

General projection operator formalism for the dynamics and thermodynamics of complex fluids

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By applying the projection operator method, we derive the general equation for the nonequilibrium reversible-irreversible coupling (GENERIC) that, in previous work [Phys. Rev. E **56**, 6620 (1997); **56**, 6633 (1997)], was obtained by empirical arguments. We find microscopic expressions for the building blocks of GENERIC, and we generally derive the rules for passing from any given level of description to a more macroscopic one. [S1063-651X(98)15802-6]

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I. INTRODUCTION

We here derive the general form of the time-evolution equations for nonequilibrium systems, proposed as GENERIC in [1,2], by projection operator techniques. The general time-evolution equation can be written in the form

$$\frac{dx}{dt} = L(x) \frac{\delta E(x)}{\delta x} + M(x) \frac{\delta S(x)}{\delta x}, \quad (1)$$

where x represents a set of independent variables required for a complete description of the nonequilibrium system, the real-valued functionals E and S are the total energy and entropy expressed in terms of the state variables x , and L and M are certain matrices. Since x typically contains position-dependent fields, such as mass, momentum, and energy densities, the state variables are usually labeled by continuous (position) labels in addition to discrete ones. A matrix multiplication, or the application of a linear operator, hence implies not only summations over discrete labels but also integrations over continuous labels, and $\delta/\delta x$ typically implies functional rather than partial derivatives.

In the GENERIC framework, Eq. (1) is supplemented by the complementary degeneracy requirements

$$L(x) \frac{\delta S(x)}{\delta x} = 0, \quad (2)$$

and

$$M(x) \frac{\delta E(x)}{\delta x} = 0. \quad (3)$$

The requirement that the gradient $\delta S/\delta x$ is in the null space of L in Eq. (2) expresses the reversible nature of the L contribution to the dynamics: the functional form of the entropy is such that it cannot be affected by the operator generating the reversible dynamics. The requirement that the gradient $\delta E/\delta x$ is in the null space of M in Eq. (3) expresses the conservation of the total energy by the M contribution to the dynamics. Furthermore, it is required that the matrix L is antisymmetric, whereas M is symmetric and positive-semidefinite. Both the complementary degeneracy requirements (2), (3) and the symmetry properties are extremely

important for formulating proper L and M matrices when modeling concrete nonequilibrium problems [2]. The two contributions to the time evolution of x generated by the energy E and the entropy S in Eq. (1) are called the reversible and irreversible contributions to GENERIC, respectively.

Many important examples of nonequilibrium systems have been expressed in the GENERIC form [2]: hydrodynamics, polymer kinetic theory (including hydrodynamic interaction, rigid constraints, reptation models, and polymer heat conductivity), and chemical reactions. Moreover, the bracket formalism of Beris and Edwards [3], which includes the linear thermodynamics of irreversible processes, has been reproduced, and the relationship to extended irreversible thermodynamics has been elaborated.

The key innovation in the GENERIC structure is the use of two separate generators for the reversible and irreversible dynamics, together with the symmetric degeneracy requirements (see [3–10] and references therein for previous thermodynamic approaches which aim to describe the dynamical behavior of complex fluids). While nonequilibrium dynamics is usually expressed in terms of a single generator (the effective Hamiltonian or free energy functional [3]), the two-generator idea, which leaves more flexibility in the choice of variables, allows us to formulate the mutual degeneracy conditions and hence actually increases the predictive power of GENERIC [1,2]. In particular, the requirement (2) has very strong implications, such as the Gibbs-Duhem equation for the local equilibrium systems of hydrodynamics or the Kramers expression for the stress tensor in polymer kinetic theory. In new applications, results of similar significance can be expected. It is therefore very important to justify the two-generator idea and the degeneracy requirements, originally discovered by empirical observations, also by microscopic arguments.

The time evolution (1) is deterministic, but fluctuations can be added very naturally [1]. This can be done most conveniently by formulating the following diffusion equation or Fokker-Planck equation for the time-evolution of the configurational distribution function, $f(x,t)$,

$$\begin{aligned} \frac{\partial f(x,t)}{\partial t} = & - \frac{\partial}{\partial x} \left[\left(L \frac{\delta E}{\delta x} + M \frac{\delta S}{\delta x} \right) f(x,t) \right] \\ & + k_B \frac{\partial}{\partial x} \left[M \frac{\partial}{\partial x} f(x,t) \right]. \end{aligned} \quad (4)$$

The Fokker-Planck equation (4) can equivalently be rewritten as a stochastic differential equation [11],

$$dx = L \frac{\delta E}{\delta x} dt + M \frac{\delta S}{\delta x} dt + k_B \frac{\delta M}{\delta x} dt + B dW_t, \quad (5)$$

where B is a matrix with

$$BB^T = 2k_B M, \quad (6)$$

k_B is Boltzmann's constant, and W_t is a multicomponent Wiener process, that is, a Gaussian process with first and second moments given by

$$\langle W_t \rangle = 0, \quad \langle W_t W_{t'}^T \rangle = \min(t, t') 1, \quad (7)$$

or, more formally,

$$\left\langle \frac{dW_t}{dt} \right\rangle = 0, \quad \left\langle \frac{dW_t}{dt} \frac{dW_{t'}}{dt'} \right\rangle = \delta(t-t') 1. \quad (8)$$

The fluctuations can be eliminated from Eq. (5) to obtain Eq. (1) by going to the limit $k_B \rightarrow 0$ (without changing the GENERIC building blocks E, S, L, M), so that k_B may be regarded as a small parameter controlling the fluctuations.

