Notes

Polymer Self-Diffusion in Bimodal Semidilute Solutions†

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Polymer self-diffusion in semidilute and concentrated solutions has become a field of relatively great interest in recent years, this due to the development of the reptation model for self-diffusion. And at this point there is a fairly extensive experimental literature on self-diffusion measurements in unimodal solutions which verify the essential features of the reptation model. These measurements include forced Rayleigh scattering,[1] pulsed field gradient nuclear magnetic resonance[2,3] luminescence quenching,[4] Rutherford backscattering,[5] forward recoil spectrometry,[6] radioactive tracers,[7,8] and infrared spectroscopy from deuterium-labeled chains.[9] Although this list of techniques is impressive, little work has been done on the study of reptation in semidilute bimodal solutions, where the "solvent" polymers have a different molecular weight than the "labeled" polymer. In fact, the study of this problem has begun only recently using the technique of dynamic light scattering[10–16] from isorefractive, ternary solutions. The ternary solutions consist of a solvent polymer, suitably chosen to index match a simple solvent, and a labeled polymer, chosen for good optical contrast and compatibility. In these solutions the labeled polymer (polystyrene (PS)) is dilute and the solvent polymer (poly(vinyl methyl ether) (PVME)) is semidilute, so dynamic light scattering detects self-diffusion of the labeled chains in a semidilute host. This labeled-chain technique lends itself to the study of bimodal solutions, and it is expected that quite a bit of experimental progress will made in this area in the future.

Recently, the scaling laws for reptation in unimodal solutions have been extended to bimodal solutions by applying the concept of a Stokes–Einstein/reptation crossover, which Daoud and de Gennes developed for melts,[17] to semidilute solutions.[12] Aside from the usual good solvent and Θ solvent cases, scaling laws were derived for a case which had not been considered in the literature: "thermodynamically" unscreened chains in good solvents.[12] This case is important in the interpretation of data from ternary solutions, since the labeled chains are chemically different from the solvent chains and excluded volume interactions are not, in general, screened by the solvent chains. In this paper we present data which are in qualitative agreement with the Stokes–Einstein/reptation crossover concept and show that these data are consistent with the predictions of scaling in bimodal solutions.

Experimental Section

Equipment. The details of the dynamic light scattering apparatus and data analysis are described elsewhere.[12]

Materials. The paucidisperse polystyrenes were obtained from Pressure Chemical Co., of number-average molecular weights 900 000, 420 000, 100 000, and 50 000. Respectively, the polydispersity indices were 1.10, 1.06, 1.06, and 1.06. Poly(vinyl methyl ether) was obtained from GAF (Gantrez M-556). Gel permeation chromatography indicated that the PVME was fairly polydisperse. Intrinsic viscosity data taken in benzene gave a molecular weight of 110 000.[18]

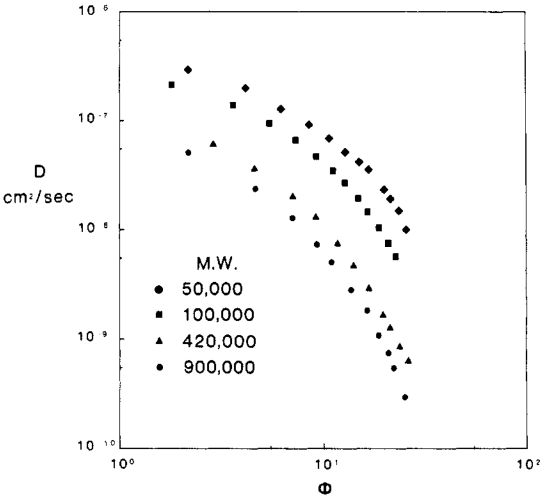

Figure 1. The dependence of the diffusion constant on ϕ, the percent volume fraction, is shown for the four polystyrene samples investigated.

