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Intrinsic viscosity for a polymer chain with self-avoiding interactions

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The complex intrinsic viscosity for a single polymer chain in the presence of self-avoiding interactions is calculated renormalization-group theoretically directly from the Green-Kubo formula. The universal functional form to $O(\varepsilon)$ ($\varepsilon \equiv 4-d$, d being the spatial dimensionality) is presented.

The intrinsic viscosity, which is the most fundamental quantity of dilute polymer solutions, has so far been calculated within the Kirkwood-Riseman approximation.[1] This calculation[2] was performed in the presence of hydrodynamic and self-avoiding interactions to lowest order in the couplings, starting from the Kramers formula.[3]

Recently in Ref. 4 the limited reliability of the Kirkwood-Riseman scheme was studied by calculating the frequency-dependent intrinsic viscosity starting directly from the Green-Kubo formula.[5] By considering a Gaussian chain with hydrodynamic interactions only, it was found that in the zero-frequency limit the Green-Kubo formalism and the Kirkwood-Riseman formalism give identical results to the lowest nontrivial order (i.e., to order $\varepsilon = 4-d$, d being the spatial dimensionality) even without using the hydrodynamic preaveraging approximation. However, in the presence of self-avoiding interactions, the two formalisms are expected to give different results to $O(\varepsilon)$, for the following reason: The self-avoiding interaction modifies not only the equilibrium state, but also the dynamics of the chain-solvent system. Whereas the equilibrium state and the solvent velocity-field motion can also be treated within the Kirkwood-Riseman formalism, the modification of the chain motion due to the direct monomer-monomer interaction cannot be thus taken into account.

In the present report we calculate the intrinsic viscosity at arbitrary frequencies for a single self-avoiding chain in the vacuum, i.e., without hydrodynamic interaction, starting from the Green-Kubo formula, and thus incorporate the influence of the monomer-monomer interaction on the chain motion. We start from the following Langevin equation for the conformation $[\underset{\sim}{c}(\tau,t)]_{\tau=0}^{N_0}$ where τ is the contour variable, t the time, and N_0 the total (bare) length:

$$\frac{\partial \underset{\sim}{c}}{\partial t} = \frac{1}{\zeta_0} \frac{\delta H_E}{\delta \underset{\sim}{c}(\tau,t)} + \underset{\sim}{\theta}(\tau,t) \ . \tag{1}$$

Here H_E is the Edwards Hamiltonian:[6]

$$H_E = \tfrac{1}{2} \int_0^{N_0} d\tau \left[\frac{\partial \underset{\sim}{c}}{\partial \tau} \right]^2 + \tfrac{1}{2} v_0 \int_0^{N_0} d\tau \int_0^{N_0} d\sigma\, \delta[\underset{\sim}{c}(\tau,t) - \underset{\sim}{c}(\sigma,t)] \ , \tag{2}$$

while $\underset{\sim}{\theta}(\tau,t)$ is a Gaussian white noise with the average zero, satisfying

$$\langle \underset{\sim}{\theta}(\tau,t) \underset{\sim}{\theta}(\sigma,s) \rangle = 2\zeta_0^{-1} \delta(\tau-\sigma) \delta(t-s) I \ . \tag{3}$$

v_0 is the bare excluded-volume parameter, ζ_0 is the bare translational friction constant per chain unit, and I is the $d \times d$ unit matrix. It is implicitly understood that (2) contains an appropriate cutoff to eliminate unphysical self-interaction.

Explicitly (1) is

$$\frac{\partial \underset{\sim}{c}(\tau,t)}{\partial t} = \frac{1}{\zeta_0} \frac{\partial^2 \underset{\sim}{c}(\tau,t)}{\partial \tau^2} - \frac{v_0}{\zeta_0} \nabla \rho(\underset{\sim}{r},t) \,|_{\underset{\sim}{r}=\underset{\sim}{c}(\tau,t)} + \underset{\sim}{\theta} \tag{4}$$

with the monomer density field $\rho(\underset{\sim}{r}) = \int_0^{N_0} d\tau\, \delta[\underset{\sim}{r} - \underset{\sim}{c}(\tau)]$. Introducing the following Green's function with free-end condition:

$$G(\tau,\sigma \,|\, t) = \frac{1}{N_0} \left[1 + 2 \sum_{p=1}^{\infty} \cos(\hat{p}_0 \tau) \cos(\hat{p}_0 \sigma) e^{-\hat{p}_0^2 t/\zeta_0} \right] , \tag{5}$$

where $\hat{p}_0 = \pi p / N_0$, (4) can be formally solved as

$$\underset{\sim}{c}(\tau,t) = \underset{\sim}{c}_0(\tau,t) - \frac{v_0}{\zeta_0} \int_0^{N_0} d\sigma \int_0^t ds\, G(\tau,\sigma \,|\, t-s) \nabla \rho(\underset{\sim}{r},s) \,|_{\underset{\sim}{r}=\underset{\sim}{c}(\sigma,s)} \tag{6}$$

with

$$\underset{\sim}{c}_0(\tau,t) = \int_0^{N_0} d\sigma\, G(\tau,\sigma \,|\, t) \underset{\sim}{c}(\sigma,0) + \int_0^{N_0} d\sigma \int_0^t ds\, G(\tau,\sigma \,|\, t-s) \underset{\sim}{\theta}(\sigma,s) \ . \tag{7}$$

We assume that the initial ensemble is in equilibrium, and $\underset{\sim}{c}(0,0)=0$.

The Green-Kubo formula for the intrinsic viscosity reads[7]

$$[\eta] = \frac{N_A}{M k_B T \eta_0} \int_0^{\infty} \langle J_p(t) J_p(0) \rangle dt \ , \tag{8}$$

where $J_p(t)$ is the xy component of the momentum flux tensor for the polymer chain, N_A is the Avogadro constant, M is the molecular weight of the chain, and η_0 is the solvent viscosity. As pointed out in Ref. 4, (8) is reliable only to the lowest nontrivial order $[O(\varepsilon)]$ of the renormalized perturbation theory. Thus we have to calculate the correlation function

$$C(t)=\langle J_p(t)J_p(0)\rangle \tag{9}$$

to $O(\varepsilon)$ where $\langle\ \rangle$ is the average over the initial equilibrium ensemble and over the Gaussian noise. J_p can be written as

$$J_p(t)=-\int_0^{N_0} d\tau\, c_y(\tau,t)\frac{\delta H_E}{\delta c_x(\tau,t)}\ . \tag{10}$$

Using (1) and (2) in (9) and solving iteratively, we can discard terms of higher order than v_0, and in terms of order v_0 we can replace $\underset{\sim}{c}$ with $\underset{\sim}{c}_0$, given by (7). In order to obtain a result which is valid in the large-t limit we cannot naively exponentiate the results obtained to $O(\varepsilon)$. Rather we have to use the idea of singular perturbation theory[8] and exploit the asymptotic behavior of the relaxation times as dictated by the renormalization-group equation.[9] For the case of hydrodynamic interactions this procedure was explained in detail in Ref. 4. To $O(\varepsilon)$ we find the relaxation spectrum

$$\lambda_{pp}=2\lambda_p\exp\left[\frac{\varepsilon}{8}\left[8\frac{[1-(-1)^p]}{(\pi p)^4}+\frac{1}{4}\frac{\pi}{(\pi p)^3}[50B(2p)-35B(p)-27B(3p)+4B(4p)-12pA(2p)+12pA(p)]\right]\right]\ , \tag{11}$$

where

$$\lambda_p=\frac{1}{\zeta}\left[\frac{\pi p}{N}\right]^2\left[\frac{L_P}{2N}\right]^{\varepsilon/8}\exp\left[\frac{\varepsilon}{8}\left[\hat{\gamma}-\mathrm{ci}(\pi p)-\frac{3}{2}-\frac{2}{(\pi p)^2}[1-(-1)^p]+\frac{3\mathrm{si}(\pi p)}{\pi p}-\frac{2\mathrm{si}(2\pi p)}{\pi p}+\frac{1}{2p}\right]\right]\ . \tag{12}$$

