,0)\frac{\partial^2}{\partial\sigma^2}cx(\sigma,0)\Big\rangle_0. \tag{4.4}$$

Introducing a generating functional as in the case of self-avoiding interactions, we can express all averages in (4.2)-(4.4) again as products of free correlation functions. Then one can show [8] that $C_1(t)$ can be written as a sum

$$C_1(t)=C_{11}(t)+C_{12}(t)+C_{13}(t)+C_{14}(t) \tag{4.5}$$

and that $2C_{14}(t)$ will cancel the contribution $C_2(t)$. We then find (putting $g_0^2=\eta_0^{-1}=1$ as both couplings are not renormalised to $\mathrm{O}(\varepsilon)$) using the Markov approximation as mentioned in § 2:

$$C(t)=C_0(t)+2C_{11}(t)+2C_{12}(t)+2C_{13}(t) \tag{4.6}$$

where $C_0(t)$ is the free contribution already given in (3.5) and (3.6). The other contributions are given by

$$C_{11}^{\mathrm{R}}(t)=-8N_0^{-3}t\int_0^{N_0}\mathrm{d}\alpha\int_0^{N_0}\mathrm{d}\beta\int_k\frac{1}{k^2}(1-k_y^2/k^2)$$
$$\times\exp\{-\tfrac{1}{2}k^2[|\alpha-\beta|-(1/N_0)(\alpha-\beta)^2]\}$$
$$\times\sum_{p=1}^{\infty}(\pi p)^2\cos 2\hat{p}_0(\alpha-\beta)\exp(-2\lambda_p^{\mathrm{R}}t) \tag{4.7}$$

for the ring (R) and

$$C_{11}^{\mathrm{L}}(t)=-2N_0^{-3}t\int_0^{N_0}\mathrm{d}\alpha\int_0^{N_0}\mathrm{d}\beta\int_k\frac{1}{k^2}(1-k_y^2/k^2)\exp(-\tfrac{1}{2}k^2|\alpha-\beta|)$$
$$\times\sum_{p=1}^{\infty}(\pi p)^2\cos\hat{p}_0\alpha\cos\hat{p}_0\beta\exp(-2\lambda_p^{\mathrm{L}}t) \tag{4.8}$$

for the linear chain (L),

$$C_{12}^{\mathrm{R}}(t)=4N_0^{-2}\int_0^{N_0}\mathrm{d}\alpha\int_0^{N_0}\mathrm{d}\beta\int_k\frac{1}{k^2}k_x^2(1-k_y^2/k^2)$$
$$\times\exp\{-\tfrac{1}{2}k^2[|\alpha-\beta|-(1/N_0)(\alpha-\beta)^2]\}$$
$$\times\sum_{p=1}^{\infty}\sum_{p'=1}^{\infty}[\cos 2\hat{p}_0(\alpha-\beta)-1][1-\cos 2\hat{p}_0'(\alpha-\beta)]$$
$$\times\int_0^t\mathrm{d}s\exp(-2\lambda_p^{\mathrm{R}}s)\exp[-2\lambda_{p'}^{\mathrm{R}}(t-s)] \tag{4.9}$$

$$C_{12}^{\mathrm{L}}(t)=4N_0^{-2}\int_0^{N_0}\mathrm{d}\alpha\int_0^{N_0}\mathrm{d}\beta\int_k\frac{1}{k^2}k_x^2(1-k_y^2/k^2)\exp(-\tfrac{1}{2}k^2|\alpha-\beta|)$$
$$\times\sum_{p=1}^{\infty}\sum_{p'=1}^{\infty}\cos\hat{p}_0\beta(\cos\hat{p}_0\alpha-\cos\hat{p}_0\beta)\cos\hat{p}_0'\alpha(\cos\hat{p}_0'\alpha-\cos\hat{p}_0'\beta)$$
$$\times\int_0^t\mathrm{d}s\exp(-2\lambda_p^{\mathrm{L}}s)\exp[-2\lambda_{p'}^{\mathrm{L}}(t-s)] \tag{4.10}$$

and finally

$$C_{13}^{R}(t) = -4N_0^{-2} \int_0^{N_0} d\alpha \int_0^{N_0} d\beta \int_k \frac{k_x^2 k_y^2}{k^4} \exp\{-\tfrac{1}{2}k^2[|\alpha-\beta| - (1/N_0)(\alpha-\beta)^2]\}$$
$$\times \sum_{p=1}^{\infty} \sum_{p'=1}^{\infty} [\cos 2\hat{p}_0(\alpha-\beta) - 1][1-\cos 2\hat{p}_0'(\alpha-\beta)]$$
$$\times \int_0^t ds \exp(-2\lambda_p^R s) \exp[-2\lambda_{p'}^R (t-s)] \qquad (4.11)$$

