Equilibrium properties of polymers from the Langevin equation: Gaussian self-consistent approach

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We investigate here the dynamics of polymers at equilibrium by means of a self-consistent approximation that can be applied to arbitrary Hamiltonians. In particular we show that for the case of two-and three-body excluded volume effects, and the Oseen hydrodynamic interaction, the Gaussian self-consistent approach can recapture what we believe to be the essential features across the collapse transition. This method is based on the approximation of the complete Langevin equation by a Gaussian stochastic ensemble obeying a linear equation of motion with some unknown effective potential $\Delta V_q(t)$ and friction. Self-consistency equations for this potential are derived and studied in a variety of regimes across the collapse transition. Here we have calculated the friction ζ_q scaling behavior. The results of a simple power counting analysis of the equations, applicable for sufficiently large polymers, confirm the expected law $\zeta_q \propto N^{\nu} q^{1-\nu}$, and give exponent values $\nu=\frac{3}{5}$ for the Flory coil, $\nu=\frac{1}{2}$ for so-called θ point, and $\nu=\frac{1}{3}$ for the collapsed globule phase. Further applications of the method for various experimental observables of interest, e.g., the dynamic structure factor of light scattering, are presented, and again simple applications are discussed.

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I. INTRODUCTION

The equilibrium properties of polymers in dilute solution have been studied a great deal in recent years, yielding many interesting insights. There are well founded scaling [1] and statistical mechanical methods [2] that can be applied, and computer simulation has proved to be a particularly powerful tool [3]. However, methods that permit us to study dynamics and kinetic phenomena are much less well developed, and the traditional methods of nonequilibrium statistical mechanics [4] are not so readily applied. Furthermore, computer simulation of these properties is often prohibitively time consuming [5]. These are unfortunate limitations for two reasons. First, the principal experimental information on the structure and dynamics of polymers comes from dynamic light scattering [6], and one would therefore like to have a simple and general method to calculate the dynamical structure factor for any dilute polymer system of interest. Secondly, there is growing interest in the kinetics and nonequilibrium processes in conformational transitions such as the polymer- and protein-folding transition [7], and it would be useful to have a single method to calculate the dynamics and kinetics of such phenomena. The present paper offers an approach to the first of these problems, determination of the dynamics, and in a subsequent publication we shall show that an extension is possible to deal with nonequilibrium phenomena.

The present method has the benefit that it can be applied to any dilute polymer system with potential interaction that can be Fourier transformed. It may be shown to equilibrate to a variationally determined Gaussian ensemble, and in a sense we can say that the method we here present is the direct extension of such equilibrium methods to the realm of dynamics. Related ideas have been applied to describe the dynamics of concentrated solutions [8–10], when the formulation in terms of collective density variables rather than polymer coordinates is more appropriate.

II. METHOD

We proceed from the Langevin equation

$$\dot{x}_q^{\alpha}(t)=\sum_{a',q'} H_{qq'}^{\alpha\alpha'}(x(t))\left[-k_{q'}x_{q'}^{\alpha'}-\frac{\partial V}{\partial x_{-q'}^{\alpha'}}+\eta_{q'}^{\alpha'}(t)\right] \tag{1}$$

written for simplicity for cyclic polymers satisfying boundary conditions $x_{m+N}=x_m, m=0,\ldots,N-1$. The case of open polymers may be easily recovered from our formulas, there being only minor differences from the definition of the form of Fourier transformation which we write for rings as follows:

$$\mathbf{x}_q=\frac{1}{N}\sum_{n=0}^{N-1}\exp\left[\frac{i2\pi nq}{N}\right]\mathbf{x}_n,$$
$$\mathbf{x}_n=\sum_{q=0}^{N-1}\exp\left[\frac{-i2\pi nq}{N}\right]\mathbf{x}_q\ . \tag{2}$$

In principle the potential V includes contributions from excluded volume effects up to two- and three-body interactions,

$$V=V_2+V_3=u_2\sum_{mm'}\delta(\mathbf{x}_m-\mathbf{x}_{m'}) +u_3\sum_{mm'm''}\delta(\mathbf{x}_m-\mathbf{x}_{m'})\delta(\mathbf{x}_{m'}-\mathbf{x}_{m''})\ , \tag{3}$$

where u_2, u_3 are virial coefficients and $m\neq m'\neq m''$. However, we note that the present method can be readily applied to any potential that can be Fourier transformed.