II. PROJECTION OF HAMILTON'S EQUATIONS OF MOTION

We here derive the GENERIC structure and microscopic expressions for the building blocks E , S , L , and M by comparing the above Fokker-Planck equation to the one obtained by the projection operator technique. The standard tool of projection operators (see, for example, [12,13]) is here most conveniently used in the form developed in [14] (with the only exception that we here assume a microcanonical rather than a canonical ensemble). Since all the details of the projection operator derivation are worked out in [14], we here only need to compile the results obtained by comparing the equations.

The starting point for the projection operator approach is the purely reversible (fully microscopic) time-evolution equation

$$\frac{dz}{dt} = L_0 \frac{\delta E_0(z)}{\delta z}, \quad (9)$$

which corresponds to Hamilton's equations of motion; here $E_0(z)$ is the microscopic Hamiltonian, and the antisymmetric matrix L_0 (generating the Poisson bracket) does not depend on z .

The variables x of the coarse-grained description are obtained as phase space functions Π from the microscopic variables z , that is, $x = \Pi(z)$. It is crucial for the application of the projection operator method that there is a clear separation of time scales: the time-evolution of x (and all functions of x) is assumed to be much slower than of all the other variables in the system. In the projection operator approach, the quantity

$$\exp\left\{ \frac{S(x)}{k_B} \right\} = \int \delta(\Pi(z) - x) dz, \quad (10)$$

plays a central role. Equation (10) means that the entropy is obtained by counting the number of microscopic states z consistent with a more macroscopic state x ; this corresponds to a natural generalization of the Gibbs entropy formula from equilibrium thermodynamics.

The matrix $M(x)$ can be identified uniquely from the second-order derivative terms in the Fokker-Planck equation obtained by the projection operator method,

$$M(x) = \frac{1}{k_B} \exp\left\{ -\frac{S(x)}{k_B} \right\} \int_0^\tau dt \int \delta(\Pi(z) - x) \times [\dot{x}_0(z) - \dot{x}_1(x)] [\dot{x}_0(z(t)) - \dot{x}_1(x)] dz, \quad (11)$$

where

$$\dot{x}_0(z) = \frac{\delta \Pi(z)}{\delta z} L_0 \frac{\delta E_0(z)}{\delta z}, \quad (12)$$

$$\dot{x}_1(x) = \exp\left\{ -\frac{S(x)}{k_B} \right\} \int \dot{x}_0(z) \delta(\Pi(z) - x) dz, \quad (13)$$

$z(t)$ is the solution of the time-evolution equation (9) with $z(0) = z$, and τ is a time scale large enough for the time integral to converge and small enough for x to be still considered as independent of time (such an intermediate time scale exists due to the previously mentioned assumption of clearly separated time scales for the slow and fast variables).

While \dot{x}_0 is a state variable that varies on a very rapid, microscopic time scale, \dot{x}_1 depends only on $x = \Pi(z)$ and hence has a much slower time evolution. Thus, $\dot{x}_0 - \dot{x}_1$ describes fluctuation effects, which are incorporated in a white-noise approximation when going from Eq. (1) to Eq. (5). Equation (11), which holds for general nonequilibrium systems, has the form of the Green-Kubo expressions for transport coefficients known from linear response theory. Here we did not extend the time integral in Eq. (11) to infinity because then it might be necessary to consider the slow time evolution of \dot{x}_1 in the second factor.

After identifying the irreversible dynamics, it is a simple exercise to find the building blocks associated with the reversible dynamics. In the GENERIC approach it is assumed that, as a very good approximation, the total energy $E_0(z)$ can be expressed in terms of the relevant state variables x , or

$$E_0(z) = E(\Pi(z)) = E(x). \quad (14)$$

Finally, by coarse-graining L_0 , one naturally obtains

$$L(x) = \exp\left\{ -\frac{S(x)}{k_B} \right\} \int \frac{\delta \Pi(z)}{\delta z} L_0 \frac{\delta \Pi(z)}{\delta z} \delta(\Pi(z) - x) dz. \quad (15)$$

The resulting identity

$$\dot{x}_1(x) = L(x) \frac{\delta E(x)}{\delta x} \quad (16)$$

might be useful in employing simulation techniques (molecular dynamics) for determining M from Eq. (11).