$$C_{13}^{L}(t) = -4N_0^{-2} \int_0^{N_0} d\alpha \int_0^{N_0} d\beta \int_k \frac{k_x^2 k_y^2}{k^4} \exp(-\tfrac{1}{2}k^2|\alpha-\beta|)$$
$$\times \sum_{p=1}^{\infty} \sum_{p'=1}^{\infty} \cos \hat{p}_0\beta(\cos \hat{p}_0\alpha - \cos\hat{p}_0\beta) \cos \hat{p}_0'\alpha(\cos \hat{p}_0'\alpha - \cos \hat{p}_0'\beta)$$
$$\times \int_0^t ds \exp(-2\lambda_p^L s) \exp[-2\lambda_{p'}^L (t-s)]. \qquad (4.12)$$

Collecting terms, we find for the ring (R) in the presence of hydrodynamic interactions

$$C^{R}(t) = 2\sum_{p=1}^{\infty} \exp(-2\lambda_p^R t) - 16tN_0^{-3} \int_0^{N_0} d\alpha \int_0^{N_0} d\beta \int_k \frac{1}{k^2}(1-k_y^2/k^2)$$
$$\times \exp\{-\tfrac{1}{2}k^2[|\alpha-\beta| - (1/N_0)(\alpha-\beta)^2]\}$$
$$\times \sum_{p=1}^{\infty} (\pi p)^2 \cos 2\hat{p}_0(\alpha-\beta) \exp(-2\lambda_p^R t)$$
$$+ 8N_0^{-2} \int_0^{N_0} d\alpha \int_0^{N_0} d\beta \int_k \frac{k_x^2}{k^2}(1-2k_y^2/k^2)$$
$$\times \exp\{-\tfrac{1}{2}[|\alpha-\beta| - (1/N_0)(\alpha-\beta)^2]\}$$
$$\times \sum_{p=1}^{\infty} \sum_{p'=1}^{\infty} [\cos 2\hat{p}_0(\alpha-\beta) - 1][1-\cos 2\hat{p}_0'(\alpha-\beta)]$$
$$\times \int_0^t ds \exp(-2\lambda_p^R s) \exp[-2\lambda_p^R (t-s)] \qquad (4.13)$$

and for the linear chain (L)

$$C^{L}(t) = \sum_{p=1}^{\infty} \exp(-2\lambda_p^L t) - 4tN_0^{-3} \int_0^{N_0} d\alpha \int_0^{N_0} d\beta \int_k \frac{1}{k^2}(1-k_y^2/k^2) \exp(-\tfrac{1}{2}k^2|\alpha-\beta|)$$
$$\times \sum_{p=1}^{\infty} (\pi p)^2 \cos \hat{p}_0\alpha \cos \hat{p}_0\beta \exp(-2\lambda_p^L t)$$
$$+ 8N_0^{-2} \int_0^{N_0} d\alpha \int_0^{N_0} d\beta \int_k \frac{k_x^2}{k^2}(1-2k_y^2/k^2) \exp(-\tfrac{1}{2}k^2|\alpha-\beta|)$$
$$\times \sum_{p=1}^{\infty} \sum_{p'=1}^{\infty} \cos \hat{p}_0\beta(\cos \hat{p}_0\alpha - \cos \hat{p}_0\beta) \cos \hat{p}_0'\alpha(\cos \hat{p}_0'\alpha - \cos \hat{p}_0'\beta)$$
$$\times \int_0^t ds \exp(-2\lambda_p^L s) \exp[-2\lambda_{p'}^L (t-s)]. \qquad (4.14)$$

Now we consider the zero-frequency ($\omega = 0$) limit. We know from our previous study [8] that for the case of hydrodynamic interactions Green–Kubo formalism and Kirkwood–Riseman formalism give identical results to lowest order ($O(\varepsilon)$). Following the same steps which have been performed in the case of self-avoiding interactions in § 3, we obtain for the ring (R):

$$\int_0^\infty \mathrm{d}t\, C^{\mathrm{R}}(t) = \tfrac{1}{24}\zeta_0 N_0^2[1-\zeta_0(2\pi)^{-2}(2\pi N_0)^{\varepsilon/2}(3/2\varepsilon+\tfrac{5}{8})+\zeta_0(2\pi)^{-2}\tfrac{7}{4}]. \tag{4.15}$$