We may note also that here $H_{qq'}^{\alpha\alpha'}$ is the Oseen hydrodynamic interaction tensor and the noise has the second order correlation function

$$\langle \eta_q^{\alpha}(t)\eta_{q'}^{\alpha'}(t')\rangle=(H^{-1})_{qq'}^{\alpha\alpha'}2k_BT\delta(t-t')\delta_{\alpha\alpha'}\delta_{-qq'} . \quad (4)$$

The explicit form of the Oseen tensor, describing the relation between generalized velocities and forces $v_n^{\alpha}=\sum_{\alpha' n'}H_{nn'}^{\alpha\alpha'}F_{n'}^{\alpha'}$, will be specified in Sec. IV. For some situations it is feasible to neglect the hydrodynamic interaction and, in any case it is instructive to discuss the simplest case where we take a diagonal constant mobility tensor

$$H_{qq'}^{\alpha\alpha'}=\zeta_q^{-1}\delta_{\alpha\alpha'}\delta_{qq'} . \quad (5)$$

In the absence of hydrodynamics $\zeta_q=N\zeta$ is simply a constant. If we include hydrodynamics the mobility would exhibit nontrivial q and N dependence. We begin by formally integrating the Langevin equation to obtain

$$x_q^{\alpha}(t)=x_q^{\alpha}(0)+\int_0^t dt_1\sum_{\alpha' q'}H_{qq'}^{\alpha\alpha'}(x(t_1))\times\left[-k_{q'}x_{q'}^{\alpha'}(t_1)-\frac{\partial V}{\partial x_{-q'}^{\alpha'}(t_1)}+\eta_{q'}^{\alpha'}(t_1)\right] . \quad (6)$$

For a diagonal mobility tensor it is more convenient to integrate as follows:

$$x_q^{\alpha}(t)=G_q^0(t)x_q^{\alpha}(0)+\frac{1}{\zeta_q}\int_0^t dt_1 G_q^0(t-t_1)\times\left[\eta_q^{\alpha}(t_1)-\frac{\partial V}{\partial x_{-q}^{\alpha}(t_1)}\right] , \quad (7)$$

$$G_q^0(t)=\exp\left[-\frac{k_q}{\zeta_q}t\right] . \quad (8)$$

In our self-consistent approach the dynamics of the full Langevin equation (1) is approximated by the Gaussian stochastic ensemble, which in diagonal form is

$$\zeta_q\dot{x}_q^{\alpha}(t)=-\Delta V_q(t)x_q^{\alpha}+\eta_q^{\alpha}(t) , \quad (9)$$

with unknown functions $\Delta V_q(t)$ and ζ_q to be determined later. We may note that this is the most general Gaussian theory, and later we shall find that, for equilibrium dynamics the effective potential has no time explicit dependence. Now, the noise distribution is considered to be Gaussian with correlations (4) where $H_{qq'}^{\alpha\alpha'}$ is set equal to (5). The formal solution is

$$x_q^{\alpha}(t)=G_q^V(t)x_q^{\alpha}(0)+\frac{1}{\zeta_q}\int_0^t dt_2 G_q^V(t-t_2)\eta_q^{\alpha}(t_2) , \quad (10)$$

$$G_q^V(t)=\exp\left[-\frac{1}{\zeta_q}\int_0^t dt_1\Delta V_q(t_1)\right] , \quad (11)$$

where $\Delta V_q(t)$ must be determined self-consistently.

Now, the Langevin ensemble possesses the equilibration property that, given any initial condition $\mathbf{x}_q(0)$, asymptotically $\mathbf{x}_q(t)$ reaches the equilibrium distribution. We restrict our attention to the case where the initial distribution is already at equilibrium. In this case one can solve the dynamics equations exactly. Note that the equilibrium distribution is space isotropic, and therefore all spatial components give equal contributions in the averages. It is also important to note the difference between the $q=0$ diffusive mode and other modes describing internal motions of the polymer. Thus

$$\langle|\mathbf{x}_q|^2(t)\rangle=\langle|\mathbf{x}_q|^2(0)\rangle \quad (q\neq 0) , \quad (12)$$

$$\langle|\mathbf{x}_0(t)|^2\rangle=\langle|\mathbf{x}_0(0)|^2\rangle+6Dt , \quad (13)$$

$$\langle\mathbf{x}_0(t)\cdot\mathbf{x}_0(0)\rangle=\langle|\mathbf{x}_0(0)|^2\rangle , \quad (14)$$

where D is, by definition, the diffusion constant. The only surviving correlation function with nontrivial time dependence for finite q will be $\langle\mathbf{x}_{-q}(0)\cdot\mathbf{x}_q(t)\rangle$. It may be shown that for equilibrium dynamics one can assume ΔV_q is independent of time without any additional assumptions.

