

# Dynamic renormalization in the framework of nonequilibrium thermodynamics

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We show how the dynamic renormalization of nonequilibrium systems can be carried out within the general framework of nonequilibrium thermodynamics. Whereas the renormalization of Hamiltonians is well known from equilibrium thermodynamics, the renormalization of dissipative brackets, or friction matrices, is the main new feature for nonequilibrium systems. Renormalization is a reduction rather than a coarse-graining technique; that is, no new dissipative processes arise in the dynamic renormalization procedure. The general ideas are illustrated for dilute polymer solutions where, in renormalizing bead-spring chain models, dissipative hydrodynamic interactions between different smaller beads contribute to the friction coefficient of a single larger bead.

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## I. INTRODUCTION

The renormalization group is a well-established, powerful tool for understanding critical phenomena in the statistical mechanics of equilibrium systems [1–4]. The basic idea is to compensate for a decimation in the number of degrees of freedom by a renormalization of the parameters in the Hamiltonian. Such transformations, which can be iterated, contain important information about the long-range properties of self-similar systems. The Hamiltonian and the transformation of the parameters in it clearly play a central role in the renormalization of equilibrium systems.

If we turn our interest to time-dependent nonequilibrium systems, what are the key objects on which a renormalization should be performed? This is the question we address with the methods of modern nonequilibrium thermodynamics, which expresses time evolution in terms of fundamental building blocks.

We first provide the required background from nonequilibrium thermodynamics by summarizing the general equation for nonequilibrium reversible-irreversible coupling (GENERIC) framework (Sec. II). In particular, we describe the rules for model reduction and coarse graining. The dynamic renormalization group has been applied very successfully to the calculation of rheological properties of dilute polymer solutions [5–10]. We hence choose this example for illustrating our ideas about dynamic renormalization and sketch the required background from polymer kinetic theory (Sec. III). With the background from nonequilibrium thermodynamics and polymer kinetic theory, we are in a position to explain dynamic renormalization from a thermodynamic perspective and to preclude some general lessons (Sec. IV). Most importantly, it turns out that dynamic renormalization is performed on dissipative brackets, or friction matrices, and nevertheless does not require consideration of any time-dependent properties or processes.

## II. NONEQUILIBRIUM THERMODYNAMICS

Time-evolution equations for nonequilibrium systems have a well-defined structure in which reversible and irre-

versible contributions are specified separately. In particular, the reversible contribution is generally assumed to be of Hamiltonian form and hence requires an underlying geometric structure (a Poisson bracket) which reflects the idea that the reversible time evolution should be “under mechanistic control.” The remaining irreversible contribution is driven by the nonequilibrium entropy by means of a dissipative bracket.

### A. GENERIC framework

Our discussion is based on the GENERIC formulation of the time evolution for nonequilibrium systems [11–13]. If  $A$  is an arbitrary observable—that is, a sufficiently regular real-valued function or functional of a set of independent variables  $x$  required for a complete description of a given nonequilibrium system—the time evolution of  $A$  is given by

$$\frac{dA}{dt} = \{A, E\} + [A, S]. \quad (1)$$

The observables  $E$  and  $S$  generating time evolution are the total energy and entropy, and  $\{\cdot, \cdot\}$  and  $[\cdot, \cdot]$  are Poisson and dissipative bracket, respectively. The bracket of two observables  $A$  and  $B$  is another observable with a linear dependence on  $A$  and  $B$  (a more complete characterization of Poisson and dissipative brackets is given below). The two contributions to the time evolution of  $A$  generated by the total energy  $E$  and the entropy  $S$  in Eq. (1) are the reversible and irreversible contributions, respectively. Equation (1) is supplemented by the complementary degeneracy requirements

$$\{S, A\} = 0 \quad (2)$$

and

$$[E, A] = 0 \quad (3)$$

for all observables  $A$ . The requirement that the entropy be a degenerate functional of the Poisson bracket expresses the reversible nature of the first contribution to the dynamics: the functional form of the entropy is such that it cannot be affected by the Poisson-bracket contribution to the dynamics, no matter which observable  $A$  is used as a generator  $E=A$  of

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reversible dynamics. The requirement that the energy be a degenerate functional of the dissipative bracket expresses the conservation of the total energy in a closed system by the dissipative contribution to the dynamics.

For completeness, we give the defining properties of Poisson and dissipative bracket. The Poisson bracket possesses the antisymmetry property

$$\{A, B\} = -\{B, A\} \quad (4)$$

and satisfies the product or Leibniz rule

$$\{AB, C\} = A\{B, C\} + B\{A, C\} \quad (5)$$

and the Jacobi identity

$$\{A, \{B, C\}\} + \{B, \{C, A\}\} + \{C, \{A, B\}\} = 0, \quad (6)$$

where  $A$ ,  $B$ , and  $C$  are arbitrary observables. These properties are well known from the Poisson bracket of classical mechanics, and they capture the essence of reversible dynamics. The Jacobi identity (6), which is a highly restrictive condition for formulating proper reversible dynamics, expresses the invariance of Poisson brackets in the course of time (time-structure invariance).

The dissipative bracket satisfies the symmetry condition (for a more sophisticated discussion of the Onsager-Casimir symmetry properties of the dissipative bracket, see Secs. 3.2.1 and 7.2.4 of [13])

$$[A, B] = [B, A] \quad (7)$$

and the non-negativeness condition

$$[A, A] \geq 0. \quad (8)$$

This non-negativeness condition, together with the degeneracy requirement (2), guarantees that the entropy is a non-decreasing function of time:

$$\frac{dS}{dt} = [S, S] \geq 0. \quad (9)$$

The condition (8) may hence be regarded as a strong formulation of the second law of nonequilibrium thermodynamics.

The formulation of GENERIC in terms of Poisson and friction operators instead of brackets can be found in [12,13]. One then formulates a time-evolution equation for the independent variables  $x$ .

