Draining in Dilute Polymer Solutions and Renormalization

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In a recent paper,[1] Douglas and Freed question the validity of our model[3] of the draining effect in dilute polymer solutions and criticize the renormalization-group calculation scheme[4] employed. It is shown below that both these affirmations are erroneous.

Douglas and Freed's first argument is that no new physics emerges from the introduction of the "mode-coupling" parameter λ_0 (see below) as introduced in ref 3, since the parameter λ_0 is a removable scale factor.

They provided the "proof" of the above statement by a set of scale transformations of the kinetic equations:

$$\frac{\partial \mathbf{c}(\tau,t)}{\partial t} = -\zeta_0^{-1}\frac{\delta \mathbf{H}\{\mathbf{c}\}}{\delta \mathbf{c}(\tau,t)} + \lambda_{\mathrm{M}}\int \mathbf{dr}\, \mathbf{u}(\mathbf{r},t)\, \delta(\mathbf{r}-\mathbf{c}(\tau,t)) + \mathbf{f}_{\mathrm{c}}(\tau,t)$$

$$\frac{\partial \mathbf{u}(\mathbf{r},t)}{\partial t} = \mathcal{T}\left[\eta_{\mathrm{e}}\nabla^2\mathbf{u}(\mathbf{r},t) - \lambda_{\mathrm{M}}\int \mathrm{d}\tau\, \frac{\delta \mathbf{H}\{\mathbf{c}\}}{\delta \mathbf{c}(\tau,t)}\, \delta(\mathbf{r}-\mathbf{c}(\tau,t)) + \mathbf{f}_u(\mathbf{r},t)\right] \tag{1}$$

Here $\mathbf{c}(\tau,t)$ is the position vector of the monomer segment at the contour position τ ($0 \le \tau \le N_0$) at time t. The solvent velocity field $\mathbf{u}(\mathbf{r},t)$ at a space-time point $(\mathbf{r},t)$ is assumed to be incompressible, hence the appearance of the projection operator $\mathcal{T}$ to select the transverse part of the vector field. The bare friction coefficient per segment of the chain is denoted by ζ_0. The coefficient η_{e} is a bare Onsager coefficient and must be interpreted as the local approximation for the solvent viscosity η_{s}. The stochastic forces $\mathbf{f}_{\mathrm{c}}$ and $\mathbf{f}_u$ are assumed to be Gaussian distributed and are such that they drive the system toward an equilibrium state with the probability distribution $\propto \exp(-\mathbf{H}\{\mathbf{c}\} - 1/2\int \mathbf{dr}\, \mathbf{u}^2)$; $\mathbf{H}\{\mathbf{c}\}$ is the free energy functional associated with a polymer chain of configuration $\{\mathbf{c}\}$. In eq 1 we have denoted the mode-coupling parameter as λ_{M} to avoid unnecessary confusion in the subsequent discussion.

It is to be clearly understood, first of all, that the dynamic parameter λ_0 of Shiwa and Oono[3] (SO) is given by

$$\lambda_0^{\,2} = \eta_{\mathrm{e}}/\eta_{\mathrm{s}} \tag{2}$$

and that this SO parameter λ_0 bears no relation to the mode-coupling parameter λ_{M}. It is simply not correct to identify λ_0 with λ_{M}.

Though the parameter λ_{M} is normally equal to unity, it can with an appropriate choice of units differ from unity. In fact, Douglas and Freed have shown that λ_{M} is merely a factor that converts units. An alternative way to show this result is via Poisson brackets. We recall from the work of Mori and collaborators[5] that the mode-coupling parameter λ_{M} of the streaming velocity terms is constructed from the Poisson brackets

$$\{\mathbf{c}(\tau),\mathbf{g}(\tau')\} = \mathbf{I}\lambda_{\mathrm{M}}\delta(\tau-\tau') \tag{3}$$

Here $\mathbf{g}(\mathbf{r},t)$ is the momentum density at $(\mathbf{r},t)$, and $\mathbf{I}$ is the unit tensor. The coefficient λ_{M} differs from unity if the units of the momentum of the polymer segment differ from those of the canonical momentum.

In summary, the authors of ref 1 are in error in identifying the phenomenological parameter λ_0 of SO with the mode-coupling parameter λ_{M}. The parameter λ_0 is the parameter "reflecting the local viscosity of the solvent which is perturbed in the proximity of the polymer chain". It differs from the mode-coupling parameter λ_{M}, which is involved in the streaming velocity of the generalized Langevin equations.

Douglas and Freed's second argument is that the renormalization-group (RG) calculations of polymer properties (equilibrium or dynamical) by Oono and co-workers are faulty, since only a portion of the second order in ϵ contributions is retained in these computations ($\epsilon \equiv 4 - d$, d being the spacial dimension). The important point that has been missed in their erroneous understanding of the RG calculations is that in the renormalization procedure the coupling constants (e.g., the usual parameters u and ξ, corresponding to the excluded-volume interaction and hydrodynamic interaction, respectively) and the dimensional parameter ϵ must be considered as two independent (expansion) parameters.[6] The dependence of a physical quantity (e.g., the friction coefficient, f) on the (renormalized) coupling parameters is determined by the RG equation. Thus, in practice, integrating the RG equation by using the perturbative (*in powers of the coupling constants*) results for β- and γ-functions, one gets the expression for the physical quantity. As an illustration, the result for f at the fixed point is[4]

$$f = \frac{\eta_{\mathrm{e}}}{2\pi}\xi^* \exp\left(\frac{\xi^*}{32\pi^2}\right)L^{d/2-1}\left(\frac{2\pi N}{L}\right)^{1-3\xi^*/16\pi^2} \tag{4}$$

to the lowest nontrivial order in ξ^* (the fixed point value of ξ), showing that the functional form conforms to the required scaling properties; N is the renormalized polymerization degree, with L being a phenomenological reference contour length.

At this juncture Douglas and Freed argue that computing ξ^* in (4) only up to *first order in* ϵ (as in ref 4) is insufficient since the expression (4) results from *the second order in* ξ expansion. However, as already emphasized, to determine the fixed-point value of the coupling constants is, in principle, an independent step one may perform. Thus, with an ϵ-expansion, one finds

$$u^* = \pi^2\epsilon/2, \quad \xi^* = 2\pi^2\epsilon \tag{5}$$

at first order in ϵ as a nontrivial fixed point. A better estimate may be obtained by the higher order (in ϵ) calculation or by an interpolation formula as used by des Cloizeaux.[7] Either is perfectly permissible, but for now it is not of our main concern.

To summarize, there is nothing at fault in the RG calculation scheme of Oono and co-workers, and their predictions as to equilibrium and dynamical properties are of the first order in ϵ.

References and Notes

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(6) See, for example: Ramond, P. *Field Theory: A Modern Primer*; Addison-Wesley: Reading, MA, 1989.
(7) des Cloizeaux, J. *J. Phys. (Paris)* **1981**, *42*, 635.

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