Addendum to "Dynamics of Copolymer and Homopolymer Mixtures in Bulk and in Solution via the Random-Phase Approximation"

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In a paper with the above title, which is henceforth referred to as I, we have presented a formulation of the dynamics of polymer mixtures with an arbitrary number of components using the random-phase approximation. In particular, we have obtained an equation (eq 16 of I) to calculate the partial dynamic scattering functions $S_{\alpha\beta}(q,t)$ in terms of the dynamic scattering functions $S^0_{\alpha\beta}(q,t)$ in the bare system and the Flory interaction parameters. In this paper, we cast this equation into a form that simplifies the calculations and makes the underlying physics more transparent. We also comment on the distinction between the short and long time mobilities.

We start with eq 16 of I and rewrite it as

$$\mu(q,s)^{-1} = \mu^0(q,s)^{-1} + q^2 k_B T \mathbf{v}'(q,s) \quad (1)$$

by introducing $\mu(q,s)$ through

$$\mu(q,s) = \beta \mathbf{D}(q,s)\,\mathbf{S}(q) \quad (2)$$

which can be identified as a generalized q- and s-dependent mobility. The $\mu^0(q,s)$ denotes the generalized mobility in the bare system. The $\mathbf{v}'(q,s)$ in eq 1 was defined by eq 18b of I as

$$\mathbf{v}'(q,s) = \frac{\beta}{s}\left[\frac{1}{\chi^0_{cc}(q,s)} - \frac{1}{\chi^0_{cc}(q,s=0)}\right]\mathbf{E}\mathbf{E}^T \quad (3)$$

where $\mathbf{E}\mathbf{E}^T$ is a square matrix with elements that are all equal to unity, and the other symbols are defined in I. We show in this paper that $\mathbf{v}'(q,s)$ defined in eq 3 in terms of the dynamic response function $\chi^0_{cc}(q,s)$ of the component "c", which is taken to be the "matrix" component and eliminated using incompressibility, can be simplified and expressed in terms of the mobility $\mu^0_{cc}(q,s)$ of the matrix in the bare system as

$$\mathbf{v}'(q,s) = \frac{\beta}{q^2}\frac{1}{\mu^0_{cc}(q,s)}\mathbf{E}\mathbf{E}^T \quad (4)$$

The derivation proceeds as follows: We first express the dynamic response function $\chi^0_{cc}(q,s)$ in eq 3 in terms of the dynamic scattering function $S^0_{cc}(q,t)$ in the bare system using the linear response theory

$$\chi^0_{cc}(q,t) = -\beta\frac{\partial}{\partial t}S^0_{cc}(q,t) \quad (5)$$

which, upon Laplace-transforming both sides, reads

$$\chi^0_{cc}(q,s) = -\beta[sS^0_{cc}(q,s) - S^0_{cc}(q)] \quad (6)$$

Following the same procedure as used in I leading to eq 1 here, we introduce the q- and s-dependent diffusion coefficient $D^0_{cc}(q,s)$ through

$$S^0_{cc}(q,s) = \frac{S^0_{cc}(q)}{s + q^2 D^0_{cc}(q,s)} \quad (7)$$

We note that $D^0_{cc}(q,s)$ and $\mu^0_{cc}(q,s)$ are also related to each other as $\mu^0_{cc}(q,s) = \beta D^0_{cc}(q,s)\,S^0_{cc}(q)$ by definition (see eq 2). Substitution of $S^0_{cc}(q,s)$ from eq 7 into eq 6 yields

$$\frac{1}{\chi^0_{cc}(q,s)} = \frac{s}{q^2}\frac{1}{\mu^0_{cc}(q,s)} + \frac{1}{\beta S^0_{cc}(q)} \quad (8)$$

Since the static response function $\chi^0_{cc}(q,s=0) = \chi^0_{cc}(q)$ in eq 3 is related to the static structure factor $S^0_{cc}(q)$ by $\chi^0_{cc}(q) = \beta S^0_{cc}(q)$ according to the linear response theory, we immediately arrive at eq 4 by substituting eq 8 into eq 3 and obtain from it the main contribution of this paper:

$$\mu(q,s)^{-1} = \mu^0(q,s)^{-1} + \frac{1}{\mu^0_{cc}(q,s)}\mathbf{E}\mathbf{E}^T \quad (9)$$

This equation expresses the generalized mobility matrix $\mu(q,s)$ in the interacting system in terms of its counterpart $\mu^0(q,s)$ in the bare system and the bare mobility $\mu^0_{cc}(q,s)$ of the "matrix" component. As we show below, it lends itself better to physical interpretation than eq 16 of I, from which it is derived. The form of eq 9 is the same as that of eq 23 of I; i.e.