III. MODEL WITHOUT HYDRODYNAMIC INTERACTIONS

For (12) to be true, we obtain from (10) after multiplication by $x_{-q}^{\alpha}(t)$ and integration over t_1,

$$\langle|\mathbf{x}_q|^2(t)\rangle=\langle|\mathbf{x}_q|^2(0)\rangle=\frac{3k_BT}{\Delta V_q} . \quad (15)$$

Similarly, multiplication of the same equation by $x_{-q}^{\alpha}(0)$ gives

$$\langle\mathbf{x}_{-q}(0)\cdot\mathbf{x}_q(t)\rangle=G_q^V(t)\langle|\mathbf{x}_q|^2(0)\rangle . \quad (16)$$

From (7) we obtain the second equation,

$$\langle\mathbf{x}_{-q}(0)\cdot\mathbf{x}_q(t)\rangle=G_q^0(t)\langle|\mathbf{x}_q|^2(0)\rangle-\frac{1}{\zeta_q}\int_0^t dt_1 G_q^0(t-t_1)\times\left\langle\mathbf{x}_q(0)\cdot\frac{\partial V}{\partial\mathbf{x}_{-q}(t_1)}\right\rangle . \quad (17)$$

Using the results (A6) and (A10) from Appendix A and carrying out the integration over time, we obtain an equation for ΔV_q,

$$k_q-\Delta V_q=\hat{u}_2\sum_{m'm''}\frac{d_{q,m'-m''}}{\mathcal{D}_{m'-m''}^{5/2}}+\hat{u}_3\sum_{mm'm''}\frac{d_{q,m_1}\mathcal{D}_{m_2}+d_{q,m_2}\mathcal{D}_{m_1}-2e_{q,m_1m_2}\mathcal{E}_{m_1m_2}}{(\mathcal{D}_{m_1}\mathcal{D}_{m_2}-\mathcal{E}_{m_1m_2}^2)^{5/2}} , \quad (18)$$

where $m_1=m-m'$, $m_2=m''-m'$, and also $\hat{u}_2=u_2/(2\pi)^{3/2}$, $\hat{u}_3=u_3/(2\pi)^3$.

Given the relations (15), (A7), (A8), (A11), and (A12) we now have a closed equation for ΔV_q. In principle this may be solved numerically. However [11], to exact some conclusions about its properties we suppose that, for small q, we can seek solutions with the properties

$$\Delta V_q = NA^{-1}\bar{q}^{2\beta}, \quad \bar{q}\equiv\frac{2\pi q}{N} , \tag{19}$$

where A is some, as yet unknown, constant. For large N and small q we obtain

$$\mathcal{D}_m = \frac{2Ak_BT}{N}\sum_{\bar{q}=2\pi/N}^{2\pi}\frac{1-\cos m\bar{q}}{\bar{q}^{2\beta}} \simeq Ak_BTm^{2\beta-1} . \tag{20}$$

If we define parameters b and ν by the relation

$$\tfrac{1}{3}\langle(\mathbf{x}_m-\mathbf{x}_{m'})^2\rangle = \mathcal{D}_{m-m'} = b^2|m-m'|^{2\nu} , \tag{21}$$

then $\nu=\beta-\frac{1}{2}$ and $b\simeq\sqrt{Ak_BT}$. Therefore for small $\bar{q}$ Eq. (18) reduces to the dominant balance equation,

$$k\bar{q}^2 - A^{-1}\bar{q}^{2\nu+1} = I'u_2b^{-5}\bar{q}^{5\nu-1} + I''u_3b^{-8}\bar{q}^{8\nu-2} . \tag{22}$$

Here, I', I'' are simple numerical constants. In fact, from this analysis we may extract three different regimes. When $u_2>0$ we find dominant balance between the order $\bar{q}^2$ and the u_2 term then given the Flory exponent $\nu=\frac{3}{5}$ and $b^2\sim(u_2/k)^{2/5}$. When $u_2=0$ we have a balance between $\bar{q}^2$ and the u_3 term, and the so-called θ point results: $\nu=\frac{1}{2}$, $b^2\sim(u_3/k)^{1/4}$. Finally, when $u_2<0$, we are in a collapsed state with balance between the two-body and three-body terms giving $\nu=\frac{1}{3}$ and $b^2\sim(-u_3/u_2)^{2/3}$. Evidently, using Eq. (13) we find $D=k_BT/\zeta_0$, and without hydrodynamics $D=k_BT/(N\zeta)$.