Performing renormalisation with

$$N = Z_N N_0 \tag{4.16a}$$

$$\zeta = Z_\zeta \zeta_0 \tag{4.16b}$$

$$\xi = \zeta L^{\varepsilon/2}. \tag{4.16c}$$

Where $Z_N = 1$ and $Z_\xi = 1 - 3\xi/8\pi^2\varepsilon$ to lowest order, we obtain at the fixed point $\xi^* = \frac{8}{3}\pi^2\varepsilon$ (non-draining Gaussian limit):

$$[\eta]^{\mathrm{R}} MkT/N_{\mathrm{A}} = \tfrac{1}{36}\varepsilon(2\pi N)^{d\nu}\exp(\tfrac{3}{4}\varepsilon) \tag{4.17}$$

where $d = 4-\varepsilon$ and $\nu = \frac{1}{2}$. For the linear chain (L) we obtain

$$[\eta]^{\mathrm{L}}\frac{MkT}{N_{\mathrm{A}}} = \tfrac{1}{18}\varepsilon(2\pi N)^{d\nu}\exp(\tfrac{7}{9}\varepsilon) \tag{4.18}$$

in agreement with [11].

Introducing as before effective eigenvalues for the relaxation times, we find at the fixed point $\xi^* = \frac{8}{3}\pi^2\varepsilon$:

$$\lambda_{pp}^{\mathrm{R}} = 2\lambda_p^{\mathrm{R}}\exp\left[\varepsilon\left(\frac{1}{18(\pi p)^2}(A^{\mathrm{R}}(4p)-4A^{\mathrm{R}}(2p))\right)\right] \tag{4.19}$$

with

$$\lambda_p^{\mathrm{R}} = \frac{3}{2\varepsilon}\frac{1}{(2\pi)^{2-\varepsilon/2}}\left(\frac{2\pi p}{N}\right)^{2-\varepsilon/2}\exp\{\varepsilon[\tfrac{1}{2}\mathrm{ci}(2\pi p)-\tfrac{1}{2}\hat{\gamma}+\tfrac{5}{12})]\} \tag{4.20}$$

for the ring (R), and

$$\lambda_{pp}^{\mathrm{L}} = 2\lambda_p^{\mathrm{L}}\exp\left\{\varepsilon\left[\frac{1}{9(\pi p)^2}\left(-4-6A^{\mathrm{L}}(p)+2A^{\mathrm{L}}(2p) + \frac{1}{2p}(11B^{\mathrm{L}}(p)-10B^{\mathrm{L}}(2p)+3B^{\mathrm{L}}(3p))\right)\right]\right\} \tag{4.21}$$

with

$$\lambda_p^{\mathrm{L}} = \frac{3}{2\varepsilon}\frac{1}{(2\pi)^{2-\varepsilon/2}}\left(\frac{\pi p}{N}\right)^{2-\varepsilon/2} \times\exp\left[\varepsilon\left(\tfrac{1}{2}\mathrm{ci}(\pi p)-\tfrac{1}{2}\hat{\gamma}+\tfrac{5}{12}-\frac{1}{2\pi p}(\mathrm{si}(\pi p)+\tfrac{1}{2}\pi)\right)\right] \tag{4.22}$$

for the linear chain (L). Then we can write the real and imaginary part of the complex intrinsic viscosity $\bar{\eta}(\bar{\omega}) = (N_{\mathrm{A}}/MkT)\bar{C}(\bar{\omega})$ in the general form:

$$\mathrm{Re}\,\bar{C}(\bar{\omega}) = a\sum_{p=1}^{\infty}\frac{1}{\bar{\lambda}_{pp}(1+\bar{\omega}^2/\bar{\lambda}_{pp}^2)} + \frac{\varepsilon}{9\pi^2}\sum_{p\neq p'=1}^{\infty}\frac{Q_{pp'}^{(1)}}{p^2-p'^2} \times\left(\frac{1}{\bar{\lambda}_{pp}(1+\bar{\omega}^2/\bar{\lambda}_{pp}^2)}-\frac{1}{\bar{\lambda}_{p'p'}(1+\bar{\omega}^2/\bar{\lambda}_{p'p'}^2)}\right) \tag{4.23a}$$

$$\operatorname{Im}\bar{C}(\bar{\omega})=a\sum_{p=1}^{\infty}\frac{\bar{\omega}/\bar{\lambda}_{pp}}{\bar{\lambda}_{pp}(1+\bar{\omega}^2/\bar{\lambda}_{pp}^2)}+\frac{\varepsilon}{9\pi^2}\sum_{p\neq p'=1}^{\infty}\frac{Q_{pp'}^{(1)}}{p^2-p'^2}\times\left(\frac{\bar{\omega}/\bar{\lambda}_{pp}}{\bar{\lambda}_{pp}(1+\bar{\omega}^2/\bar{\lambda}_{pp}^2)}-\frac{\bar{\omega}/\bar{\lambda}_{p'p'}}{\bar{\lambda}_{p'p'}(1+\bar{\omega}^2/\bar{\lambda}_{p'p'}^2)}\right) \tag{4.23b}$$

where $a=2$ for the ring (R) and $a=1$ for the linear chain (L) and $Q_{pp'}^{\mathrm{R}(1)}$ and $Q_{pp'}^{\mathrm{L}(1)}$ $(p\neq p')$ are given in the appendix. This concludes our discussion of the hydrodynamic interactions.

