Szleifer, Wilson, and Loring (SWL)\(^1\) have recently suggested a dynamic disorder model for polymer dynamics in melts, based on a non-Markovian analog of earlier work of Loring and co-workers.\(^2\) They suggest a solution to their non-Markovian master equation based on a non-Markovian generalization of the dynamical effective medium approximation (DEMA) of Harrison and Zwanzig (HZ).\(^3\) In this comment we argue that the result offered by SWL is not a proper solution of the non-Markovian generalization of the HZ model.

For clarity we disregard the polymer context and state the model using the HZ notation. We consider a particle hopping on a lattice characterized by dynamical bond disorder. The walker dynamics is described by the set of stochastic master equations for the probability \(P_i(t)\) to be at site \(i\) at time \(t\)

\[
\frac{d}{dt} P_i = - \sum_a \sigma_a(t) V_{ai} P_i - W_i P_i,
\]  

where \(\sigma_a(t)\) corresponds to a bond \((ij)\) between the nearest-neighbor sites \(i\) and \(j\) and where

\[
V_a = (|i| - |j|)(|i| - |j|).
\]

and

\[
P = \sum_i P_i |i|.
\]

(with \(|i| = \delta_{ij}\)). Here, \(\sigma_a(t)\) are stochastic variables which take the values 0 or 1. The SWL model assumes that these fluctuations occur according to the non-Markovian rate equation

\[
\frac{\partial}{\partial t} \phi_a(0,t) = \int_0^t dt' \Gamma(t-t') \left( \frac{-1}{p} \right) \phi_a(1,t')
\]

where \(\phi_a(\sigma, t)\) is the probability that the bond \(\sigma = (ij)\) has the value \(\sigma = 0\) or \(1\) at time \(t\), \(p\) is the average fraction of open bonds (\(\sigma = 1\)), and \(\Gamma(t)\) is a memory kernel.

In the Markovian limit where \(\Gamma(t) = 2y\delta(t)\), Eq. (4) reduces to the kinetic equation used by HZ. In this case the Laplace transform \([D(s) = \int_0^\infty dt e^{-st} D(t)]\) of the time-dependent diffusion coefficient is obtained to be

\[
D(s, \gamma) = D_0(s + \gamma),
\]

where \(D_0(s)\) is associated with the corresponding medium with static disorder \((\gamma = 0)\). According to SWL, in the more general case of arbitrary function \(\Gamma(t)\), the DEMA result is

\[
D(s, \gamma(s)) = D_0[s + y(s)],
\]

where \(y(s)\) is the Laplace transform of \(\Gamma(t)\). We now show that Eq. (6) does not follow from extending the HZ approach to the model defined by Eqs. (1)–(4). The starting point of HZ is a “Liouville-master” (LM) equation for the joint probability distribution \(f(P, \sigma, t)\), to find (at time \(t\)) the probability array \(P\) and the collective bond state \(\sigma = (\sigma_1, \sigma_2, \ldots, \sigma_m)\). Equation (6) is obtained (in the DEMA) from an extension of this LM equation written in the form

\[
\frac{\partial}{\partial t} f(t) = \frac{\partial}{\partial P} [W \cdot P(f(t)) + \int_0^t \hat{\Omega}(t-t') f(t') dt'],
\]

where

\[
\hat{\Omega}(t) = \sum_a \hat{\Omega}_a(t).
\]

[The LM equation of HZ is similar to Eq. (7), except that the last term is replaced by \(\hat{\Omega} f(t)\) where the constant operator \(\hat{\Omega}\) is associated with the Markovian analog of Eq. (4)]. Equation (7) can be used to construct an equation for the time evolution of the partial average

\[
P(\sigma, t) = \int dPf(P, \sigma, t)
\]

which leads (in the DEMA) to the result (5).

Our objection follows from the observation that even though Eq. (7) appears to generalize the form of the LM equation of HZ, it does not follow from the model Eqs. (1)–(4). To realize this, consider an example where the dynamics of the random walker does not depend on the state \(\sigma(t)\) of the bond. The random walker is then governed by a given static disorder [so that in Eq. (1) \(\sigma_a(t)\) are replaced by time-independent constants] while there is some property \(\sigma_a(t)\) of each bond \(\sigma\) which evolves according to Eq. (4) but has no effect on the walker. In this case the joint distribution \(f(P, \sigma)\) must decouple to \(f_1(P) f_2(\sigma)\), which is a solution to an equation similar to (7) with the last term replaced by \(f_1(P) \cdot f_2(\sigma) \hat{\Omega}(t-t') f_2(\sigma)\). However this decoupled form is not a solution of Eq. (7) itself, unless \(\Gamma(t) \sim \delta(t)\). In fact, Eq. (7) creates unusual time-dependent correlations between \(P\) and \(\sigma\).
and $\sigma$ that are not present in the model Eqs. (1)–(4). We conclude that the SWL result Eq. (6) must possess an inherent error.

We should add that in spite of this weakness of Eq. (6), it may provide a useful approximation in many cases. Indeed, we have used similar ideas in our studies of tracer diffusion in a noninteracting lattice gas (i.e., particles with only excluded volume interactions) on a static percolating network. We have used (as an ansatz) the collective (chemical) diffusion coefficient $D_c$ of the lattice-gas as a measure of the environment fluctuation rate $\gamma$, which was then used in the DEMA result (5) to obtain the tracer diffusion coefficient. We have found that this ansatz works well far from the percolation threshold of the static network. (However it yields a critical exponent for the tracer diffusion coefficient which is twice that of the single particle diffusion coefficient, in contradiction to simulation results which suggest that these exponents are identical).

We conclude that while Eq. (6) might be a useful approximation in some cases, it can not be obtained from the DEMA solution to Eqs. (1)–(4). Caution must be taken in drawing conclusions from results relying on this equation.

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