Here $\hat{\gamma}$ is Euler's constant, $\mathrm{ci}(x)=-\int_x^\infty dt\,\cos t_t$ and $\mathrm{si}(x)=-\int_x^\infty dt\,\sin t/t$. In (11) we have used the functions $A(p)$ and $B(p)$ which are defined by

$$A(p)=(-1)^{p+1}-\mathrm{ci}(\,|\pi p|\,)+\ln(\,|\pi p|\,)-\pi p\left[\mathrm{si}(\pi p)+\frac{\pi}{2}\right]\ , \tag{13}$$

$$B(p)=p[\mathrm{ci}(\,|\pi p|\,)-\ln(\,|\pi p|\,)]\ . \tag{14}$$

Besides we have introduced in (12) the renormalized quantities N and ζ. L is some phenomenological length scale. λ_p was derived in Ref. 10 for the calculation of the time-dependent correlation function $\langle\underset{\sim}{c}(\tau,t)\cdot\underset{\sim}{c}(\tau,t)\rangle$ in the presence of self-avoiding interactions. λ_{pp} is the reciprocal of the relaxation time of the doubly excited p mode. $\lambda_{pp}/2\lambda_p$ describes the interference effect of two p modes in the presence of self-avoiding interactions. We should point out that $\lambda_p \sim p^{2+\varepsilon/8}$ asymptotically, as required by the renormalization group.[9] (Note that $p^{2+\varepsilon/8}=p^{2v+1}=p^{vz}$, z being the dynamical exponent, $z=2+1/v$, and $v=\frac{1}{2}+\varepsilon/16$ the Flory exponent to lowest order.) Finally, using (11), (12), and performing a Fourier transformation, we obtain the real and imaginary part of the complex intrinsic viscosity $[\overline{\eta}(\overline{\omega})]=(N_A/M\eta_0k_BT)\overline{C}(\overline{\omega})$ at the free-draining self-avoiding fixed point:

$$\mathrm{Re}\overline{C}(\overline{\omega})=\sum_{p=1}^{\infty}\frac{1}{\overline{\lambda}_{pp}}\frac{1}{1+\overline{\omega}^2/\overline{\lambda}_{pp}^2}\exp\left[\frac{\varepsilon}{4}E(p)\right]+\frac{\varepsilon}{4\pi^2}\sum_{p\neq p'=1}^{\infty}\frac{1}{\overline{\lambda}_{p'p'}}\frac{[Q_1(p,p')+Q_2(p,p')]}{1+\overline{\omega}^2/\overline{\lambda}_{p'p'}^2}$$
$$+\frac{\varepsilon}{4\pi^2}\sum_{p\neq p'=1}^{\infty}\frac{1}{\overline{\lambda}_{pp}}Q_3(p,p')\frac{1}{1+\overline{\omega}^2/\overline{\lambda}_{pp}^2}\ , \tag{15}$$

$$\mathrm{Im}\overline{C}(\overline{\omega})=\sum_{p=1}^{\infty}\frac{1}{\overline{\lambda}_{pp}}\frac{\overline{\omega}/\overline{\lambda}_{pp}}{1+\overline{\omega}^2/\overline{\lambda}_{pp}^2}\exp\left[\frac{\varepsilon}{4}E(p)\right]+\frac{\varepsilon}{4\pi^2}\sum_{p\neq p'=1}^{\infty}\frac{1}{\overline{\lambda}_{p'p'}}\frac{[Q_1(p,p')+Q_2(p,p')]}{1+\overline{\omega}^2/\overline{\lambda}_{p'p'}^2}\frac{\overline{\omega}}{\overline{\lambda}_{p'p'}}$$
$$+\frac{\varepsilon}{4\pi^2}\sum_{p\neq p'=1}^{\infty}\frac{1}{\overline{\lambda}_{pp}}Q_3(p,p')\frac{\overline{\omega}/\overline{\lambda}_{pp}}{1+\overline{\omega}^2/\overline{\lambda}_{pp}^2}\ . \tag{16}$$

The functions $E(p),Q_i(p,p')$ are given in the Appendix. $\overline{\lambda}_{pp}=2\lambda_{pp}/\lambda_{pp}(p=1)$ and $\overline{C}(\overline{\omega})=C(\overline{\omega})\lambda_{pp}(p=1)$ are universal quantities, with $\overline{\omega}=\omega/\lambda_{pp}$ $(p=1)$ a new frequency unit. Equations (15) and (16) are illustrated in Figs. 1 and 2 for $\varepsilon=1$ $(d=3)$. Note that these curves are universal curves.