### B. Elimination of degrees of freedom

Within the GENERIC framework, there are systematic recipes for reducing the number of degrees of freedom in a system, which is a classical problem of statistical mechanics. For the general discussion of coarse graining, we assume that we have more or less detailed levels of description in terms of the variables  $x$  and  $y$ , respectively. We then need a probability density  $\rho_y(x)$ , which represents the probability of a more detailed state  $x$  contributing to the properties of the less detailed state  $y$ . We further assume that there exists a function  $\Pi(x)$  such that the variables  $y$  can be obtained by averaging:

$$y = \int \Pi(x) \rho_y(x) \mathcal{D}x = \langle \Pi \rangle_y, \quad (10)$$

where we have introduced the notation  $\langle \cdots \rangle_y$  for averages performed with  $\rho_y(x)$ . For example,  $\rho_y(x)$  might be given by a generalized canonical or microcanonical ensemble for non-equilibrium systems [13–15]. The function  $\Pi(x)$  can be interpreted as the more detailed expression for the coarser variables.

Now, if we know the generators  $E(x)$  and  $S(x)$  and the brackets  $\{.,.\}$  and  $[.,.]$  on the more detailed level, how can we determine the building blocks on the less detailed level by means of  $\Pi(x)$  and  $\rho_y(x)$  in terms of the variables  $y$ ? The answer to this question is briefly summarized in the rest of this section. Detailed derivations and explanations can be found in [13–16].

The energy of the less detailed level is obtained by straightforward averaging with  $\rho_y(x)$ . The transformation rule for the entropy depends on the underlying ensemble. For a linear expression for the slow variables in terms of the more detailed variables,  $\Pi(x) = Q^\Pi x$ , it makes sense to introduce Lagrange multipliers on both levels of description because the underlying generalized canonical ensemble is invariant under linear transformations. The generalized canonical ensembles on the more and less detailed levels are given in terms of the longer list  $\lambda(x)$  and the shorter list  $\Lambda(y)$  of Lagrange multipliers. The conditional probability density  $\rho_y(x)$  for given  $y$  is then obtained by calculating the Lagrange multipliers  $\Lambda(y)$  associated with  $y$  and choosing the longer list of Lagrange multipliers,

$$\lambda(x) = \Lambda(y) Q^\Pi, \quad (11)$$

thus representing merely the coarser physics on the finer level of description. All microstates contributing to  $y = \langle \Pi \rangle_y = Q^\Pi \langle x \rangle_y$  then contribute in an equivalent way to a properly matched state  $x$  associated with  $\lambda(x)$ . We hence have

$$\rho_y(x) = \left| \det \left( \frac{\partial \lambda(x)}{\partial x} \right) \right| \delta(\lambda(x) - \Lambda(y) Q^\Pi). \quad (12)$$

Moreover, the entropy  $S'(y)$  is then given by  $S(x)$ , provided that the Lagrange multipliers associated with  $y$  and  $x$  are related by Eq. (11). This transformation rule for the entropy can also be expressed in the surprisingly simple form

$$S'(y) = \int S(x) \rho_y(x) \mathcal{D}x = \langle S \rangle_y. \quad (13)$$

No new entropy arises upon eliminating degrees of freedom when the relation between the levels, which can be handled by generalized canonical ensembles, is linear. The assumption of a linear transformation should not be regarded as a sign of untypical simplicity, but rather indicates that we rely on a rich level of description in terms of configurational distribution functions. For example, Fokker-Planck equations for stochastic processes or the Schrödinger equation of quantum mechanics are linear in probability densities or wave functions, respectively, but they typically represent highly nonlinear configurational processes. The passage to reduced distributions and moments is a linear transformation. At the

same time, there is a natural Boltzmann-type entropy associated with probability densities.

We now turn from the generators to the brackets. For two observables  $A(y)$  and  $B(y)$  on the coarse-grained level, we can consider the observables  $A(\Pi(x))$  and  $B(\Pi(x))$  on the more detailed level, for which we know how to evaluate a Poisson bracket. The result is a new observable depending on  $x$ . By averaging this new observable with  $\rho_y(x)$ , we obtain an observable on the less detailed level, which we take as our new coarse-grained Poisson bracket. This construction can be summarized by the equation

$$\{A, B\}' = \langle \{A, B\} \rangle_y. \quad (14)$$

If the same construction happens to provide the full dissipative bracket,

$$[A, B]' = \langle [A, B] \rangle_y, \quad (15)$$

then we speak of a reduction procedure. The dissipative processes on both levels are the same; they are merely described with different resolution in terms of different variables. It often happens, however, that new dissipative processes arise upon eliminating degrees of freedom because some fast reversible processes are eliminated, so that new fluctuations and hence dissipation arise. We then deal with coarse graining (see [17] for more information on the implications of the fundamental distinction between model reduction and coarse graining). The relevant background for coarse graining is that of the fluctuation-dissipation theorem and Green-Kubo formulas [13]. An additional contribution

$$[A, B]'' = \frac{1}{2k_B} \frac{d}{d\tau} \langle A(\Pi(x(\tau))) B(\Pi(x(\tau))) \rangle_y \quad (16)$$

to the dissipative bracket arises. The trajectory  $x(\tau)$  is constructed by means of the GENERIC evolution on the detailed level from initial conditions  $x(0)$  distributed according to  $\rho_y(x)$ , and  $k_B$  is Boltzmann's constant. For a clear separation of time scales between the variables eliminated and kept in passing to the less detailed level of description, the expression (16) should be independent of  $\tau$ , provided that  $\tau$  is intermediate between the fast and slow time scales. Fast degrees of freedom of the more detailed level are turned into random fluctuations of the coarse level so that we lose mechanistic control of some processes and new dissipative processes arise.