5. Self-avoiding and hydrodynamic interactions

To lowest order ($O(\varepsilon)$) there are no cross terms between self-avoiding and hydrodynamic interactions and therefore we can just add the results (3.33) and (4.13) for the ring (R) and (3.34) and (4.14) for the linear chain (L) (counting the free term only once). Considering the $\omega=0$ limit, we find for the ring (R)

$$\int_0^\infty \mathrm{d}t\, C^{\mathrm{R}}(t)=\tfrac{1}{24}\zeta_0 N_0^2\left\{1-\frac{u_0}{(2\pi)^2}\left[-\frac{2}{\varepsilon}-\ln\left(\frac{2\pi N_0}{L}\right)\right]-\frac{\xi_0}{(2\pi)^2}\left[\frac{3}{2\varepsilon}+\tfrac{3}{4}\ln\left(\frac{2\pi N_0}{L}\right)-\frac{9}{8}\right]\right\}. \tag{5.1}$$

Performing the renormalisation as before with

$$Z_\xi=1-\frac{2}{\varepsilon}\frac{u}{(2\pi)^2}-\frac{3}{8\pi^2\varepsilon}\xi \qquad Z_N=1+\frac{2}{\varepsilon}\frac{u}{(2\pi)^2}$$

to lowest order, we secure at the fixed point $u^*/(2\pi)^2=\frac{1}{8}\varepsilon$, $\xi^*/(2\pi)^2=\frac{1}{2}\varepsilon$ (non-draining self-avoiding limit) for the ring (R)

$$[\eta]^{\mathrm{R}}\frac{MkT}{N_{\mathrm{A}}}=\frac{1}{48}\varepsilon\left(\frac{2\pi N}{L}\right)^{d\nu}L^{d/2}\exp\left(\tfrac{9}{16}\varepsilon\right) \tag{5.2}$$

with $d=4-\varepsilon$ and $\nu=\frac{1}{2}+\frac{1}{16}\varepsilon$. For the linear chain (L), we secure [11]

$$[\eta]^{\mathrm{L}}\frac{MkT}{N_{\mathrm{A}}}=\tfrac{1}{24}\varepsilon\left(\frac{2\pi N}{L}\right)^{d\nu}L^{d/2}\exp\left(\tfrac{43}{96}\varepsilon\right). \tag{5.3}$$

For finite frequency ω we can write the real and imaginary parts of the complex intrinsic viscosity $\bar{\eta}(\bar{\omega})=(N_{\mathrm{A}}/MkT)\bar{C}(\bar{\omega})$ in the general form

$$\operatorname{Re}\bar{C}(\bar{\omega})=a\sum_{p=1}^{\infty}\frac{1}{\bar{\lambda}_{pp}(1+\bar{\omega}^2/\bar{\lambda}_{pp}^2)}\exp\left(\tfrac{1}{4}\varepsilon E(p)\right)+\frac{\varepsilon}{\pi^2}\sum_{p\neq p'=1}^{\infty}\left(\frac{Q_{pp'}^{(2)}}{p'^2(p'^2-p^2)}+\frac{Q_{pp'}^{(2)}}{p^2p'^2}+\frac{\tilde{Q}_{pp'}^{(1)}}{p'^2-p^2}\right)\frac{1}{\bar{\lambda}_{p'p'}(1+\bar{\omega}^2/\bar{\lambda}_{p'p'}^2)}+\frac{\varepsilon}{\pi^2}\sum_{p\neq p'=1}^{\infty}\left(\frac{Q_{pp'}^{(2)}}{p'^2(p^2-p'^2)}+\frac{\tilde{Q}_{pp'}^{(1)}}{p^2-p'^2}\right)\frac{1}{\bar{\lambda}_{pp}(1+\bar{\omega}^2/\bar{\lambda}_{pp}^2)} \tag{5.4a}$$