Preparation. The method of sample preparation has been detailed previously[12] but will be repeated here for clarity. PVME was diluted with toluene to ca. 15 wt % polymer and prefiltered through a 3-μm Millipore MF filter. This solution was then injected through a 0.45-μm MF filter into ca. 25-mL sample containers. GPC analysis on the filtered PVME indicated no decrease in the polymer molecular weight due to scission in the filtering process. After these samples were weighed, a dilute polystyrene solution (2.0 mg/mL) was injected into each sample through a 0.45-μm MF filter. The semidilute crossover for polystyrene of molecular weight 900 000 is ~17 mg/mL and so these samples were well within the dilute regime. The final concentrations were attained by either diluting the samples with 0.2-μm-filtered toluene or slowly evaporating the samples in a dust-free oven with a steady circulation of 0.2-μm-filtered air. Final concentrations were determined gravimetrically and samples showing signs of dust were discarded. Volume fractions were calculated from the gravimetric data using 1.154 and 0.98 mL/g for the specific volumes of toluene and PVME, respectively. Finally, viscosity data for PVME were taken from ref 12, where measurements were made with Cannon-Ubbelohde viscometers.

Theory

The need for a theory of diffusion in bimodal solutions is obvious from the data in Figure 1. From these data it is clear that there is no apparent scaling regime for the concentration dependence of the diffusion coefficient; instead, the data show a progressively greater dependence on concentration at high ϕ, this increasing to as much as ϕ^{-4} at the highest molecular weight. In a previous paper,[12] it was suggested that these data could be understood in terms of a crossover from Stokes–Einstein (SE) diffusion to reptation. The idea is simple enough: in a bimodal solution consisting of a semidilute solution of short chains and a dilute solution of long chains, the long chain simply diffuses in a mean-field environment whose viscosity is that of the semidilute solution itself. Finally, at a critical concentration ϕ_r of the short chains ($\phi_r > \phi^*$, the semidilute crossover) the mean-field approximation for the effective viscosity breaks down and the long chains cross over to reptation.

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Table I

solvent	ϕ_r		ηD		γ
	bimodal	unimodal	bimodal	unimodal	
Θ	$N^{1/2}/P$	$N^{-1/2}$	$N^{-2}P^3\phi^3$	$N\phi^3$	3
good	$(N^{1/2}/P)^{8/5}$	$N^{-4/5}$	$N^{-2}P^3\phi^2$	$N\phi^2$	$^{15}/_8$
good, un-screened	$(N^{2/5}/P)^{4/3}$	$N^{-4/5}$	$N^{-9/5}P^3\phi^{9/4}$	$N^{6/5}\phi^{9/4}$	$^{9}/_4$

Originally, the crossover from SE diffusion to reptation was calculated by taking the ratio of the scaling form of the reptation diffusion coefficient, D_r, to the SE diffusion coefficient, D_s, using the scaling form for the semidilute viscosity.[12] The SE/reptation crossover, ϕ_r, was calculated by setting this ratio to unity. Although this procedure may seem somewhat arbitrary, we can now show that the crossovers calculated in this way are consistent with the theory of reptation and can be used to directly obtain reptation results. We begin by writing a scaling form for the diffusion coefficient of the long chains

$$D = D_s f(\phi/\phi_r)$$

where $D_s = T/6\pi\eta_p R$. Here, T is the temperature in units of energy, η_p is the viscosity of the semidilute chains of P monomers, and R is the radius of the dilute chains of N monomers, where $N > P$. The scaling form of the viscosity of the semidilute chains is $\eta_p \sim TP/g^3$, where g is the number of monomers per concentration blob. For $\phi \ll \phi_r$ the function $f(x) \sim 1$, whereas for $\phi \gg \phi_r$, $f(x) \sim x^\gamma$. The power γ can be computed by insisting that in the reptation regime the self-diffusion coefficient of the dilute chains is independent of the molecular weight of the semidilute chains.

$$D = D_s(\phi/\phi_r)^\gamma \sim P^0 \qquad \text{for } \phi \gg \phi_r$$

In Θ systems $g \sim \phi^{-2}$, $R \sim N^{1/2}$, and $\phi_r \sim N^{1/2}/P$, which gives $\gamma = 3$ and the reptation result $D_r \sim \phi^{-3}N^{-2}$. For good solvent systems $g \sim \phi^{-5/4}$, $R \sim N^{1/2}\phi^{-1/8}$, and $\phi_r \sim (N^{1/2}/P)^{8/5}$. This gives $\gamma = {}^{15}/_8$ and $D_r \sim \phi^{-7/4}N^{-2}$. These results for the reptation diffusion coefficient in bimodal solutions demonstrate that bimodal scaling is consistent with, and is a natural extension of, unimodal reptation theory. The crossover ϕ_r is just the bimodal generalization of the unimodal semidilute crossover, ϕ^*.