### III. POLYMER SOLUTIONS

For discussing dynamic renormalization from a thermodynamic perspective, we here consider dilute polymer solutions. The starting point for our discussion of the flow behavior of dilute polymer solutions is the Rouse model [18]. In that model, the polymers are represented by linear chains of identical, spherical “beads” connected by Hookean “springs.” The solvent is modeled as a Newtonian fluid, which is completely characterized by its viscosity. The assumption of purely entropic Hookean springs—that is, the absence of finite-extensibility and excluded-volume effects—requires long chains and a suitable, poor solvent

quality ( $\Theta$  point; see, for example, Sec. II.2 of [19]). An important physical effect, which is studied here, but was neglected in the original Rouse model, is the perturbation of the solvent flow field caused by the beads of the polymer chains on moving through the solvent. Such perturbations propagate through the solvent and hence influence the motion of the other beads. This complicated nonlinear phenomenon is known as “hydrodynamic interaction” [20,21]. The simple bead-spring model is known to be successful in predicting the universal properties of dilute polymer solutions which result from the self-similarity of long-chain molecules.

#### A. Diffusion equation

Our development is based on conventional polymer kinetic theory—that is, on the Kirkwood diffusion equation for the polymer dynamics—generalized to  $d$ -dimensional space. The generalization to  $d$  dimensions does not introduce any fundamental changes or practical difficulties, but makes our discussion more directly comparable to previous calculations which make use of the fact that hydrodynamic interaction effects become weak near  $d=4$  and can thus be treated perturbatively.

In the bead-spring model, the conformation of a polymer chain can be characterized by the  $N$  bead-position vectors  $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N$  with respect to the origin of a laboratory-fixed coordinate frame. The velocity field of the incompressible Newtonian solvent in which these polymer chains are suspended is assumed to be homogeneous—that is,  $\mathbf{v}(\mathbf{r}) = \mathbf{v}_0 + \boldsymbol{\kappa}(t) \cdot \mathbf{r}$ , with a constant vector  $\mathbf{v}_0$  and a traceless transpose velocity gradient tensor  $\boldsymbol{\kappa}(t)$  independent of the position  $\mathbf{r}$ , but possibly dependent on the time  $t$ . Then, the diffusion equation for the configurational distribution function  $\psi = \psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$  of the bead-spring model with Hookean springs and configuration-dependent hydrodynamic interactions is [see, for example, Eqs. (15.1-4) and (15.4-4) of [22] or Eq. (4.63) of [23]]

$$\begin{aligned} \frac{\partial \psi}{\partial t} = & - \sum_{\mu=1}^N \frac{\partial}{\partial \mathbf{r}_\mu} \cdot \left[ \mathbf{v}(\mathbf{r}_\mu) + \frac{1}{\zeta} \mathbf{F}_\mu + \sum_{\nu=1}^N \boldsymbol{\Omega}(\mathbf{r}_\mu - \mathbf{r}_\nu) \cdot \mathbf{F}_\nu \right] \psi \\ & + \frac{k_B T}{\zeta} \sum_{\mu=1}^N \frac{\partial}{\partial \mathbf{r}_\mu} \cdot \frac{\partial}{\partial \mathbf{r}_\mu} \psi \\ & + k_B T \sum_{\substack{\mu, \nu=1 \\ \mu \neq \nu}}^N \frac{\partial}{\partial \mathbf{r}_\mu} \cdot \boldsymbol{\Omega}(\mathbf{r}_\mu - \mathbf{r}_\nu) \cdot \frac{\partial}{\partial \mathbf{r}_\nu} \psi, \end{aligned} \quad (17)$$

where the force  $\mathbf{F}_\mu$  on bead  $\mu$  consists of two spring contributions with spring constant  $H$  (the first contribution is missing for  $\mu=1$ ; the second contribution is missing for  $\mu=N$ ):

$$\mathbf{F}_\mu = H(\mathbf{r}_{\mu-1} - \mathbf{r}_\mu) + H(\mathbf{r}_{\mu+1} - \mathbf{r}_\mu). \quad (18)$$

Furthermore,  $T$  is the absolute temperature,  $\zeta$  is the bead friction coefficient, and  $\boldsymbol{\Omega}(\mathbf{r})$  is the hydrodynamic-interaction tensor. The only way in which the space dimension  $d$  affects the above equations is through the concrete form of the hydrodynamic-interaction tensor  $\boldsymbol{\Omega}(\mathbf{r})$ . In three dimensions, the well-known Oseen tensor can be derived by

solving the Navier-Stokes equation for an external force exerted at a single point in space on a Newtonian solvent. In doing so, the Navier-Stokes equation is linearized—that is, advection-terms are neglected—and the solvent relaxation is assumed to be very fast compared to typical polymer relaxation processes (at least, on a length scale comparable to the radius of gyration of a polymer) [24]. In other words, the Oseen tensor is the Green's function for the time-independent, linearized Navier-Stokes equation in  $d$  dimensions. An explicit expression for the Oseen tensor can be constructed by Fourier transformation:

$$\mathbf{\Omega}(\mathbf{r}) = \frac{1}{(2\pi)^d} \int \frac{1}{\eta_s k^2} \left( \mathbf{1} - \frac{\mathbf{k}\mathbf{k}}{k^2} \right) e^{i\mathbf{k}\cdot\mathbf{r}} d^d k, \quad (19)$$

where  $k$  is the length of the wave vector  $\mathbf{k}$  and  $\eta_s$  is the solvent viscosity. Note that the divergence of  $\mathbf{\Omega}(\mathbf{r})$  vanishes. The occurrence of  $\eta_s$  in the expression (19) shows the dissipative character of hydrodynamic interactions. When comparing the second-order-derivative terms in the diffusion equation (17), we are led to introduce the dimensionless parameter

$$\xi = \frac{\zeta}{\eta_s} \left( \frac{k_B T}{H} \right)^{(2-d)/2}, \quad (20)$$

where  $(k_B T/H)^{1/2}$  is a characteristic length scale of a connector spring. The dimensionless parameter  $\xi$  characterizes the strength of hydrodynamic interactions compared to single-bead friction on the bead level.

The validity of the description of hydrodynamic interactions through Oseen tensors may be questioned because it describes only the behavior at large distances and without considering a finite propagation speed. However, at least to first order in the deviation from four dimensions, the Oseen-tensor approximation has been shown to be sufficient and a coupled dynamic treatment of the polymer molecules and the solvent is not required [24–27].