IV. MODEL WITH OSEEN HYDRODYNAMIC TENSOR

To determine the effects of including the hydrodynamic interactions, let us return to the integral equation (6). The Oseen tensor can be presented as follows:

$$H^{\alpha\alpha'}_{qq'}(x(t)) = \frac{1}{\eta_sN^2}\sum_{nn'}e^{(i2\pi/N)(q'n'-qn)} \times\int\frac{d\mathbf{w}}{(2\pi)^3}\frac{\mathcal{P}_{\alpha\alpha'}(\hat{\mathbf{w}})}{\mathbf{w}^2} \times\exp\left[-i\mathbf{w}\cdot\sum_p c_p^{nn'}\mathbf{x}_p(t)\right]+\frac{1}{N\zeta_b} , \tag{23}$$

$$\mathcal{P}_{\alpha\alpha'}(\hat{\mathbf{w}})\equiv\delta_{\alpha\alpha'}-\hat{w}_\alpha\hat{w}_{\alpha'} , \quad \hat{w}_\alpha=w_\alpha/w .$$

Here η_s denotes the viscosity of the solvent. We may note that there is an additional bare friction term ζ_b that arises from the diagonal element of the Oseen tensor $H^{\alpha\alpha'}_{nn}$. Its contribution may easily be calculated from the results [(A6) and (A10)] in Appendix A, but it is suppressed here because its effects vanish in the large-N limit, as we shall see later in Eq. (31). Now in place of Eq. (17) we would have

$$\langle\mathbf{x}_{-q}(0)\cdot\mathbf{x}_q(t)\rangle = \langle|\mathbf{x}_q|^2(0)\rangle + \int_0^t\sum_{\alpha\alpha',q'}\left[-k_q\langle x^\alpha_{-q}(0)H^{\alpha\alpha'}_{qq'}(x(t_2))x^{\alpha'}_{q'}(t_2)\rangle - \left\langle x^\alpha_{-q}(0)H^{\alpha\alpha'}_{qq'}(x(t_2))\frac{\partial V}{\partial x^{\alpha'}_{-q'}(t_2)}\right\rangle + \langle x^\alpha_{-q}(0)H^{\alpha\alpha'}_{qq'}(x(t_2))\eta^{\alpha'}_{q'}(t_2)\rangle\right] . \tag{24}$$

We note that the final term in the above equation vanishes. Details of the evaluation of the other two terms are given in Appendix B. Now, including up to two-body terms we find

$$k_q\zeta_q\frac{1}{3(2\pi^3)^{1/2}\eta_sN^2}\sum_{nn'}\frac{\cos[2\pi q(n-n')/N]}{\mathcal{D}^{1/2}_{n-n'}} - \Delta V_q = \zeta_q\frac{2u_2}{3(2\pi)^3\eta_sN}\sum_{mm'n}\frac{\cos(2\pi qm_1/N)-\cos(2\pi qm_2/N)}{\mathcal{D}^2_{m_1-m_2}}[(\mathcal{D}_{m_1-m_2}\mathcal{D}_{m_1}-\mathcal{C}^2_{m_1m_1-m_2})^{-1/2} - (\mathcal{D}_{m_1-m_2}\mathcal{D}_{m_2}-\mathcal{C}^2_{m_2m_1-m_2})^{-1/2}] , \tag{25}$$

where $m_1=m-n, m_2=m'-n$. Now for large N and small q power counting gives

$$J'k\bar{q}^2\zeta_q\frac{1}{N\eta_s}\frac{\bar{q}^{\nu-1}}{b} - A^{-1}\bar{q}^{2\nu+1} = J''u_2\zeta_q\frac{1}{N\eta_s}\frac{\bar{q}^{6\nu-2}}{b^6} , \tag{26}$$

where J', J'' are again some numerical constants. By comparison with Eq. (22) one finds

$$\zeta_q\simeq b\eta_sN^\nu q^{1-\nu} . \tag{27}$$

In principle one might retain three-body terms in Eq. (26), but this reproduces the same balance equation (22), essentially because ζ_q is a common factor in all interaction terms.

The above analysis is valid for all but the $q=0$ diffusive mode. Thus instead of (17) we should consider the equation for $\langle|\mathbf{x}_0|^2(t)\rangle$ and the dynamics is now trivial,

$$x^\alpha_0(t) = x^\alpha_0(0)+\frac{1}{\zeta_0}\int_0^t dt'\eta^\alpha_0(t') , \tag{28}$$

from which we find (13). One can see that $k_0=0$ and $c_0^{mm'}=0$. Therefore neither V nor $H^{\alpha\alpha'}$ contain x_0. Thus the correlation function of the interaction term with $x_0(t)$

vanishes as there is no term $\mathbf{x}_0$ with which to couple. Hence we find

$$\langle |\mathbf{x}_0|^2(t)\rangle = \langle |\mathbf{x}_0|^2(0)\rangle + \int_0^t \sum_{\alpha\alpha' q'} \langle x_0^{\alpha}(t) H_{0q'}^{\alpha\alpha'}(x(t_2)) \eta_{q'}^{\alpha'}(t_2)\rangle \ . \quad (29)$$

This leads to

$$\frac{6k_BT}{\zeta_0}t = \frac{6k_BT}{N\zeta_b}t + \frac{2k_BT}{\eta_s N^2} \times \int_0^t dt' \sum_{nn'} \int \frac{d\mathbf{w}}{(2\pi)^3}\frac{2}{\mathbf{w}^2} \times \left\langle \exp\left[-i\mathbf{w}\cdot\sum_p c_p^{nn'}\mathbf{x}_p(t')\right]\right\rangle \ . \quad (30)$$