In the zero-frequency limit we obtain

$$[\eta]\frac{M\eta_0k_BT}{N_A}=\frac{1}{12}\frac{\zeta}{(2\pi)^2}L^{d/2}\left[\frac{2\pi N}{L}\right]^{vz}\exp\left[\frac{\varepsilon}{8}\sum_{p=1}^{\infty}\overline{I}(p)\right]\exp\left[-\frac{\varepsilon}{8}\sum_{p\neq p'=1}^{\infty}\overline{Q}(p,p')\right]\ , \tag{17}$$

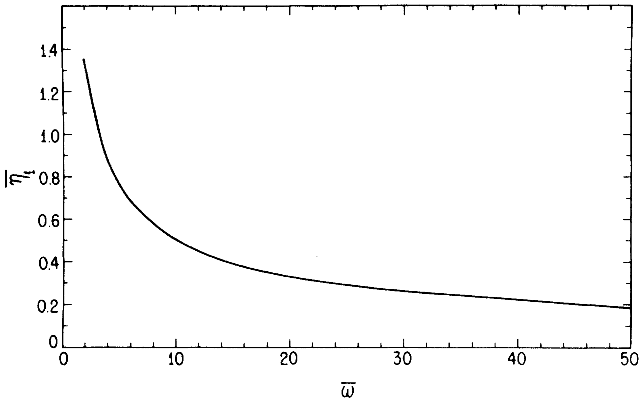

FIG. 1. The storage part of the normalized complex intrinsic viscosity $\overline{\eta}_1$ expressed in universal quantities. $\overline{\eta}_1(\overline{\omega})$ is calculated as $[\overline{\eta}_1(\overline{\omega})]=[N_A/M\eta_0\lambda_{pp}(p=1)k_BT]\mathrm{Re}\overline{C}(\overline{\omega})$, with $\overline{\omega}=\omega/\lambda_{pp}$ $(p=1)$, and $\mathrm{Re}\overline{C}(\overline{\omega})$ given in Eq. (15) to $O(\varepsilon)$.

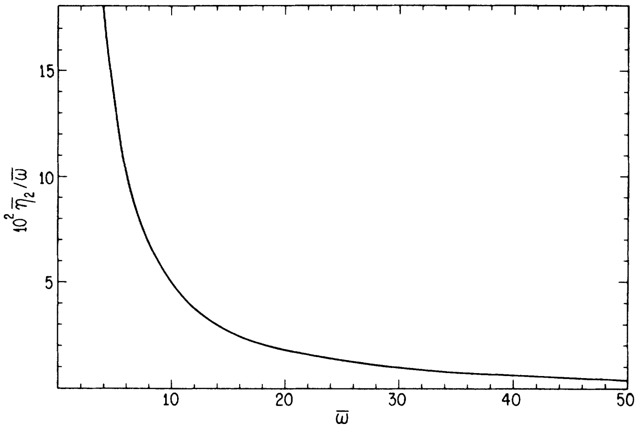

FIG. 2. The loss part of the renormalized complex intrinsic viscosity $\overline{\eta}_2$ expressed in universal quantities. $\overline{\eta}_2(\overline{\omega})$ is calculated as $[\overline{\eta}_2(\overline{\omega})]=[N_A/M\eta_0\lambda_{pp}(p=1)k_BT]\mathrm{Im}\overline{C}(\overline{\omega})$, with $\mathrm{Im}\overline{C}(\overline{\omega})$ given in Eq. (16) to $O(\varepsilon)$.

where $\overline{I}(p)$ and $\overline{Q}(p,p')$ are given in the Appendix, and $\zeta=\zeta/\eta_0L^{-\varepsilon/2}$. Performing the sums we obtain

$$[\eta]\frac{M\eta_0k_BT}{N_A}=\frac{1}{12}\frac{\zeta}{(2\pi)^2}L^{d/2}\left[\frac{2\pi N}{L}\right]^{vz}\exp(-0.586\varepsilon)\ , \tag{18}$$

which should be compared with the results obtained in Ref. 2 within the Kirkwood-Riseman formalism:

$$[\eta]\frac{M\eta_0k_BT}{N_A}=\frac{1}{12}\frac{\zeta}{(2\pi)^2}L^{d/2}\left[\frac{2\pi N}{L}\right]^{vz}\exp(-\tfrac{13}{96}\varepsilon)\ . \tag{19}$$