## B. GENERIC formulation

The GENERIC formulation of complex liquids requires hydrodynamic plus structural variables. For the bead-spring model of dilute polymer solutions, we use the variables  $x = (\rho(\mathbf{r}), \mathbf{M}(\mathbf{r}), \epsilon(\mathbf{r}), \psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N))$ , where  $\rho$  is the mass density,  $\mathbf{M}$  is the momentum density,  $\epsilon$  is the internal energy density, and  $\psi$  is the previously introduced configurational distribution function. We here do not repeat the contributions to the GENERIC building blocks associated with the hydrodynamic fields (see, for example, [12,13]) and focus on the polymer contributions to the entropy and the dissipative bracket. The energy is safely assumed to be independent of the polymer configuration, and the convection of  $\psi$  expressed in the Poisson bracket is straightforward.

The polymer contribution to the entropy is given by

$$S_p = - \int \left[ \frac{H}{2T} \sum_{\mu=1}^{N-1} (\mathbf{r}_{\mu+1} - \mathbf{r}_\mu)^2 + k_B \ln \psi \right] \psi d^d r_1 \cdots d^d r_N. \quad (21)$$

This expression highlights the entropic nature of the spring constant  $H$  associated with the larger number of coiled rather than stretched states. To obtain Eq. (21) for the extensive configurational entropy, we have assumed that the normalization of  $\psi$  is such that the integral of  $\psi$  over all bead positions gives the total number of polymer molecules in the solution.

We write the polymer contribution to the dissipative bracket as the sum of two contributions:

$$[A, B]_p = [A, B]_{\text{intra}} + [A, B]_{\text{inter}}. \quad (22)$$

The first contribution is associated with the friction coefficient of the individual beads,

$$[A, B]_{\text{intra}} = \sum_{\mu=1}^N \int \frac{T}{\zeta} \left( \frac{\partial}{\partial \mathbf{r}_\mu} \frac{\delta A}{\delta \psi} \right) \cdot \left( \frac{\partial}{\partial \mathbf{r}_\mu} \frac{\delta B}{\delta \psi} \right) \psi d^d r_1 \cdots d^d r_N, \quad (23)$$

whereas the second one represents the hydrodynamic interactions between different beads,

$$[A, B]_{\text{inter}} = \sum_{\substack{\mu, \nu=1 \\ \mu \neq \nu}}^N \int T \left( \frac{\partial}{\partial \mathbf{r}_\mu} \frac{\delta A}{\delta \psi} \right) \cdot \mathbf{\Omega}(\mathbf{r}_\mu - \mathbf{r}_\nu) \cdot \left( \frac{\partial}{\partial \mathbf{r}_\nu} \frac{\delta B}{\delta \psi} \right) \psi d^d r_1 \cdots d^d r_N. \quad (24)$$

When introduced into the fundamental GENERIC equation (1), the polymer contributions to the entropy (21) and to the dissipative bracket (22) reproduce all irreversible terms in the diffusion equation (17)—that is, all terms except for the reversible velocity term.

## IV. DYNAMIC RENORMALIZATION

The bead concept is a fictitious one. Relevant predictions should not depend on whether we choose smaller or larger beads. In passing from smaller to larger beads, interactions between several smaller beads must be accommodated in the properties of a single larger bead. This is the essence of renormalization. In our example, hydrodynamic interactions between different small beads are expected to contribute to the friction coefficient of a larger bead. Dissipative processes associated with the bracket contribution  $[A, B]_{\text{inter}}$  for small beads are moved into the dissipative-bracket contribution  $[A, B]_{\text{intra}}$ . The only reversible process contributing to polymer dynamics—namely, convection—is present on all length scales and does not lead to additional dissipation on larger scales.

In summary, dynamic renormalization is deeply linked with the reshuffling of terms from  $[A, B]_{\text{inter}}$  to  $[A, B]_{\text{intra}}$ . Whereas we could imagine converting self-similar reversible processes on all length and time scales into dissipation, this clearly is not the case for our example of dilute polymer

solutions. The dynamic renormalization of hydrodynamic interactions can hence be classified as a reduction technique rather than a coarse-graining procedure. We expect the reshuffling of dissipative terms to be a rather natural and general scenario. In fact, it would be interesting to find an example of dynamic renormalization in which reversible processes, on all length and time scales, are turned into dissipative processes—that is, an example of coarse graining.

### A. Entropy

We now apply the general rules for eliminating degrees of freedom to the polymer contributions to the entropy (21) and to the dissipative bracket (22). To do so, we introduce the following decimation procedure of the linear type:

$$\Psi(\mathbf{R}_1, \dots, \mathbf{R}_M) = \int \left[ \prod_{m=1}^M \delta \left( \mathbf{R}_m - \frac{1}{K} \sum_{\mu \in I_m} \mathbf{r}_\mu \right) \right] \times \psi(\mathbf{r}_1, \dots, \mathbf{r}_N) d^d r_1 \cdots d^d r_N, \quad (25)$$

where the number of bead vectors has been reduced by a factor of  $K$  from  $N$  to  $M=N/K$  and each  $I_m$  is a set of  $K$  consecutive integers,

$$I_m = \{(m-1)K+1, \dots, mK\}, \quad m = 1, \dots, M. \quad (26)$$

In words,  $K$  consecutive beads of the original bead-spring chain are collapsed into a single new bead at the center-of-mass location. The choice of the center-of-mass position is preferable over other possibilities because it is fully consistent with iterating the decimation procedure. For a functional  $A$  of  $\Psi$ , which can be expressed as a functional  $A$  of  $\psi$  by inserting Eq. (25), it is useful to know the functional derivative

$$\frac{\delta A}{\delta \psi(\mathbf{r}_1, \dots, \mathbf{r}_N)} = \int \left[ \prod_{m=1}^M \delta \left( \mathbf{R}_m - \frac{1}{K} \sum_{\mu \in I_m} \mathbf{r}_\mu \right) \right] \times \frac{\delta A}{\delta \Psi(\mathbf{R}_1, \dots, \mathbf{R}_M)} d^d R_1 \cdots d^d R_M. \quad (27)$$