$$\operatorname{Im}C(\bar{\omega})=a\sum_{p=1}^{\infty}\frac{\bar{\omega}}{\bar{\lambda}_{pp}}\frac{1}{(1+\bar{\omega}^2/\bar{\lambda}_{pp}^2)}\exp\left(\tfrac{1}{4}\varepsilon E(p)\right)+\frac{\varepsilon}{\pi^2}\sum_{p\neq p'=1}^{\infty}\frac{\bar{\omega}}{\bar{\lambda}_{p'p'}}\frac{1}{\bar{\lambda}_{p'p'}(1+\bar{\omega}^2/\bar{\lambda}_{p'p'}^2)}\left(\frac{Q_{pp'}^{(2)}}{p'^2(p'^2-p^2)}+\frac{Q_{pp'}^{(2)}}{p^2p'^2}+\frac{\tilde{Q}_{pp'}^{(1)}}{(p'^2-p^2)}\right)+\frac{\varepsilon}{\pi^2}\sum_{p\neq p'=1}^{\infty}\frac{\bar{\omega}}{\bar{\lambda}_{pp}}\frac{1}{\bar{\lambda}_{pp}(1+\bar{\omega}^2/\bar{\lambda}_{pp}^2)}\left(\frac{Q_{pp'}^{(2)}}{p'^2(p^2-p'^2)}+\frac{\tilde{Q}_{pp'}^{(1)}}{(p^2-p'^2)}\right). \tag{5.4b}$$

As before, $a=2$ for the ring (R) and $a=1$ for the linear chain (L). We have here introduced the function $\tilde{Q}^{(1)}_{pp'}=\frac{1}{12}Q^{(1)}_{pp'}$, where both $Q^{(1)}_{pp'}$ and $Q^{(2)}_{pp'}$ have been defined already. We have defined (as in § 3) $\bar{\lambda}_{pp}=2\lambda_{pp}/\lambda_{pp}$ $(p=1)$ and $\bar{\omega}=\omega/\lambda_{pp}$ $(p=1)$. In the presence of both types of interactions we find for the relaxation spectrum for a ring (R):

$$\lambda^{R}_{pp}=2\lambda^{R}_{p}\exp\{\varepsilon[\tfrac{1}{8}Q^{R(2)}_{pp}+\tfrac{1}{24}Q^{R(1)}_{pp}/(\pi p)^2]\} \tag{5.5}$$

with

$$\lambda^{R}_{p}=\frac{1}{2\pi^2\varepsilon}\left(\frac{2\pi p}{N}\right)^{2-\varepsilon/4}\left(\frac{L}{2\pi}\right)^{-\varepsilon/4} \times\exp\left[\tfrac{1}{4}\varepsilon\left(\tfrac{1}{2}+\mathrm{ci}(2\pi p)-\hat{\gamma}+\frac{3}{4}\frac{1}{(\pi p)^2}A^{R}(2p)\right)\right]. \tag{5.6}$$

For the linear chain (L) we have

$$\lambda^{L}_{pp}=2\lambda^{L}_{p}\exp\{\varepsilon[\tfrac{3}{4}Q^{L(2)}_{pp}-\tfrac{1}{3}Q^{L(1)}_{pp}/(\pi p)^2]\} \tag{5.7}$$

with

$$\lambda^{L}_{p}=\frac{1}{2\pi^2\varepsilon}\left(\frac{\pi p}{N}\right)^{2-\varepsilon/4}\left(\frac{L}{2\pi}\right)^{-\varepsilon/4} \times\exp\left[\tfrac{1}{4}\varepsilon\left(\tfrac{1}{2}+\mathrm{ci}(\pi p)-\hat{\gamma}-\frac{1}{(\pi p)^2}(1-(-1)^p)-\frac{\mathrm{si}(2\pi p)}{\pi p}-\frac{1}{2p}\right)\right]. \tag{5.8}$$

$Q^{R(2)}_{pp}$, $Q^{L(2)}_{pp}$ have been given in (3.54) and (3.56), while $Q^{R(1)}_{pp}$, $Q^{L(1)}_{pp}$ are given in the appendix. In order to give an example for the universal quantities presented here, we have plotted $\bar{\lambda}^{L}_{pp}(p)$ (figure 1) and the real and imaginary parts of the normalised intrinsic viscosity (figure 2) for a linear chain (L).

