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Response to "Draining in Dilute Polymer Solutions and Renormalization", *Macromolecules* 1995, *28*, 4039

Karl F. Freed*

James Franck Institute and Department of Chemistry, University of Chicago, Chicago, Illinois 60637

Jack F. Douglas

Polymers Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899

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Our recent papers discuss how the competition between hydrodynamic and excluded volume interactions influences the hydrodynamic properties of polymers in dilute solution. These works provide a summary of our renormalization group (RG) computations for dilute polymer solution hydrodynamic properties.[1,2] References 1 and 2 note some deficiencies of the alternative RG calculations by Shiwa and Oono,[3] whose work is based on similar computational methods and addresses similar polymer properties. Shiwa[4] has claimed in a recent letter that two of our criticisms are erroneous. We are entirely unconvinced by his rebuttal, and we take this opportunity to respond to his criticisms and to reiterate our previous claims.

Two matters are under dispute by Shiwa.[4] The first problem relates to the fundamental issue associated with the treatment of hydrodynamic interactions within a polymer chain, while the second point involves a technical issue regarding the mathematically consistent method of performing ϵ-expansion calculations based on RG theory.

It is useful to begin our response by providing some background concerning the disagreements between Shiwa and ourselves. Shiwa and Oono[3] motivate the introduction of an additional parameter λ_0 by claiming that the free-draining hydrodynamic limit is not physically meaningful. This conclusion apparently derives from an earlier finding by Oono and Kohmoto[5] that Gaussian chains have no dependence on hydrodynamic interactions, i.e., that Gaussian chains are *always* in the nondraining limit. To extricate themselves from this mathematical difficulty, which represents a gross departure from all prior treatments, they effectively introduce a different bead friction coefficient in the Oseen tensor than in the term which gives rise to the free-draining contribution to the polymer friction. This formal mathematical maneuver is further motivated by the reasonable physical idea that the local viscosity η_e in the vicinity of the chain differs from that η_s in the bulk medium.

A subsequent work by[6] us notes that the absence of a free-draining limit in the Oono−Kohmoto calculation arises because they did not notice the presence of an improper limit in their setting of the excluded volume interaction to zero. When this Gaussian chain limit is taken properly using l'Hopital's rule, the result demonstrates that the dynamics of Gaussian chains do indeed depend on the strength of the hydrodynamic interactions in exactly the manner previously obtained by Kirkwood.[7] In addition, by developing the theory from the outset for the Gaussian chain limit, we further demonstrate that the (crossover) dependence of polymer friction on hydrodynamic interactions takes the identical mathematical form as the crossover dependence of equilibrium properties on the strength of the excluded volume interactions.[8] Thus, in contrast to the claims of Oono and Kohmoto, the free-draining limit does not require the vanishing of the monomer friction coefficient, but only that the monomer friction ζ_0 is weak. A weak hydrodynamic interaction in polymers could, in principle, arise when the polymer beads are widely separated, a situation implying that the sum of the monomer friction coefficients provides a good approximation to the friction of the chain as a whole, as discussed by Traytak[9] in the closely related problem of diffusion-limited reaction rates of bead arrays. The translational friction coefficient f of a polymer chain with widely separated beads has the asymptotic "free-draining" scaling with polymerization index N,

$$f \sim N\zeta_0 + O(h) \tag{1}$$

where the dimensionless hydrodynamic interaction parameter h is small. Reference 1 provides a Ginzburg-type criterion to precisely define the width of this weak hydrodynamic coupling regime in terms of chain parameters. Shiwa and Oono,[3] on the other hand, maintain the absence of a dependence of Gaussian chains on hydrodynamic interactions and instead invoke a model with the additional coupling parameter λ_0 whose physical relevance is one point of the present dispute.

Shiwa indicates that while the analysis of ref 1 is correct for the "mode-coupling" parameter λ_M in the kinetic equations we present [see eq 2 of ref 3 or eqs A.1 and A.2 of ref 1 with $\lambda_M \rightarrow \lambda_0$], these conclusions do not apply to the λ-parameter λ_0 used by Shiwa and Oono in ref 3. The λ_0-parameter is defined by Shiwa and Oono[3] as

$$\lambda_0^{\,2} = \eta_s/\eta_e \tag{2}$$

where η_e is an "effective local viscosity" in the vicinity of the polymer chain and η_s is the pure solvent viscosity. Earlier drafts of the authors' manuscript identify λ_0 as the "mode-coupling" parameter λ_M in eq 1 of ref 3 or the λ_0 of eqs A.1 and A.2 of ref 1. We did not recognize their changed definition because all the final results are entirely unchanged. However, the same criticisms presented in ref 1 for the λ_M parameter apply to the Shiwa−Oono[3] λ_0-parameter in eq 2 above, but with a slightly different proof as follows.