Note that the transformation  $\psi \rightarrow \Psi$  is linear and maps a probability density onto another one. According to Eqs. (6.147) and (6.151) of [13], for probability densities, the Lagrange multipliers of the generalized canonical ensemble can be interpreted as dimensionless “effective potentials” in the representation

$$\psi(\mathbf{r}_1, \dots, \mathbf{r}_N) \propto \omega(\mathbf{r}_1, \dots, \mathbf{r}_N) e^{-\lambda(\mathbf{r}_1, \dots, \mathbf{r}_N)}, \quad (28)$$

where  $\omega(\mathbf{r}_1, \dots, \mathbf{r}_N)$  is the number of microstates consistent with beads at the positions  $\mathbf{r}_1, \dots, \mathbf{r}_N$  and the entropy is given by

$$S = k_B \int [\ln \omega - \ln \psi] \psi d^d r_1 \cdots d^d r_N. \quad (29)$$

By comparison with Eq. (21), we find the natural Gaussian result

$$\omega(\mathbf{r}_1, \dots, \mathbf{r}_N) = \left( \frac{2\pi k_B T}{H} \right)^{-d(N-1)/2} \times \exp \left\{ -\frac{H}{2k_B T} \sum_{\mu=1}^{N-1} (\mathbf{r}_{\mu+1} - \mathbf{r}_\mu)^2 \right\}. \quad (30)$$

For the further discussion, in which correlations between neighboring connector vectors occur, it is actually convenient to consider the more general version

$$\omega(\mathbf{r}_1, \dots, \mathbf{r}_N) = \left[ \left( \frac{2\pi k_B T}{H} \right)^{N-1} \det \sigma \right]^{-d/2} \exp \left\{ -\frac{H}{2k_B T} \sum_{\mu, \nu=1}^{N-1} \sigma_{\mu\nu}^{-1} (\mathbf{r}_{\mu+1} - \mathbf{r}_\mu) \cdot (\mathbf{r}_{\nu+1} - \mathbf{r}_\nu) \right\}, \quad (31)$$

from which the special case in Eq. (30) is recovered for strictly local correlations  $\sigma_{\mu\nu} = \delta_{\mu\nu}$ .

We similarly have

$$\Psi(\mathbf{R}_1, \dots, \mathbf{R}_M) \propto \Omega(\mathbf{R}_1, \dots, \mathbf{R}_M) e^{-\Lambda(\mathbf{R}_1, \dots, \mathbf{R}_M)}, \quad (32)$$

where  $\Omega(\mathbf{R}_1, \dots, \mathbf{R}_M)$  now is the number of microstates consistent with the larger beads at the positions  $\mathbf{R}_1, \dots, \mathbf{R}_M$  and the entropy is given by

$$S = k_B \int [\ln \Omega - \ln \Psi] \Psi d^d R_1 \cdots d^d R_M. \quad (33)$$

The consistency (11) of the Lagrange multipliers on both levels of description can be expressed as

$$\lambda(\mathbf{r}_1, \dots, \mathbf{r}_N) = \Lambda \left( \frac{1}{K} \sum_{\mu \in I_1} \mathbf{r}_\mu, \dots, \frac{1}{K} \sum_{\mu \in I_M} \mathbf{r}_\mu \right), \quad (34)$$

and Eq. (25) then gives the following intuitive relationship expressing proper successive counting:

$$\Omega(\mathbf{R}_1, \dots, \mathbf{R}_M) = \int \left[ \prod_{m=1}^M \delta \left( \mathbf{R}_m - \frac{1}{K} \sum_{\mu \in I_m} \mathbf{r}_\mu \right) \right] \times \omega(\mathbf{r}_1, \dots, \mathbf{r}_N) d^d r_1 \cdots d^d r_N. \quad (35)$$

With this identification, the constants of proportionality in Eqs. (28) and (32) are equal. In terms of the respective Fourier transforms  $\tilde{\Omega}$  and  $\tilde{\omega}$ , which facilitate the subsequent calculations, this identity can be rewritten as

$$\tilde{\Omega}(\mathbf{Q}_1, \dots, \mathbf{Q}_M) = \tilde{\omega} \left( \frac{\mathbf{Q}_1}{K}, \dots, \frac{\mathbf{Q}_1}{K}, \dots, \frac{\mathbf{Q}_M}{K}, \dots, \frac{\mathbf{Q}_M}{K} \right), \quad (36)$$

where, on the right-hand side, each argument occurs  $K$  consecutive times. Because the Fourier transforms of Gaussians are Gaussians, all practical calculations can be reduced to operations on matrices of second moments. For the general form (31) of  $\omega$ , the Fourier transform is given by

$$\tilde{\omega}(\mathbf{q}_1, \dots, \mathbf{q}_N) = (2\pi)^d \delta\left(\sum_{\mu=1}^N \mathbf{q}_\mu\right) \exp\left\{-\frac{1}{2} \frac{k_B T}{H} \times \sum_{\mu, \nu=1}^{N-1} F_{\mu\nu}^{(N)} \mathbf{q}_\mu \cdot \mathbf{q}_\nu\right\}, \quad (37)$$

where the matrix

$$F_{\mu\nu}^{(N)} = \sum_{j,k=1}^{N-1} B_{\mu j} \sigma_{jk} B_{\nu k} \quad (38)$$

is most conveniently defined in terms of the auxiliary matrix expressing the transformation from connector vectors  $\mathbf{r}_{\mu+1} - \mathbf{r}_\mu$  to bead positions  $\mathbf{r}_\mu$  (see p. 23 of [22]):

$$B_{\mu j} = \begin{cases} j/N & \text{for } \mu > j \\ (j/N) - 1 & \text{for } \mu \leq j. \end{cases} \quad (39)$$

The  $\delta$  function in Eq. (37) is associated with freedom of overall translations of the polymer molecules.