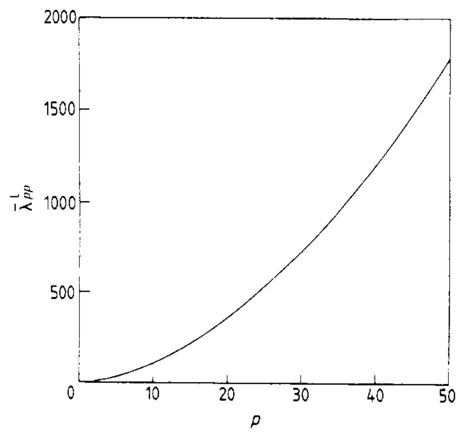

Figure 1. The normalised effective eigenvalue $\bar{\lambda}^{L}_{pp}$ for a linear chain (L) plotted as a function of p.

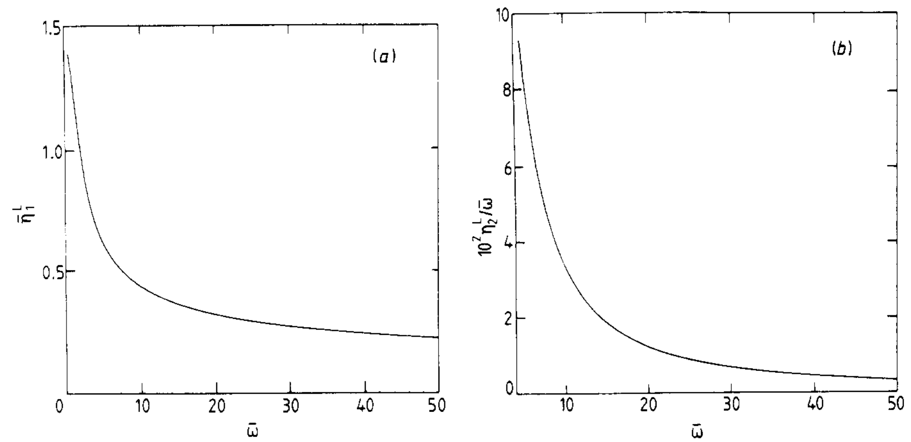

Figure 2. (a) The storage part (real part) of the normalised complex intrinsic viscosity $\bar{\eta}_1^{\mathrm{L}}(\bar{\omega})$ (see equation (5.4a)) expressed in universal quantities for a linear chain (L) in $d=3$ ($\varepsilon=1$) dimensions. (b) The loss part (imaginary part) of the normalised complex intrinsic viscosity $\bar{\eta}_2^{\mathrm{L}}(\bar{\omega})/\bar{\omega}$ (see equation (5.4b)) expressed in universal quantities for a linear chain (L) in $d=3$ ($\varepsilon=1$) dimensions.

6. Conclusions

We have presented the calculation of the intrinsic viscosity for simple ring polymers and linear chains in the presence of both self-avoiding and hydrodynamic interactions, starting from the Green–Kubo formula. The calculation was performed to lowest order in the couplings and we have derived the universal functional form of the intrinsic viscosity to $O(\varepsilon)$.

From our results given in §§ 3–5, we can derive universal amplitude ratios $[\eta]^{\mathrm{R}}/[\eta]^{\mathrm{L}}$ in the zero-frequency limit. In the absence of self-avoiding and hydrodynamic interactions we obtain, from equations (3.5) and (3.6) after performing the time integration, the ratio

$$[\eta]_0^{\mathrm{R}}/[\eta]_0^{\mathrm{L}}=\tfrac{1}{2}. \tag{6.1}$$

In the presence of self-avoiding interactions only, we find

$$[\eta]^{\mathrm{R}}/[\eta]^{\mathrm{L}}=\tfrac{1}{2}\exp(\tfrac{13}{96}\varepsilon)=0.573(d=3). \tag{6.2}$$

In the presence of hydrodynamic interactions only, we find

$$[\eta]^{\mathrm{R}}/[\eta]^{\mathrm{L}}=\tfrac{1}{2}\exp(-\tfrac{1}{36}\varepsilon)=0.486(d=3). \tag{6.3}$$

In the presence of both self-avoiding and hydrodynamic interactions, we find

$$[\eta]^{\mathrm{R}}/[\eta]^{\mathrm{L}}=\tfrac{1}{2}\exp(\tfrac{11}{96}\varepsilon)=0.561(d=3). \tag{6.4}$$

We should note that although the functional form of the intrinsic viscosity (as of any other physical quantity) can be determined from the RG equation, the exponentiation of the $O(\varepsilon)$ terms chosen here is only one possible choice. There is an inevitable ambiguity in postulating the correct interpolation formula from a perturbative calculation (e.g. the ε expansion).