The parameter λ_0 in eq 2 arises in the Shiwa−Oono theory by treating the viscosity factor in the Oseen tensor as a free parameter, since it is presumed that the polymer alters the local fluid viscosity in the vicinity of the polymer chain. Importantly, the bead friction at the leading order free-draining theory is assumed to be uninfluenced by this local viscosity renormalization. Apart from the completely *ad hoc* nature of this model, this mathematical construction leads to no new physics in basically the same fashion described in Appendix A of ref 1 for the λ_M-parameter as we now demonstrate. Continuing the Shiwa−Oono procedure[3] to all orders in the hydrodynamic interactions would lead to a power series representation of the intrinsic viscosity $[\eta]$ of the form

$$[\eta] = (\zeta_0/\eta_s) \sum_{k=0}^{\infty} c_k(N)(\zeta_0/\eta_e)^k \tag{3}$$

where ζ_0 is the bead friction coefficient corresponding to the solvent having viscosity η_0 and $c_k(N)$ are constants

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depending on the polymerization ratio. Reference 3 defines one bare coupling constant in terms of $\xi_0 \propto \lambda_0^2\zeta_0/\eta_s$ and the other in terms of $\lambda_0^2 = \eta_e/\eta_s$ to give them two allegedly independent coupling constants. However, if the product of $\lambda_0^2 = \eta_e/\eta_s$ and ζ_0/η_s are absorbed together into the definition, the coupling constant becomes $\xi_0 \propto \lambda_0^2\zeta_0/\eta_s = \zeta_0/\eta_e$. This equally valid representation of the coupling constant transforms eq 3 into

$$[\eta] = \lambda_0^{-2}\xi_0 \sum_{k=0}^{\infty} c_k(N)(\xi_0)^k \tag{4}$$

thereby producing an overall rescaling of $[\eta]$ by a factor of λ_0^{-2} as presented in Appendix A of ref 1 with what Shiwa[4] calls the λ_M-parameter, but which is written in ref 1 as λ_0. The fixed-point value of the coupling constant ξ_0 is found from the RG method as a power series in ϵ, so the Shiwa–Oono procedure merely results in a rescaling of $[\eta]$ by the factor λ_0^{-2}. No new physics is produced!

The second matter of disagreement regards the correct method of truncating the perturbative ϵ-expansion in RG theory. Shiwa[4] argues that the dimensionless hydrodynamic and excluded volume coupling parameters and the expansion parameter ϵ must all be taken as independent expansion parameters. However, RG theory dictates that these expansion parameters be truncated at a *consistent* order by formally treating the two coupling parameters as of order ϵ. More explicitly, the fixed-point value of the final computed intrinsic viscosity in the Shiwa–Oono formalism would be of the form

$$[\eta] = D[a\epsilon + b\epsilon^2] \tag{5}$$

where D is a collection of dimensional quantities and a and b are pure numbers. The coefficient a would remain unchanged in higher order calculations, but the coefficient b would be changed in the next order. This procedure deviates from the customary practice in which lower order coefficients in the ϵ-expansion are unchanged in higher orders. Thus, we have termed such calculations as being of "one and one half order". Our calculations proceed with an allowable different definition of the coupling parameters, a choice that is introduced to minimize the errors incurred by the ϵ-expansion in reproducing well-known exactly solvable hydrodynamic models. Apart from an overal factor with dimensional quantities like D in eq 4, the final expressions for dimensionless properties at the fixed point may be expressed entirely in terms of ϵ *alone*, and these ϵ-expansions are *invariant* to the arbitrary definition of the coupling constants. The determination of the coupling constants is not an independent step from the ϵ-expansion calculation.

References 1 and 2 discuss practical difficulties[10] emerging as consequences of the dubious ϵ-expansion procedure of Shiwa and Oono, whose calculational methods are inconsistent with previous RG calculations by ourselves[1,2] and others.[11] The Shiwa–Oono methods are shown to produce unreasonable estimates for the magnitude of preaveraging errors for polymer frictional properties, and their reexponentiation procedure yields large errors when applied to exactly solvable models.[1,11] To summarize, we are entirely unconvinced by Shiwa's rebuttal of our previous criticisms. A new proof is given that their λ_0-parameter may be removed to *all orders* by a simple rescaling operation. The introduction of this parameter is without theoretical justification apart from the trivial exercise of maintaining proper dimensions. Finally, we still believe that their ϵ-expansion calculations are mathematically inconsistent. Thus, the basic conclusions produced on the basis of their calculations are suspect.

References and Notes

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(7) See eqs 2.1 to 2.7 of ref 1 for the comparison showing that our first-order RG calculation differs from the exact preaveraged Kirkwood–Riseman theory by a slight difference in the overall prefactor.
(8) Oono, Y.; Freed, K. F. *J. Phys. A.* **1982**, *15*, 1931.
(9) Traytak, S. O. *Chem. Phys.* **1995**, *193*, 351.
(10) For example, see the paragraph containing eq 2.9 in ref 1.
(11) See Appendix D of ref 2.

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