Summarizing, we have calculated the complex intrinsic viscosity for a polymer chain with self-avoiding interaction to $O(\varepsilon)$, starting from the Green-Kubo formula. In the $\omega\to 0$ limit, performing the sums numerically, we find a result which differs from that obtained in Ref. 2, using the Kirkwood-Riseman scheme. It remains to exhibit the analytical form of the correction.

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APPENDIX

The functions $E(p),Q_1(p,p')$ in Eqs. (15) and (16) are

$$E(p)=\frac{3}{2p}+8\frac{[1-(-1)^p]}{(\pi p)^4}+\frac{1}{4}\frac{\pi}{(\pi p)^3}[50B(2p)-35B(p)-27B(3p)+4B(4p)-12pA(2p)+12pA(p)]\ , \tag{A1}$$

$$Q_1(p,p')=\frac{Q(p,p')}{p^2p'^2}\ , \tag{A2}$$

$$Q_2(p,p')=\frac{Q(p,p')}{2p'^2(p'^2-p^2)}\ , \tag{A3}$$

$$Q_3(p,p')=-Q_2(p,p')\ , \tag{A4}$$

where

$$Q(p,p')=-\frac{4}{\pi^2}[(-1)^p+(-1)^{p'}-(-1)^{p+p'}-1]-G_1(p,p')-G_1(p,-p')-G_2(p,p')-G_2(p',p)+p^2A(p)+p'^2A(p')-\tfrac{1}{2}(p+p')^2A(p+p')-\tfrac{1}{2}(p-p')^2A(p-p')\ , \tag{A5}$$

with

$$G_1(p,p')=-\tfrac{3}{2}(p+p')B(p+p')-\tfrac{1}{2}(p+p')B(2p+2p')-\frac{1}{2}\frac{(p+p')^2}{p'}B(p+p')-\frac{1}{2}\frac{(p+p')^2}{p}B(p+p')+\frac{1}{4}\frac{(2p+p')^2}{p+p'}B(2p+p')+\frac{1}{4}\frac{(p+2p')^2}{p+p'}B(p+2p') \tag{A6}$$

and

$$G_2(p,p')=3pB(p)-2pB(2p)+\frac{1}{4}\frac{p^2}{p-p'}B(p)+\frac{1}{4}\frac{p'^2}{p+p'}B(p')-\frac{p^2}{4p'}B(p)+\frac{1}{4p'}(p+2p')^2B(p+2p')$$
$$+\frac{1}{2}\frac{p'^2}{p-p'}B(2p')+\frac{1}{4p}(2p-p')^2B(2p-p')+\frac{p'^2}{4p}B(p')-\frac{1}{2}\frac{p'^2}{p+p'}B(2p')\ . \tag{A7}$$

The functions $\overline{I}(p),\overline{Q}(p,p')$ in Eq. (18) are given by

$$\overline{I}(p)=\frac{6}{(\pi p)^2}I(p)\ , \tag{A8}$$

$$I(p)=\frac{5}{2p}+\operatorname{ci}(\pi p)-\hat{\gamma}-\ln(\pi p)+\frac{3}{2}+\frac{2}{(\pi p)^2}[1-(-1)^p]-\frac{3\operatorname{si}(\pi p)}{\pi p}+\frac{2\operatorname{si}(2\pi p)}{\pi p}+8\frac{[1-(-1)^p]}{(\pi p)^4}$$
$$+\frac{1}{4}\frac{\pi}{(\pi p)^3}[50B(2p)-35B(p)-27B(3p)+4B(4p)-12pA(2p)+12pA(p)]\ , \tag{A9}$$

$$\overline{Q}(p,p')=\frac{6}{\pi^4}\frac{Q(p,p')}{p'^4p^2}\ . \tag{A10}$$

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