In the ternary systems studied here, the solvent is a good solvent for both the dilute and semidilute chains. However, the usual good solvent scaling laws must be modified since the dilute chains are not chemically identical with the semidilute chains and are therefore not a priori thermodynamically screened. The reptation diffusion coefficient can be derived by using $g \sim \phi^{-5/4}$, $R \sim N^{1/2}$, and $\phi_r \sim (N^{2/5}/P)^{4/3}$. This gives $\gamma = {}^9/_4$ and $D_r \sim \phi^{-3/2}N^{-9/5}$. The bimodal scaling results are collected in Table I.

Since much of the experimental data presented here are in the crossover regime where $\phi \sim \phi_r$, we must make some conjecture about the form of the scaling function $f(\phi/\phi_r)$. To estimate this scaling function we make the physically reasonable empirical assumption that the diffusion due to reptation occurs in a reference frame which is comoving with a reference frame in which the Stokes–Einstein part of the diffusion is stationary—the observed diffusion coefficient is simply the sum of the Stokes–Einstein and reptation diffusion coefficients. This gives

$$D = D_s[1 + C(\phi/\phi_r)^\gamma]$$

where C is a constant which is to be determined experimentally and the exponent γ is defined above and included in Table I. For good solvent, unscreened chains the scaling prediction for the concentration and molecular weight dependence is

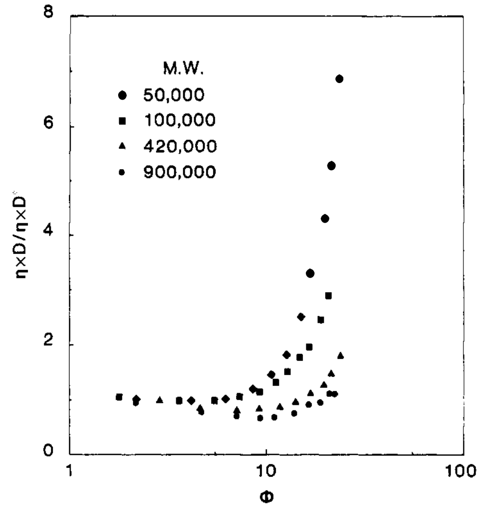

Figure 2. The ordinate-scaled ηD data illustrate the divergence from Stokes–Einstein behavior at high concentrations. The divergence is especially pronounced for the lowest molecular weight sample.

$$D = D_s[1 + C\phi^{9/4}P^3/N^{6/5}] \tag{1}$$

We will use this semiempirical equation to interpret the molecular weight dependence of the diffusion coefficient in the non-power-law regime $\phi \sim \phi_r$.

Results and Discussion

Concentration Dependence. The SE/reptation crossover is examined by plotting the product ηD vs. concentration. In the SE regime ηD should be $T/6\pi R$, independent of concentration, whereas in the reptation regime ηD becomes very concentration dependent, scaling like $N^{-9/5}P^3\phi^{9/4}$. In Figure 2 it is observed that for the polystyrene of M_n = 900 000 this product is very nearly independent of concentration, indicating a Stokes–Einstein regime that extends well into the semidilute regime ($\phi^* \sim 4\%$). At lower molecular weights, the crossover occurs at lower concentrations and so the data deviate much more strongly from Stokes–Einstein behavior at large ϕ.

The diffusion data should form a master curve on a plot of $\eta D/\eta D^*$ (the asterisk indicates data taken at ϕ^*) vs. ϕ/ϕ_r. For the good solvent, unscreened case shown here, ϕ_r should scale like $M^{0.53}$, but if this is used as the abscissa scale factor the data do not form a well-defined master curve. Instead, it is empirically observed that the data collapse onto a master curve if the abscissa is scaled by $M^{0.3}$, as in Figure 3. At this time this apparent disagreement with bimodal scaling is not understood, but it may simply be due to a weak dependence of the polystyrene radius on PVME concentration. On the other hand, it is observed that beyond ϕ_r the ηD data are in good agreement with the $\phi^{9/4}$ prediction of bimodal scaling; however, this agreement should be viewed with due caution since the high-concentration regime is somewhat limited.