Using methods other than RG one can write the zero-frequency limit of the intrinsic viscosity according to [20] as a product of the mean-square radius of gyration S^2 times a sum over eigenvalues λ. In these theories both S^2 and the eigenvalues λ depend on a parameter which describes the influence of self-avoiding interactions. Then it is certainly unexpected to find such a simple universal ratio as is obtained in equation (6.2). The fact that we find $[\eta]^R/[\eta]^L$ in the presence of self-avoiding interactions to be a universal number, independent of the (renormalised) chain length N, stems from the finding reported in [18] that, to lowest order in ε, linear chains and simple rings have the same critical exponents (i.e. the dependence on N is the same). Of course, it is not clear if this is also valid to higher orders in a RG calculation.

Besides its simplicity, we find our results, e.g. (6.2), also to agree with the ratio for the mean-square radius of gyration S^2 [21]

$$(S^2)^R/(S^2)^L = \tfrac{1}{2}\exp(\tfrac{13}{96}\varepsilon). \tag{6.5}$$

Whereas results from other than RG calculations [20] predict $[\eta]^R/[\eta]^L = 0.662$ in the absence of self-avoiding interactions, it seems that in [20] and [22] there are opposing conclusions about the influence of self-avoiding interactions on the ratio $[\eta]^R/[\eta]^L$. Physically, in agreement with equation (6.5), we expect that ring polymers exhibit properties having a greater sensitivity with respect to self-avoiding interactions than have linear chains. Comparing (6.4) to (6.3) we conclude that, at least to $O(\varepsilon)$, the presence of self-avoiding interactions increases the ratio of $[\eta]^R/[\eta]^L$. In order to compare with experimental results, we should point out again that our ratios to $O(\varepsilon)$ are independent of the chain length N and that the RG predictions are only valid in the asymptotic ($N\to\infty$) regime. Results reported in [22] give for the ratio $[\eta]^R/[\eta]^L$ measured for cyclic and linear PDM $(CH_3S_iO)x$ values between 0.58 and 0.67 depending on the type of solvent. The ratio $[\eta]^R/[\eta]^L = 0.58$ determined for cyclohexane (a good solvent) compares quite well with our result, equation (6.4). The ratio $[\eta]^R/[\eta]^L = 0.67$ in a 2-butanone (a θ-solvent), however, is much larger than our result (equation (6.3)). At present we do not see the possibility of making a more rigorous comparison with experiment. Judging from the experimentally investigated N dependence it seems that our asymptotic ($N\to\infty$) results are not applicable to most of the experiments performed so far. From the theoretical point of view there are two ways to improve the present situation.

One way is to perform our calculation in a restricted geometry where N can be finite. This is of considerable difficulty but certainly would allow a better comparison with available experimental data and possible numerical simulations. The second and easier achievable way is to perform a static calculation to see if, to $O(\varepsilon^2)$, the critical exponents for linear chains and simple rings are still the same, or if there is a different dependence on N. In the latter case a fixed result like (6.2) would not be valid to $O(\varepsilon^2)$. Instead we would then find a N-dependent ratio $[\eta]^R/[\eta]^L$ in the presence of self-avoiding interactions.

Finally, we would like to comment on the finite-frequency behaviour of the intrinsic viscosity. As the effective eigenmodes $\lambda_{pp}\sim p^{z\nu}$ asymptotically, we find that in the large-ω limit the sums over p which appear in real and imaginary parts of $\bar{C}(\bar{\omega})$ can be approximated by integrals

$$\int \mathrm{d}p\,\frac{1}{\bar{\lambda}_{pp}}\,\frac{1}{1+\bar{\omega}^2/\bar{\lambda}_{pp}^2}\sim\frac{\bar{\omega}^{1/z\nu}}{(\bar{\omega}^{1/z\nu})^{z\nu}}=\bar{\omega}^{1/z\nu-1} \tag{6.6}$$

and therefore $[\eta](\omega)\sim\omega^{1/z\nu-1}$. This gives for both ring and linear chain the predictions $[\eta](\omega)\sim\omega^{-0.531}$ in the presence of self-avoiding interactions only $[\eta](\omega)\sim\omega^{-0.375}$ in the presence of hydrodynamic interactions only and $[\eta](\omega)\sim\omega^{-0.438}$ in the presence of both interactions ($d=3$). In order to have a quantitative comparison with experimental data (for ω finite) one needs to have simultaneous measurements of $[\eta](\omega)$ and either λ_{pp} ($p=1$) or λ_p ($p=1$) (since we have a relation between λ_{pp} and λ_p).