For the standard assumption of uncorrelated connector vectors ( $\sigma_{jk} = \delta_{jk}$ ), the matrix  $F_{\mu\nu}^{(N)}$  has the explicit form

$$F_{\mu\nu}^{(N)} = \frac{(N+1)(2N+1)}{6N} + \frac{\mu(\mu-1) + \nu(\nu-1)}{2N} - \max(\mu, \nu), \quad (40)$$

with the interesting property

$$\sum_{\mu \in I_m} \sum_{\nu \in I_n} F_{\mu\nu}^{(N)} = K^3 F_{mn}^{(M)} + \frac{1}{6} K(K^2 - 1) \left( \frac{1}{M} - \delta_{mn} \right), \quad (41)$$

which is important when it comes to evaluating the right-hand side of Eq. (36). Without the underlined last term, which actually is only a small correction term, the entropy on the less detailed level of description would be of the same form as in Eqs. (21) and (30) for the more detailed starting level, however, with the renormalized spring constant

$$H' = \frac{H}{K}. \quad (42)$$

The underlined term in Eq. (41) signals that, if one starts with uncorrelated connector vector in the formulation of  $\omega$ , there must be correlations in the connectors on the less detailed level. The development of such correlations under coarse graining has been discussed before [28]. They are limited to nearest-neighbor correlations, and they are a consequence of placing the coarser beads at the center of mass of a collection of smaller beads. The results of [28] suggest to choose

$$\sigma_{jk} = \delta_{jk} + \frac{1}{4} (\delta_{jk+1} + \delta_{kj+1}). \quad (43)$$

Once such nearest-neighbor correlations of relative strength 1/4 are introduced, the corresponding  $F_{\mu\nu}^{(N)}$  defined in Eq.

(38) satisfies the invariance property (41) without the underlined term or any other correction terms. In other words, the entropy associated with  $\omega$  in Eq. (31) for the almost (rather than strictly) local correlations (43) is rigorously invariant under coarse graining. The entropic springs of the famous Rouse-Zimm model are not fully appropriate because any type of bead is located at the center of mass of a collection of monomers and is hence correlated with its neighbors. The incorporation of the invariance idea (43) and the renormalization (42) of the entropic spring constant complete our calculation of the entropy (33) on the less detailed level of description from the one on the more detailed one. Note that the expression for the invariant entropic spring potential,

$$\Phi_S = -\frac{\hat{H}}{2} \sum_{\mu, \nu=1}^{N-1} \sigma_{\mu\nu}^{-1} (\mathbf{r}_{\mu+1} - \mathbf{r}_\mu) \cdot (\mathbf{r}_{\nu+1} - \mathbf{r}_\nu), \quad (44)$$

involves the inverse of the matrix  $\sigma_{jk}$  defined in Eq. (43) and hence contains contributions from all pairs of beads. We here use the symbol  $\hat{H}$  because the correlations require a spring constant stronger than  $H$  (actually, one should use  $\hat{H} = \frac{3}{2}H$ ).

## B. Dissipative bracket

For functionals  $A$  and  $B$  of  $\Psi$ , the evaluation of the dissipative bracket  $[A, B]_{\text{intra}}$  according to its definition in Eq. (23) is straightforward. By means of Eq. (27), we obtain the rigorous result

$$[A, B]_{\text{intra}} = \sum_{m=1}^M \int \frac{T}{K\zeta} \left( \frac{\partial}{\partial \mathbf{R}_m} \frac{\delta A}{\delta \Psi} \right) \cdot \left( \frac{\partial}{\partial \mathbf{R}_m} \frac{\delta B}{\delta \Psi} \right) \times \Psi d^d R_1 \cdots d^d R_M, \quad (45)$$

which has the nice feature of depending on  $\psi$  only through  $\Psi$ . Averaging hence does not change that expression any further. Note that, compared to Eq. (23), the friction coefficient  $K\zeta$  occurs instead of  $\zeta$ . From Eq. (24), we similarly obtain the rigorous reformulation

$$[A, B]_{\text{inter}} = \sum_{m,n=1}^M \int T \left( \frac{\partial}{\partial \mathbf{R}_m} \frac{\delta A}{\delta \Psi} \right) \cdot \Omega_{mn} \cdot \left( \frac{\partial}{\partial \mathbf{R}_n} \frac{\delta B}{\delta \Psi} \right) \times \Psi d^d R_1 \cdots d^d R_M, \quad (46)$$

with

$$\Omega_{mn} \Psi(\mathbf{R}_1, \dots, \mathbf{R}_M) = \frac{1}{K^2} \sum_{\substack{\mu \in I_m, \nu \in I_n \\ \mu \neq \nu}} \int \Omega(\mathbf{r}_\mu - \mathbf{r}_\nu) \times \left[ \prod_{k=1}^M \delta \left( \mathbf{R}_k - \frac{1}{K} \sum_{\mu \in I_k} \mathbf{r}_\mu \right) \right] \times \psi(\mathbf{r}_1, \dots, \mathbf{r}_N) d^d r_1 \cdots d^d r_N. \quad (47)$$

The formal appearance of Eq. (46) is very similar to Eq. (24), but the tensors  $\Omega_{mn}$  defined in Eq. (47) are much more complicated objects than the hydrodynamic interaction tensors