Molecular Weight Dependence. Empirically, it is found that the molecular weight dependence of the diffusion coefficient follows a power law at all concentrations of polymer, $D \sim M^{-\nu}$. This is shown in Figure 4, where the molecular weight dependence is given for PVME concentrations of 0%, 5%, 10%, 15%, and 20%. It is possible, using eq 1, to theoretically predict the exponent for the apparent power-law dependence of the diffusion coefficient data in the crossover regime. The procedure is simple: (1) evaluate the constant in eq 1 by fitting the

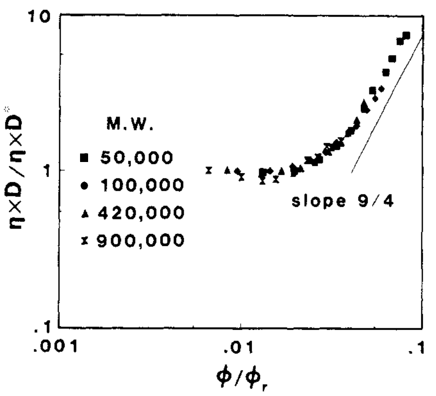

Figure 3. The product of the viscosity and the diffusion coefficient is found to superpose on properly scaled axes. The large-ϕ data are fit quite well by the line of slope $^9/_4$, which is the bimodal scaling prediction for these ternary solutions (the dimensionless ratio ϕ/ϕ_r has an arbitrary prefactor).

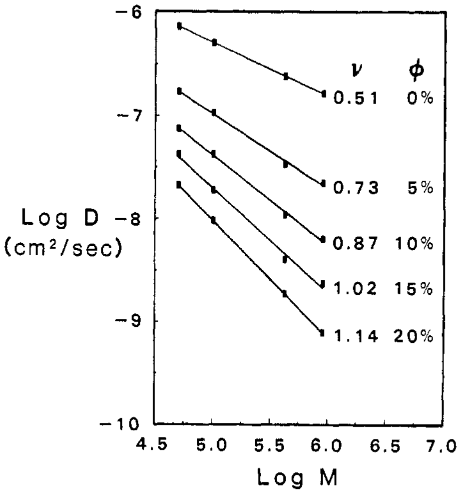

Figure 4. The exponent ν ($D \sim M^{-\nu}$) increases smoothly with PVME concentration. Diffusion data at 5%, 10%, etc. were obtained by polynomial interpolation of the slowly varying ηD data. The interpolated values of ηD were then divided by measured values of the viscosity at these concentrations.

concentration dependence of one molecular weight sample; (2) using this constant, evaluate eq 1 at ϕ = 0%, 5%, etc. for molecular weights 50 000, 100 000, 420 000, and 900 000; (3) determine the apparent exponent for each PVME concentration by plotting these calculated diffusion coefficients vs. molecular weight on logarithmic axes. This is a zero-adjustable parameter model insofar as the molecular weight dependence is concerned, since only the concentration dependence of a single molecular weight sample is used to evaluate the constant.

In practice, the molecular weight 50 000 sample was used to determine the constant in eq 1, since this sample showed the strongest dependence of ηD on concentration. The one-parameter fit to the concentration dependence of ηD is very good and is shown in Figure 5. In Figure 6 the resultant theoretical values of ν are compared to the experimental values taken from Figure 4. Given that there are no adjustable parameters, the agreement is quite good. These data demonstrate that the assumption that Stokes–Einstein diffusion and reptation are independent processes is useful in describing the salient features of the bimodal diffusion data in the complex crossover regime.

As a final point, it should be noted that the data for ν increase monotonically with concentration and do not give any indication of stopping at the maximum value observed. At very high PVME concentrations it should, therefore, be possible to discriminate between the chemically indistinguishable chain prediction $D \sim M^{-2}$ and the theoretical prediction $D \sim M^{-1.8}$ for the reptation diffusion coefficient.

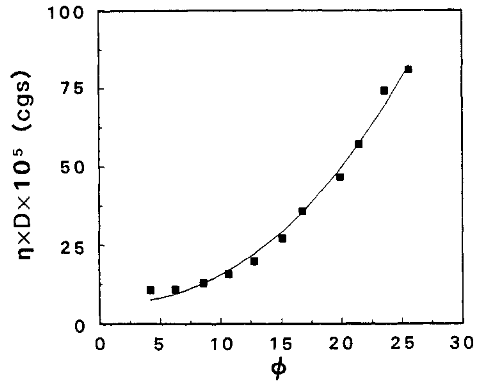

Figure 5. Single-parameter fit of eq 1 to the concentration dependence of the ηD data for molecular weight 50 000 polystyrene.