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Appendix

In this appendix we give the double sum contributions to the complex intrinsic viscosity for the ring (R) and the linear chain (L) in the presence of self-avoiding interactions (2) and hydrodynamic interactions (1):

$$\begin{aligned}Q_{pp'}^{\mathrm{R}(2)} = \tfrac{1}{32}\{&(1/\pi^2)[30A^{\mathrm{R}}(2p+2p')+30A^{\mathrm{R}}(2p-2p')-60A^{\mathrm{R}}(2p')-60A^{\mathrm{R}}(2p)]\\&+2(p+p')^2C^{\mathrm{R}}(2p+2p')+2(p-p')^2C^{\mathrm{R}}(2p-2p')-4p^2C^{\mathrm{R}}(2p)\\&-4p'^2C^{\mathrm{R}}(2p')+24pB^{\mathrm{R}}(2p)+24p'B^{\mathrm{R}}(2p')\\&-12(p+p')B^{\mathrm{R}}(2p+2p')-12(p-p')B^{\mathrm{R}}(2p-2p')\}\end{aligned} \tag{A1}$$

$$\begin{aligned}Q_{pp'}^{\mathrm{L}(2)} = &-(1/2\pi^2)\{(-1)^p+(-1)^{p'}-(-1)^{p+p'}-1\}\\&-\tfrac{1}{8}[G_3(p,p')+G_3(p,-p')+G_4(p,p')+G_4(p',p)\\&-p^2A^{\mathrm{L}}(p)-p'^2A^{\mathrm{L}}(p')+\tfrac{1}{2}(p+p')^2A^{\mathrm{L}}(p+p')+\tfrac{1}{2}(p-p')^2A^{\mathrm{L}}(p-p')]\end{aligned} \tag{A2}$$

where

$$\begin{aligned}G_3(p,p') = &-\tfrac{3}{2}(p+p')B^{\mathrm{L}}(p+p')-\tfrac{1}{2}(p+p')B^{\mathrm{L}}(2p+2p')\\&-\frac{1}{2}\frac{(p+p')^2}{p'}B^{\mathrm{L}}(p+p')-\frac{1}{2}\frac{(p+p')^2}{p}B^{\mathrm{L}}(p+p')\\&+\frac{1}{4}\frac{(2p+p')^2}{p+p'}B^{\mathrm{L}}(2p+p')+\frac{1}{4}\frac{(p+2p')^2}{p+p'}B^{\mathrm{L}}(p+2p')\end{aligned} \tag{A3}$$

and

$$\begin{aligned}G_4(p,p') = &\,3pB^{\mathrm{L}}(p)-2pB^{\mathrm{L}}(2p)+\frac{1}{4}\frac{p^2}{p-p'}B^{\mathrm{L}}(p)+\frac{1}{4}\frac{p'^2}{p+p'}B^{\mathrm{L}}(p')\\&-\frac{p^2}{4p'}B^{\mathrm{L}}(p)+\frac{1}{4p'}(p+2p')^2B^{\mathrm{L}}(p+2p')+\frac{1}{2}\frac{p'^2}{p-p'}B^{\mathrm{L}}(2p')\\&+\frac{1}{4p}(2p-p')^2B^{\mathrm{L}}(2p-p')+\frac{p'^2}{4p}B^{\mathrm{L}}(p')-\frac{1}{2}\frac{p'^2}{p+p'}B^{\mathrm{L}}(2p').\end{aligned} \tag{A4}$$

The remaining double-sum contributions which appear in (4.23*a*) and (4.23*b*) are given by

$$Q_{pp'}^{R(1)} = A^R(2p-2p') + A^R(2p+2p') - 2A^R(2p) - 2A^R(2p') \tag{A5}$$

$$Q_{pp'}^{L(1)} = G_1(p,p') + G_2(p,p') + G_1(p,-p') + G_2(p',p) + 2 + 2A^L(p) + 2A^L(p') - A^L(p+p') - A^L(p-p') \tag{A6}$$

with

$$G_1(p,p') = \frac{1}{2(p+p')}\{2B^L(p+p') - B^L(2p+p') - B^L(p+2p') - B^L(p) - B^L(p') + B^L(2p) + B^L(2p')\} \tag{A7}$$

and

$$G_2(p,p') = \frac{1}{2p}\{2B^L(2p) - 4B^L(p) + 2B^L(p+p') + 2B^L(p-p') - B^L(2p+p') - B^L(2p-p')\}. \tag{A8}$$

Finally, the single sums defined in equations (5.5) and (5.7) are given by

$$Q_{pp}^{R(1)} = A^R(4p) - 4A^R(2p) \tag{A9}$$

$$Q_{pp}^{L(1)} = 1 + \tfrac{3}{2}A^L(p) - \tfrac{1}{2}A^L(2p) - (1/8p)[11B^L(p) - 10B^L(2p) + 3B^L(3p)]. \tag{A10}$$

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