Again, at equilibrium, we find

$$\frac{1}{\zeta_0} = \frac{1}{N\zeta_b} + \frac{12}{(2\pi)^{3/2}\eta_s N^2}\sum_{n\neq n'} \mathcal{D}_{n-n'}^{-1/2} \ . \quad (31)$$

Thus for large degree of polymerization N we estimate the sum, and neglect the bare friction term, and obtain

$$\zeta_0 \simeq b\eta_s N^{\nu} \quad (32)$$

and the diffusion constant is determined to be $D = k_BT/\zeta_0$.

V. DYNAMIC STRUCTURE FACTOR OF LIGHT SCATTERING

By definition the dynamic structure factor is

$$q(\mathbf{k},t) = \frac{1}{N}\sum_{nm}\left\langle \exp\{i\mathbf{k}\cdot[\mathbf{x}_n(t)-\mathbf{x}_m(0)]\}\right\rangle \ . \quad (33)$$

The wave vector $\mathbf{k}$ is related to the wave length λ, refraction index n, and scattering angle θ as follows:

$$|k| = \frac{4\pi n}{\lambda}\sin\frac{\theta}{2} \ .$$

In the Gaussian approximation the structure factor takes the form

$$g(\mathbf{k},t) = \frac{1}{N}\sum_{nm}\exp\left\{-\frac{1}{6}\mathbf{k}^2\sum_q\left[\langle |\mathbf{x}_q|^2(t)\rangle + \langle |\mathbf{x}_q|^2(0)\rangle - 2\cos\left[\frac{2\pi q(n-m)}{N}\right] \times \langle \mathbf{x}_q(0)\cdot\mathbf{x}_q(t)\rangle\right]\right\} \ . \quad (34)$$

Now we extract contribution of the zero diffusive mode from the remaining internal modes and substitute the averages,

$$g(\mathbf{k},t) = g_0(\mathbf{k},t)g_{\rm int}(\mathbf{k},t) \ , \quad (35)$$

$$g_0(\mathbf{k},t) = \exp(-\mathbf{k}^2 Dt) \ , \quad (36)$$

$$g_{\rm int}(\mathbf{k},t) = \frac{1}{N}\sum_{nm}\exp\left\{-\mathbf{k}^2\sum_{q\neq 0}\frac{k_BT}{\Delta V_q}\left[1-\cos\left[\frac{2\pi q(n-m)}{N}\right] \times e^{-(\Delta V_q/\zeta_q)t}\right]\right\} \ . \quad (37)$$

The internal modes part may be again decomposed

$$g_{\rm int}(\mathbf{k},t) = \frac{1}{N}\sum_{mn} g_{nm}^{(0)}(\mathbf{k})\Delta g_{nm}(\mathbf{k},t) \ , \quad (38)$$

$$g_{nm}^{(0)}(\mathbf{k}) = e^{(\mathbf{k}^2/2)\mathcal{D}_{n-m}} \simeq e^{-(\mathbf{k}^2/2)b^2|n-m|^{2\nu}} \ , \quad (39)$$

$$\Delta g_{nm}(\mathbf{k},t) = \exp\left[-\mathbf{k}^2\sum_{q\neq 0}\frac{k_BT}{\Delta V_q}\cos\left[\frac{2\pi q(n-m)}{N}\right] \times (1-e^{-(\Delta V_q/\zeta_q)t})\right] \ . \quad (40)$$

In Appendix C we have presented an approach that is valid in the whole k range. However, it is possible to consider two different regimes that result in further simplifications. In the limit $k^2b^2N^{2\nu} \ll 1$ one can neglect the contribution of internal modes, and the structure factor will be given entirely by the diffusion part $g_0(\mathbf{k},t)$. In the opposite case $k^2b^2N^{2\nu} \gg 1$ the contribution of internal modes becomes essential. In fact, for large N, their distribution is almost quasicontinuous, so that we may convert the sums into integrals. If we take the formula for the friction $\zeta_q = Ib\eta_s N\bar{q}^{1-\nu}$, with I being a numerical constant, the inverse relaxation times will be

$$1/\tau_q = \frac{k_BT}{Ib^3\eta_s}\bar{q}^{3\nu} \ . \quad (41)$$

By introducing new integration variables one can obtain

$$g_{\rm int}(\mathbf{k},t) = g(\mathbf{k},0)\frac{2\nu}{\Gamma(1/2\nu)} \times \int_0^{\infty} du\, \exp[-u^{2\nu} - (\Gamma_k t)^{2/3} \times \mathcal{H}(u(\Gamma_k t)^{-1/3\nu})] \ , \quad (42)$$