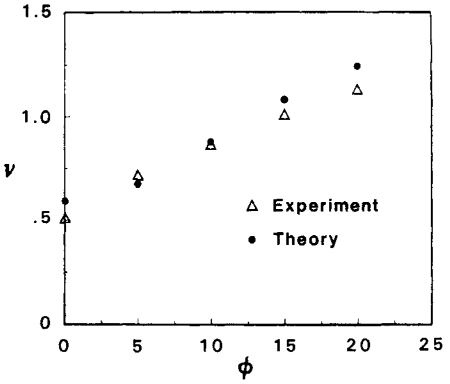

Figure 6. The concentration dependence of the apparent D vs. M exponent is compared to the semiempirical theory for this apparent exponent. For a zero-parameter theory the fit is quite good.

Conclusions

We have shown that bimodal scaling is consistent with reptation theory and that the Stokes–Einstein/reptation crossover, ϕ_r, can be used to obtain previously known scaling results for the reptation diffusion coefficient. Bimodal scaling seems to be useful in describing the gross features of the experimental data, but on close inspection the results are mixed. For instance, the concentration dependence of the diffusion coefficient data is in good agreement with the $\phi^{9/4}$ prediction of bimodal scaling for good solvent, ternary systems, but the diffusion coefficient data are found to superpose on axes with the abscissa scaled by $M^{0.3}$, in disagreement with the $M^{8/15} \cong M^{0.53}$ prediction. On the other hand, the molecular weight dependence of the diffusion coefficient data is in good agreement with the predictions of bimodal scaling coupled with the additional $D = D_s + D_r$ hypothesis for the scaling function $f(x)$.

This general type of behavior is common to critical systems which are studied in a nonasymptotic or crossover regime. The rule, rather than the exception, is that scaling behavior is found in such systems, but only with effective exponents. So although the situation is at present unclear, it is possible that better agreement will be found when comparison is made to ternary systems with higher molecular weight PVME.

Registry No. PVME (homopolymer), 9003-09-2; polystyrene (homopolymer), 9003-53-6; toluene, 108-88-3.

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Concentration Dependence of the Polymer Diffusion Coefficient

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The form of the concentration dependence of the polymer diffusion coefficient depends on the concentration of the polymer relative to the crossover concentration, c^*, between the dilute and semidilute regimes. At concentrations below c^* the diffusion is of a single polymer molecule. As the polymer concentration is increased the friction coefficient is increased, thus leading to a slowing down of the motion of individual molecules. A microscopic, hydrodynamic theory explains this behavior quite adequately.[1] As the polymer concentration approaches c^* the diffusion coefficient vs. concentration curve flattens out and, at concentrations above c^* but still in the semidilute regime, the diffusion coefficient becomes a linearly increasing function of the polymer concentration.[2] Typically, scaling approaches are employed to explain the behavior in the semidilute regime. By examining static correlations near the Θ temperature, Daoud and Jannink[3] have expressed the density–density correlation function in terms of a correlation length that is inversely proportional to the concentration. Brochard and de Gennes,[4] using dynamic scaling arguments for Θ conditions, have shown that the diffusion coefficient is inversely proportional to the correlation length and is therefore directly proportional to the concentration.

Combining the above descriptions leads to a picture that describes the experimentally observed concentration dependence of the polymer diffusion coefficient. At low concentrations the decrease of the translational diffusion coefficient is due to hydrodynamic interactions that increase the friction coefficient and thereby slow down the motion of the polymer chain. At high concentrations the system becomes an entangled network. The diffusion of the chains becomes a cooperative process, and the diffusion of the chains increases with increasing polymer concentration. This description requires two different expressions in the two concentration regimes. A microscopic, hydrodynamic theory should be capable of explaining the observed behavior at all concentrations. In this note we present such a microscopic interpretation.