$$\mathbf{m}(q)^{-1} = \mathbf{m}^0(q)^{-1} + \frac{1}{m^0_{cc}(q)}\mathbf{E}\mathbf{E}^T \quad (10)$$

which was written for the mobility matrix $\mathbf{m}(q)$ defined in terms of the first cumulant matrix $\mathbf{\Omega}(q)$ as $\mathbf{m}(q) = \beta\mathbf{\Omega}(q)\,\mathbf{S}(q)/q^2$. Since the first cumulant matrix describes the short time behavior of the intermediate scattering matrix $\mathbf{S}(q,t)$, we refer here to $\mathbf{m}(q)$ as the "short time mobility" to distinguish it from the Markov limit $\mu = \mu(0,0)$ of the generalized mobility $\mu(q,s)$, which involves the large time behavior of $\mathbf{S}(q,t)$ and hence defines the long time mobility. Returning to eq 9, we find that it is a generalization of eq 10 and is valid for all s and q. It can be inverted using the Sherman–Morrison[2] formula (incorrectly written in I as Sherman–Adams formula) as

$$\mu(q,s) = \mu^0(q,s) - \frac{\mu^0(q,s)\mathbf{E}\mathbf{E}^T\mu^0(q,s)}{\mu^0_{cc}(q,s) + \mathbf{E}^T\mu^0(q,s)\mathbf{E}} \quad (11)$$

which is identical with eq 24 of I in form but extends it to the generalized mobility. Equation 11 enables one to determine $\mu(q,s)$ in terms of the mobilities $\mu^0(q,s)$ in the bare system, whose elements can be more easily modeled than those of $\mu(q,s)$, adopting, for example, the single-chain Rouse dynamics. Once $\mu(q,s)$ is determined, it is in principle possible to obtain $\mathbf{S}(q,t)$ in the interacting system. Since these procedures have already been explained in I, we continue with the physical interpretation of eq 11, by calculating the diagonal and off-diagonal elements of $\mu(q,s)$. We assume that the mobility matrix $\mu^0(q,s)$ is diagonal, which is the case when the Rouse dynamics is used to calculate the mobilities in the bare system. Then, from eq 11 we obtain

$$\frac{1}{\mu_{aa}(q,s)} = \frac{1}{\mu^0_{aa}(q,s)} + \frac{1}{\sum_{j\neq a}\mu^0_{jj}(q,s)} \quad (12)$$

$$\frac{1}{\mu_{ab}(q,s)} = -\left[\frac{1}{\mu^0_{aa}(q,s)} + \frac{1}{\mu^0_{bb}(q,s)} + \frac{\sum_{j\neq a,b}\mu^0_{jj}(q,s)}{\mu^0_{aa}(q,s)\mu^0_{bb}(q,s)}\right] \quad (13)$$

where the summations include also the c component. Equation 12 can be interpreted as follows: In calculating

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the mobility $\mu_{aa}(q,s)$ of a given component "a", we can visualize the multicomponent system as an incompressible binary mixutre consisting of the component a and another one containing all the remaining components. The latter is a compressible mixture with an effective mobility, which, according to eq 12, is equal to the sum of the mobilities of its components. The mobility of the binary incompressible mixture is then obtained by adding the inverses of the mobilities of its two components and inverting the sum. This is a generalization of the usual superposition rule for calculating the mobility of binary incompressible mixtures to the incompressible multicomponent polymer mixtures. Another interesting consequence of eq 12 is that, if the mobility of any other component is much larger than the mobility of the a component, then $\mu_{aa}(q,s) = \mu^0{}_{aa}(q,s)$. This is also an extension of a similar conclusion reported in I for the short time mobility $m_{aa}(q)$. We were not able to attach a similar easy interpretation to the off-diagonal elements $\mu_{ab}(q,s)$ given in eq 13. We can only point out that, in an incompressible binary mixture consisting of a and b components, $\mu_{ab}(q,s) = -\mu_{aa}(q,s)$ and $\mu_{bb}(q,s) = \mu_{aa}(q,s)$.

References and Notes

(1) Akcasu, A. Z.; Tombakoglu, M. *Macromolecules* **1990**, *23*, 607.

(2) Dahlquist, G.; Björck, Å. Translated by Anderson, N. *Numerical Methods*; Prentice-Hall, Inc.: Englewood Cliffs, NJ, 1974.