$$\mathcal{H}(u) = -\frac{2^{2\beta}\Gamma(\beta)}{\pi^{1/2}\Gamma(-\nu)}\int_0^{\infty}\frac{dx}{x^{2\nu+1}}\cos(ux)(1-e^{-x^{3\nu}}) \ ,$$

where the static structure factor and Γ_k are given up to some numerical coefficients by

$$g(\mathbf{k},0) \simeq (kb)^{-1/\nu} \ , \quad (43)$$

$$\Gamma_k \simeq \frac{k_BT}{\eta_s}k^3 \ . \quad (44)$$

For large time $\Gamma_k t \gg 1$ (42) may be further simplified to give

$$g_{\rm int}(\mathbf{k},t) = g(\mathbf{k},0)\exp[-\mathcal{H}(0)(\Gamma_k t)^{2/3}] \ , \quad (45)$$

where $\mathcal{H}(0)=-2^{2\beta+1}\sqrt{\pi}\Gamma(2\beta)/[2^{3/2}\Gamma(5/3)\nu\Gamma(-\nu)]$. Also the quantity of interest is logarithmic derivative at zero time. For large k we find by simple differentiation

$$\mathcal{Q}(\mathbf{k})\equiv-\frac{d}{dt}\bigg|_{t=0} g(\mathbf{k},t)=Dk^2+C(\nu)\frac{k_BT}{\eta_s}k^3 . \quad (46)$$

The value $C(\nu)$ may be independently expressed in terms of the static structure factor $g(\mathbf{k},0)$ [2],

$$C(\nu)k^3=g(\mathbf{k},0)^{-1}\int\frac{d\mathbf{q}}{(2\pi)^3}\left[\frac{\mathbf{k}^2-(\mathbf{k}\hat{\mathbf{q}})^2}{\mathbf{q}^2}\right]g(\mathbf{k}+\mathbf{q},0) , \quad (47)$$

that is $\mathbf{k}$ independent if we use the asymptotic formula (43) for $k^2b^2N^{2\nu}\gg1$. It is interesting to note that in this regime $C(\nu)$ does not contain any polymer specific parameters, and it is therefore referred to as the universal k^3 regime. This phenomenon persists in most realistic models and is quite easily observed in experiment.

VI. CONCLUSION

We have shown that it is possible to generalize the equilibrium method of variational approximation by a Gaussian ensemble to the realm of dynamics. The present equations produce precisely these variational equations in the static limit, though the problems that beset the equilibrium approaches to infinite repulsive potentials are also present in this generalization. As at equilibrium, these problems arise from the absence of a short-ranged cutoff, and with sensible analysis they are expected to reproduce the important features in a wide range of problems. It is possible to avoid these problems by inclusion of an explicit cutoff, but the equations then become considerably more cumbersome for analytical analysis.

It will be of some interest, in future, to examine dilute polymer problems with a range of conformational transitions.

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APPENDIX A: CALCULATION OF SOME AVERAGES

We begin by expressing the potential V in terms of an integral over plane waves.

$$V_2(t_1)=u_2\sum_{mm'}\int\frac{d\mathbf{k}}{(2\pi)^3}\exp\left[i\mathbf{k}\cdot\sum_{q'}\mathbf{x}_{q'}(t_1)c_{q'}^{mm'}\right] , \quad (A1)$$

$$V_3(t_1)=u_3\sum_{mm'm''}\int\frac{d\mathbf{k}}{(2\pi)^3}\frac{d\mathbf{p}}{(2\pi)^3} \times\exp\left[i\sum_{q'}\mathbf{x}_{q'}(t_1)\cdot(\mathbf{k}c_{q'}^{mm'}+\mathbf{p}c_{q'}^{m'm''})\right] , \quad (A2)$$

where

$$c_q^{nn'}\equiv\exp\frac{i2\pi qn}{N}-\exp\frac{i2\pi qn'}{N} . \quad (A3)$$

Evaluating the derivative $\partial V/\partial x_{-1}^{\alpha}(t_1)$, multiplying it by $x_{-q}^{\alpha}(0)$, and calculating the average we find

$$\left\langle x_{-q}^{\alpha}(0)\frac{\partial V_2}{\partial x_{-q}^{\alpha}(t_1)}\right\rangle =u_2\sum_{mm'}ic_q^{mm'}\int\frac{dk^{\alpha}}{2\pi}k_{\alpha}\langle x_{-q}^{\alpha}(0) \times e^{ik_{\alpha}c_q^{mm'}x_q^{\alpha}(t_1)}\rangle\langle e^{i\sum_{q'\neq q}k_{\alpha}c_{q'}^{mm'}x_{q'}^{\alpha}(t_1)}\rangle \times\prod_{\beta\neq\alpha}\int\frac{dk_{\beta}}{2\pi}\langle e^{i\sum_{q'}k_{\beta}c_{q'}^{mm'}x_{q'}^{\beta}(t_1)}\rangle . \quad (A4)$$