$\Omega(\mathbf{r}_\mu - \mathbf{r}_\nu)$ . In principle, the tensors  $\Omega_{mn}$  could depend on all the bead positions  $\mathbf{R}_1, \dots, \mathbf{R}_M$ , and the functional form then even depends on the particular choice of  $\psi$ . According to the ensemble in Eq. (12), averaging over  $\psi$  corresponds to the proper choice (34) of Lagrange multipliers on the more detailed level. By using Eqs. (28) and (32) with equal constants of proportionality, we obtain

$$\Omega_{mn} = \Omega_{mn}(\mathbf{R}_1, \dots, \mathbf{R}_M) = \frac{1}{K^2} \sum_{\substack{\mu \in I_m, \nu \in I_n \\ \mu \neq \nu}} \langle \Omega(\mathbf{r}_\mu - \mathbf{r}_\nu) \rangle_{\mathbf{R}_1, \dots, \mathbf{R}_M}^{\text{eq}}, \quad (48)$$

where, for any function  $A(\mathbf{r}_1, \dots, \mathbf{r}_N)$ ,

$$\langle A \rangle_{\mathbf{R}_1, \dots, \mathbf{R}_M}^{\text{eq}} = \frac{\int A(\mathbf{r}_1, \dots, \mathbf{r}_N) \left[ \prod_{m=1}^M \delta\left(\mathbf{R}_m - \frac{1}{K} \sum_{\mu \in I_m} \mathbf{r}_\mu\right) \right] \omega(\mathbf{r}_1, \dots, \mathbf{r}_N) d^d r_1 \cdots d^d r_N}{\Omega(\mathbf{R}_1, \dots, \mathbf{R}_M)} \quad (49)$$

is the conditional expectation of  $A$  for given positions  $\mathbf{R}_1, \dots, \mathbf{R}_M$  of the coarse-grained beads, performed with the equilibrium distribution function.

The expression (48) is still rigorous. The occurrence of equilibrium averages is a nice simplifying feature. The physical origin of this simplification lies in the matching of the Lagrange multipliers, which implies that only the large-scale features represented by the coarser level can feel non-equilibrium effects. This simplification is a direct consequence of the fundamental assumption of a separation of time scales in nonequilibrium thermodynamics. The full complexity of this calculation without scale separation can be found in [29].

For the further discussion of the hydrodynamic-interaction tensors  $\Omega_{mn}$  in Eq. (48), we distinguish the cases  $m \neq n$  and  $m = n$ . For  $m \neq n$ , the small beads  $\mu \in I_m$  are grouped around  $\mathbf{R}_m$  and the small beads  $\nu \in I_n$  are located near  $\mathbf{R}_n$ . We may hence use the approximation

$$\Omega(\mathbf{r}_\mu - \mathbf{r}_\nu) \approx \Omega(\mathbf{R}_m - \mathbf{R}_n) \quad (50)$$

in Eq. (48). This approximation becomes exact when  $m$  and  $n$  are far apart, which, in the limit of long chains, happens for the majority of pairs  $m, n$ . For small differences  $|m - n|$ , the approximation (50) becomes better when the rescaling factor  $K$  increases. After performing the trivialized conditional average in Eq. (48), we obtain the result

$$\Omega_{mn} = \Omega(\mathbf{R}_m - \mathbf{R}_n) \quad \text{for } m \neq n. \quad (51)$$

The more interesting part of the renormalization procedure now happens for  $m = n$ . Hydrodynamic interactions between small beads  $\mu$  and  $\nu$  contribute to the friction coefficient of the large bead  $m$ . From Eq. (48), we have the exact expression

$$\Omega_{mm} = \frac{1}{K^2} \sum_{\substack{\mu, \nu \in I_m \\ \mu \neq \nu}} \langle \Omega(\mathbf{r}_\mu - \mathbf{r}_\nu) \rangle_{\mathbf{R}_1, \dots, \mathbf{R}_M}^{\text{eq}}. \quad (52)$$

The absolute position  $\mathbf{R}_m$  is irrelevant for the average  $\Omega_{mm}$ . According to the above discussion of the entropy, however, the relative positions of the neighboring coarse beads,

$\mathbf{R}_{m \pm 1} - \mathbf{R}_m$ , might have an influence on the conditional averages in Eq. (52). In the spirit of the Rouse-Zimm model, we neglect this potential correlation and approximate  $\Omega_{mm}$  by an unconditional average that is independent of the configuration and also of  $m$ :

$$\Omega_{mm} = \frac{1}{K^2} \sum_{\substack{\mu, \nu \in I_m \\ \mu \neq \nu}} \langle \Omega(\mathbf{r}_\mu - \mathbf{r}_\nu) \rangle^{\text{eq}} = \frac{D_K}{k_B T} \mathbf{1}. \quad (53)$$

Again, we expect the effect of the approximation to become negligible for large rescaling factors  $K$  because all the proper universal correlations develop within a single large bead. We introduced the symbol  $D_K$  for this equilibrium average because it actually coincides with the Kirkwood approximation for the diffusion coefficient of a polymer molecule consisting of  $K$  beads [22,30]. By incorporating  $\Omega_{mm}$  into the friction coefficient  $\zeta'$  of the large beads, we obtain from Eqs. (45) and (53)

$$\frac{1}{\zeta'} = \frac{1}{K\zeta} + \frac{D_K}{k_B T}. \quad (54)$$

The renormalization of the friction coefficient happens through adding mobilities. For large rescaling factors  $K$ , the decay of the diffusion coefficient in  $d < 4$  dimensions is weaker than  $1/K$  so that we find the following asymptotic behavior of the renormalized friction coefficient:

$$\zeta' \approx \frac{k_B T}{D_K}. \quad (55)$$

The diffusion coefficient introduced in Eq. (53) can be evaluated by inserting the hydrodynamic interaction tensor (19) and using the Fourier-transformed probability density (37):

$$\frac{D_K}{k_B T} = \frac{1}{K^2} \sum_{\substack{\mu, \nu=1 \\ \mu \neq \nu}}^K \frac{1}{(2\pi)^d} \frac{d-1}{d} \int \frac{1}{\eta_s k^2} \times \exp \left\{ -\frac{1}{2} \frac{k_B T}{H} (F_{\mu\mu}^{(K)} + F_{\nu\nu}^{(K)} - 2F_{\mu\nu}^{(K)}) k^2 \right\} d^d k. \quad (56)$$

After introducing (40) and performing the Gaussian integrations, we obtain

$$\frac{D_K}{k_B T} = \frac{1}{K^2} \sum_{\substack{\mu, \nu=1 \\ \mu \neq \nu}}^K \frac{1}{(2\pi)^{d/2}} \frac{d-1}{d(d-2)} \frac{1}{\eta_s} \left( |\mu - \nu| \frac{k_B T}{H} \right)^{-(d-2)/2}. \quad (57)$$