Theory

The diffusion coefficient is related to a microscopic variable through a Green–Kubo relation

$$D = (1/3)\int_0^\infty \mathrm{d}t \ \langle \dot{A}(t)\dot{A}^+(0)\rangle \tag{1}$$

where for diffusion the microscopic variable is the flux of the number of particles through an imaginary plane of unit area in the fluid. Thus, for diffusion $\dot{A}(t) = (\mathrm{d}x/\mathrm{d}N)\dot{N}(t)$, where $\dot{N}(t)$ is the flux of the number of particles through the plane at time t , and $\dot{N}(t)$ is a phase-space variable; that is, the flux will depend on both the positions and velocities of the polymer segments. Therefore, we can expand it in the variables $(\mathbf{x}_i, \mathbf{p}_i)$ and, using eq 1, obtain

$$D = \int_0^\infty \mathrm{d}t \ \langle \mathbf{v}_i(t)\mathbf{v}_i(0)\rangle + \int_0^\infty \mathrm{d}t \ (\mathrm{d}\mathbf{x}_i/\mathrm{d}N)^2(\mathrm{d}N/\mathrm{d}\mathbf{p}_i)^2\langle \mathbf{F}_i(t)\mathbf{F}_i(0)\rangle \tag{2}$$

where we have used the repeated index convention. Noting that the velocities of the individual segments add up to the overall polymer velocity, we see that the first term in eq 2 gives simply the relation between the polymer diffusion coefficient and the velocity–velocity correlation function. A microscopic approach yields the Einstein relation[4] $D = k_\mathrm{b}T/f_0(1 + k_\mathrm{s}c)$, where k_b is Boltzmann's constant, T is the absolute temperature, f_0 is the friction coefficient at infinite dilution, k_s is a constant, and c is the polymer concentration. Because the forces on the individual segments are not additive, the second term in eq 2 must be left in terms of segment variables.

Following Ferrell,[5] the second term in eq 2 can be expressed as a Green–Kubo integral over a flux–flux correlation function. The transport is due to a velocity perturbation caused by two driving forces, the Brownian force and frictional force. The transport coefficient due to the segment–segment interaction can be calculated from the Kubo formula.[6]

$$\lambda = (1/k_\mathrm{b}T)\int\int\int_0^\infty \mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2\,\mathrm{d}(t_2 - t_1)\langle \mathbf{J}(\mathbf{r}_2,t_2)\mathbf{J}(\mathbf{r}_1,t_1)\rangle \tag{3}$$

where $\mathbf{J}(\mathbf{r},t) = S(\mathbf{r},t)\mathbf{V}(\mathbf{r},t)$; $S(\mathbf{r},t)$ is the density fluctuation, and $\mathbf{V}(\mathbf{r},t)$ is the local velocity of the segment in the polymer solution. For simplicity,[5] we define the equal time density correlation function $G(\mathbf{r})$

$$G(\mathbf{r}_{12}) = \langle S(\mathbf{r}_1,0)S(\mathbf{r}_2,0)\rangle \tag{4}$$

and the time-integrated velocity correlation tensor $A_{ij}(\mathbf{r})$

$$A_{ij}(\mathbf{r}_{12}) = \int_0^\infty \mathrm{d}t \ \langle V_i(\mathbf{r}_1,t)V_j(\mathbf{r}_2,0)\rangle \tag{5}$$

Substituting $G(\mathbf{r})$ and $A_{ij}(\mathbf{r})$ into eq 3, we have

$$\lambda = (1/k_\mathrm{b}T)\int\int\int \mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2\,\mathrm{d}t \ \langle S(\mathbf{r}_2,t)\mathbf{V}(\mathbf{r}_2,t)S(\mathbf{r}_1,0)\mathbf{V}(\mathbf{r}_1,0)\rangle$$

$$\lambda = (1/k_\mathrm{b}T)\int\int\int \mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2\,\mathrm{d}t \ G(\mathbf{r}_{12})\langle \mathbf{V}(\mathbf{r}_2,t)\mathbf{V}(\mathbf{r}_1,0)\rangle$$

$$\lambda = (1/k_\mathrm{b}T)\int\int G(\mathbf{r}_{12})A(\mathbf{r}_{12})\,\mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2$$

$$\lambda = (V/k_\mathrm{b}T)\int G(\mathbf{r})A(\mathbf{r})\,\mathrm{d}\mathbf{r} \tag{6}$$

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