The average in a Gaussian distribution assuming a spatially isotropic initial condition is

$$\langle e^{i\sum_{q'}\mathbf{k}c_{q'}^{mm'}\cdot\mathbf{x}_{q'}(t_1)}\rangle=\exp\left[-\frac{1}{6}\mathbf{k}^2\sum_{q'}|c_{q'}^{mm'}|^2\langle|\mathbf{x}_{q'}|^2(t_1)\rangle\right] . \quad (A5)$$

The first average in (A4) may be obtained by means of differentiation with respect to auxiliary parameters. After integration over k we finally obtain

$$\left\langle\mathbf{x}_{-q}(0)\cdot\frac{\partial V_2}{\partial\mathbf{x}_{-q}(t_1)}\right\rangle=-\frac{u_2}{(2\pi)^{3/2}}\langle|\mathbf{x}_q|^2(0)\rangle G_q^V(t_1) \times\sum_{m'm''}\frac{d_{q,m'-m''}}{\mathcal{D}_{m'-m''}(t_1)^{5/2}} , \quad (A6)$$

$$\mathcal{D}_m(t_1)\equiv\tfrac{1}{3}\sum_{q'}d_{q',m}\langle|\mathbf{x}_{q'}|^2(t_1)\rangle , \quad (A7)$$

$$d_{q,m}=|c_q^m|^2=2-2\cos\frac{2\pi qm}{N} . \quad (A8)$$

Calculation of the three-body term is similar,

$$\left\langle x_{-q}^{\alpha}(0)\frac{\partial V_3}{\partial x_{-q}^{\alpha}(t_1)}\right\rangle =-u_3G_q^V(t_1)\langle|x_q^{\alpha}|^2(0)\rangle \times\sum_{mm'm''}\int\frac{d\mathbf{k}}{(2\pi)^3}\frac{d\mathbf{p}}{(2\pi)^3}|k^{\alpha}c_q^{mm'}+p^{\alpha}c_q^{m'm''}|^2 \times e^{-(1/2)\sum_{q'}|\mathbf{k}c_{q'}^{mm'}+\mathbf{p}c_{q'}^{m'm''}|^2\langle|x_{q'}|^2(t_1)\rangle} \quad (A9)$$

The result is

$$\left\langle \mathbf{x}_{-q}(0)\frac{\partial V_3}{\partial \mathbf{x}_{-q}(t_1)}\right\rangle = -\frac{u_3}{(2\pi)^3}\langle |\mathbf{x}_q|^2(0)\rangle G_q^V(t_1)\sum_{mm'm''}\frac{d_{q,m_1}\mathcal{D}_{m_2}(t_1)+d_{q,m_2}\mathcal{D}_{m_1}(t_1)-2e_{q,m_1m_2}\mathcal{E}_{m_1m_2}(t_1)}{[\mathcal{D}_{m_1}(t_1)\mathcal{D}_{m_2}(t_1)-\mathcal{E}^2_{m_1m_2}(t_1)]^{5/2}} \tag{A10}$$

$$\mathcal{E}_{m_1m_2}=\tfrac{1}{2}(\mathcal{D}_{m_1-m_2}-\mathcal{D}_{m_1}-\mathcal{D}_{m_2}) , \tag{A11}$$

$$e_{q,m_1m_2}=\tfrac{1}{2}(d_{q,m_1-m_2}-d_{q,m_1}-d_{q,m_2}) , \tag{A12}$$

where we have introduced relative coordinates $m_1=m'-m, m_2=m'-m''$.

APPENDIX B: AVERAGE FOR USE IN HYDRODYNAMICS

One may obtain the formula

$$\left\langle x^{\alpha}_{-q}(0)\exp\left[-i\mathbf{w}\cdot\sum_p c_p^{nn'}\mathbf{x}_p(t_2)\right]x_{q'}^{\alpha'}(t_2)\right\rangle=\delta^{\alpha\alpha'}\delta_{qq'}G_q^V(t_2)\langle |x_q^{\alpha}|^2(0)\exp\left[-\frac{1}{2}w^2\sum_p d_{p,nn'}\langle |x_p|^2(0)\rangle\right]+\cdots . \tag{B1}$$

The second part is equal to zero contribution after convolution with $\mathcal{P}_{\alpha\alpha'}$. After integration we obtain

$$\sum_{\alpha\alpha' q'}\langle x^{\alpha}_{-q}(0)H^{\alpha\alpha'}_{qq'}(x(t_2))x_{q'}^{\alpha'}(t_2)\rangle=\frac{1}{3(2\pi^3)^{1/2}\eta_s N^2}G_q^V(t_2)\langle |\mathbf{x}_q|^2(0)\rangle\sum_{nn'}\frac{\cos[2\pi q(n-n')/N]}{\mathcal{D}^{1/2}_{n-n'}} . \tag{B2}$$