The sums can be approximated by integrals and then evaluated to obtain the simple result

$$\frac{D_K}{k_B T} = \frac{1}{\xi^*} \frac{1}{\eta_s} \left( K \frac{k_B T}{H} \right)^{-(d-2)/2}, \quad (58)$$

with the constant prefactor

$$\xi^* = (2\pi)^{d/2} \frac{d(d-2)(4-d)(6-d)}{8(d-1)} \quad \text{for } 2 \leq d \leq 4. \quad (59)$$

In terms of the dimensionless hydrodynamic interaction parameter  $\xi$  introduced in Eq. (20), the renormalization (54) can be rewritten as

$$\frac{1}{\xi'} = K^{-(4-d)/2} \frac{1}{\xi} + \frac{1}{\xi^*}. \quad (60)$$

We thus recognize that  $\xi^*$  is the asymptotic value of  $\xi'$  for large rescaling factors  $K$ . By differentiation we obtain the following equation for the evolution of  $\xi'$  with  $K$ :

$$\frac{d\xi'}{d \ln K} = \frac{4-d}{2} \xi' \left( 1 - \frac{\xi'}{\xi^*} \right). \quad (61)$$

The solution with proper initial conditions [note that Eq. (60) holds only for large  $K$  and certainly not for  $K=1$ ] can be written as

$$\left( \frac{1}{\xi'} - \frac{1}{\xi^*} \right) = K^{-(4-d)/2} \left( \frac{1}{\xi} - \frac{1}{\xi^*} \right), \quad (62)$$

which emphasizes the role of  $\xi^*$  as the fixed point of the renormalization-group transformation. Near four dimensions, Eq. (59) implies the well-known result [7]

$$\xi^* \approx \frac{8}{3} \pi^2 (4-d) \quad (63)$$

for the fixed point.

The calculations of the renormalized entropy and dissipative bracket are strongly affected by the fact that we locate the larger beads at the center of mass of a collection of smaller beads. This leads to the particular correlations given in Eq. (43) and to the occurrence of the Kirkwood approximation to the diffusion coefficient in the renormalized friction

coefficient (54). The calculation of the exact diffusion coefficient is usually based on considering the random motion of the center of resistance rather than the center of mass [22,30]. However, such an alternative does not exist in the definition of the coarse-graining transformation because this transformation should not involve any dynamic material information.

## V. SUMMARY AND CONCLUSIONS

We have introduced the idea of performing dynamic renormalization on the building blocks of nonequilibrium thermodynamics as a generalization of the usual renormalization of Hamiltonians at equilibrium. This offers an alternative to calculating and analyzing specific observables associated with dynamic material behavior. As a concrete example, we have considered the renormalization of the entropy and the dissipative bracket, or friction matrix, for dilute polymer solutions with hydrodynamic interactions.

The usual entropy associated with independent Hookean springs is found to be not invariant under renormalization. Correlations between neighboring connector vectors need to be considered so that the invariant entropy is a more general quadratic form of the bead positions. Contrary to this invariant generalized form of the entropy, the simple transformation behavior (42) of the spring constant is well known.

The discussion of the dissipative bracket reveals that renormalization is a reduction technique. The renormalization does not require any calculation of two-time correlation functions or other dynamic information. On decimating the number of degrees of freedom, dissipative hydrodynamic interactions between different beads are incorporated into the friction coefficient of a single larger bead, which leads to a nontrivial renormalization of the friction coefficient. This renormalization of the friction coefficient has several interesting features.

(i) The renormalization is determined by the Kirkwood approximation to the diffusion coefficient (rather than the exact diffusion coefficient).

(ii) The calculation of the renormalized friction coefficient does not make use of perturbation theory or the analysis of the singular behavior of any observable.

(iii) The rigorous fixed-point value of the friction coefficient is readily calculated in any space dimension.

Analytical calculations are feasible because we work on the rich level of configurational distribution functions. The decimation procedure hence requires only the linear operation of contracting distribution functions, and as a consequence, we can benefit from the convenience of generalized canonical ensembles. The calculations are further simplified by assuming a separation of time scales, which implies that the eliminated degrees of freedom are equilibrated. The final integrations for long chains can be performed with isotropic Gaussian distributions.

Whereas we do not make any use of perturbation theory, we obtain the simple results (61) and (62) for the renormalization of the friction coefficient, which are exactly of the form that would result from first-order perturbation theory. The automatic occurrence of the simplest perturbative result

seems to be related to the fact that the exponent governing the molecular-weight dependence of the size of polymer chains ( $\nu=1/2$ ) does not change due to the presence of hydrodynamic interactions. The surprising possibility to perform the renormalization by a nonperturbative procedure may be derogated by the fact that the diffusion equation for the configurational distribution function with the Oseen-tensor approximation, which is used as a starting point of our calculations, has only been justified to first order in the deviation from four dimensions [24–27]. This may also be the reason why, starting from the diffusion equation, different estimates of the fixed point in three dimensions have been found for different observables in Eq. (9) of [31].

Once the renormalization of the thermodynamic building blocks has been carried out, the results can be used to decimate the number of degrees of freedom of the original problem represented by the diffusion or Fokker-Planck equation (17). For our polymer chains, we can use the renormalized parameters for short chains in Eq. (17), and these short

chains can be treated by simulations, perturbation theory, or any other method limited to a small number of degrees of freedom (and hence not applicable without renormalization). In practice, it turns out that one needs to keep at least seven or eight beads to represent hydrodynamic interactions in three dimensions in a meaningful way. With increasing flow rate, also the number of beads to be kept in the model increases.

The thermodynamic approach to dynamic renormalization proposed in this paper can readily be applied to other systems exhibiting self-similarity. The fact that we deal with a reduction technique offers promising possibilities for extending equilibrium results to dynamic situations without performing any time-dependent calculations.

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