For the interaction we find

$$\left\langle x^{\alpha}_{-q}(0)\exp\left[-i\mathbf{w}\cdot\sum_p c_p^{nn'}\mathbf{x}_p(t_2)\right]\frac{\partial V_2}{\partial x_{q'}^{\alpha'}(t_2)}\right\rangle=-u_2\sum_{mm'}\int\frac{d\mathbf{k}}{(2\pi)^3}k_{\alpha'}c^{mm'}_{-q}(k_{\alpha}c_q^{mm'}-w_{\alpha}c_q^{nn'})G_q^V(t_2)\langle |x_q^{\alpha}|^2(0)\rangle$$
$$\times\exp\left[-\frac{1}{2}\sum_p|\mathbf{k}c_p^{mm'}-\mathbf{w}c_p^{nn'}|^2\langle |x_p|^2(t_2)\rangle\right] . \tag{B3}$$

With the help of the integral

$$\int\frac{d\mathbf{k}}{(2\pi)^3}\frac{d\mathbf{w}}{(2\pi)^3}\frac{\mathbf{k}^2\mathbf{w}^2-(\mathbf{kw})^2}{\mathbf{w}^4}\exp[-\alpha\mathbf{k}^2-\beta\mathbf{w}^2-\gamma(\mathbf{kw})]=\frac{2}{(2\pi)^3}(2\alpha)^{-2}(4\alpha\beta-\gamma^2)^{-1/2} , \tag{B4}$$

one finds

$$\sum_{\alpha\alpha' q'}\left\langle x^{\alpha}_{-q}(0)H^{\alpha\alpha'}_{qq'}(x(t_2))\frac{\partial V_2}{\partial x_{q'}^{\alpha'}(t_2)}\right\rangle$$
$$=-\frac{2u_2}{3(2\pi)^3\eta_s N}G_q^V(t_2)\langle |\mathbf{x}_q|^2(0)\rangle\sum_{mm'n}\frac{\cos(2\pi qm_1/N)-\cos(2\pi qm_2/N)}{\mathcal{D}^2_{m_1-m_2}}$$
$$\times[(\mathcal{D}_{m_1-m_2}\mathcal{D}_{m_1}-\mathcal{E}^2_{m_1m_1-m_2})^{-1/2}-(\mathcal{D}_{m_1-m_2}\mathcal{D}_{m_2}-\mathcal{E}^2_{m_2m_1-m_2})^{1/2}] , \tag{B5}$$

where $m_1=m-n, m_2=m'-n$.

APPENDIX C: INTERNAL MODE DECOMPOSITION OF THE DYNAMIC STRUCTURE FACTOR

It is possible to derive another representation for the dynamic structure factor valid for any k. For large N we can replace double sums by integration over the relative coordinate

$$g_{\rm int}(\mathbf{k},t)/g_{\rm int}(\mathbf{k},0)=\int_0^N dn\prod_{q=1}^{N-1}\exp\left[\mathbf{k}^2G_q(t)\cos\frac{2\pi qn}{N}\right] , \tag{C1}$$

where

$$G_q(t)=\tfrac{1}{3}\langle \mathbf{x}_{-q}(0)\cdot\mathbf{x}_q(t)\rangle$$
$$=(k_BT/\Delta V_q)\exp[-(\Delta V_q/\xi_q)t] .$$

Using the generating function of the modified Bessel functions $I_m(z)$,

$$e^{z\cos q\phi}=\sum_{m=-\infty}^{\infty}e^{im\phi}I_m(z) \tag{C2}$$

for each internal mode labeled by a q, after integration over n we obtain

$$g_{\rm int}(\mathbf{k},t)/g_{\rm int}(\mathbf{k},0) = \sum_{m_1,\ldots m_{N-1}=-\infty}^{\infty} I_{m_1}(\mathbf{k}^2 G_1(t))\cdots I_{m_{N-1}}(\mathbf{k}^2 G_{N-1}(t)) , \tag{C3}$$

where summation is restricted by the condition

$$m_1+2m_2+\cdots+(N-1)m_{N-1}=0 . \tag{C4}$$

Such a representation is useful for asymptotics at large t when it is enough to consider only leading terms in the series (C3). In the simplest case, we may retain only the contribution of the first internal mode and the formula then reduces to simply

$$g_{\rm int}(\mathbf{k},t)/g_{\rm int}(\mathbf{k},0) \propto I_0(\mathbf{k}^2 G_1(t)) . \tag{C5}$$

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