III. SOME IMPLICATIONS

We can now discuss some implications of the microscopic expressions (10), (11), (14), and (15) for the building blocks of GENERIC. Equation (15) implies that L is antisymmetric. The formal expression for M , which is often referred to as a friction tensor, is symmetric, provided that the microscopic time evolution is reversible. In order to avoid problems with antisymmetric contributions to M (corresponding to dissipative dynamics without entropy production), we consider isolated systems (no external magnetic fields), and we assume that a sufficiently detailed level of description has been chosen (see problems caused by the transition from an inertial to a noninertial level of description in [15]). In any case, the symmetry of M can be traced back to the symmetry of the time correlation function in Eq. (11).

The degeneracy requirement (3) is an immediate consequence of the identity $\dot{x}_0(z)\delta E(x)/\delta x=0$ for $x=\Pi(z)$ (which, in turn, follows from the antisymmetry of L_0). In favor of the degeneracy requirement (2), we can offer the following heuristic argument: Since the projection should be such that, on microscopic time scales, $\Pi(z)=\Pi(z')$ if and only if $\Pi(z(t))=\Pi(z'(t))$, and since the microscopic time evolution preserves volume in phase space, we expect

$$\frac{dS(\Pi(z))}{dt} = -\frac{\delta E_0(z)}{\delta z} L_0 \frac{\delta S(\Pi(z))}{\delta z} = 0. \quad (17)$$

This leads to

$$\frac{\delta E(x)}{\delta x} L(x) \frac{\delta S(x)}{\delta x} = 0, \quad (18)$$

for arbitrary functionals $E(x)$ and hence to Eq. (2). Since the expression (15) implies

$$\frac{\delta}{\delta x} \left[L(x) \frac{\delta E(x)}{\delta x} \right] = \frac{1}{k_B} \frac{\delta E(x)}{\delta x} L(x) \frac{\delta S(x)}{\delta x}, \quad (19)$$

the connection between Liouville's theorem for the reversible dynamics and the degeneracy requirement (2) becomes obvious.

The positive-semidefinite character of the matrix M is not obvious from Eq. (11). However, the Fokker-Planck equation derived by the projection operator method is meaningful if and only if M is positive-semidefinite; a violation of this condition would lead to physically unacceptable properties of the fluctuating forces. We have thus derived the full GENERIC structure from the microscopic expressions for the building blocks obtained by projection operators (the Jacobi identity for the bracket associated with L matrix [1] remains to be derived).

We would here like to point out a problem with the transformation behavior of the GENERIC (1). From the microscopic expressions it can be verified that all building blocks except entropy have a simple transformation behavior. According to Eq. (10), a one-to-one transformation $x \rightarrow x'$ introduces the Jacobian of the transformation into the entropy expression. This problem can be resolved by looking at GENERIC with fluctuations. Under nonlinear transformations, the fluctuations can introduce systematic (deterministic) effects, which are exactly cancelled by the additional

entropy contribution involving the Jacobian. As long as fluctuations are irrelevant (as is the case for most applications of hydrodynamics and of the equations for multi-component systems with chemical reactions, as well as for polymer kinetic theory on the level of configurational distribution functions [2]) we can expect the additional entropy contribution to be equally irrelevant. While transformations with Jacobian unity clearly preserve the entropy, the selection of a particular natural set of variables (or the natural separation of fluctuations) is probably related to the applicability of the volume-preservation argument used in the previous paragraph for deriving the consistency requirement (2).

IV. RELATIONSHIP BETWEEN TWO COARSE-GRAINED LEVELS OF DESCRIPTION

While the microscopic expressions for the building blocks E , S , L , and M may be regarded as the analogues of the famous expression for the Helmholtz free energy in terms of the logarithm of the partition function when going from equilibrium to nonequilibrium systems, the complexity of a problem can be reduced dramatically by starting on an intermediate level of description (e.g., the viscoelastic properties of polymeric fluids are often determined from mechanical bead-rod-spring models of polymers). We therefore derive the rules for passing from any given level of description to a more macroscopic one. We consider two coarse-grained levels of description, where the level with $x=\Pi_1(z)$, $E_1(x)$, $S_1(x)$, $L_1(x)$, $M_1(x)$ is more microscopic than the level with $y=\Pi_2(z)$, $E_2(y)$, $S_2(y)$, $L_2(y)$, $M_2(y)$ (the respective intermediate time scales are τ_1 and τ_2). We assume $y=\Pi(x)$ where $\Pi_2=\Pi \circ \Pi_1$. By comparing the microscopic expressions for the building blocks of the two levels we can now construct direct transformation rules. A direct projection of the time-evolution equation from one coarse-grained level of description to another one, both based on Fokker-Planck equations, has been formulated very recently [16].

Since the total energy must, to a very good approximation, be accessible on any level of description we can obtain $E_2(y)$ by writing $E_1(x)$ in the form

$$E_1(x) = E_2(\Pi(x)). \quad (20)$$

For the entropy, we obtain the following general formula:

$$\exp\left\{\frac{S_2(y)}{k_B}\right\} = \int \exp\left\{\frac{S_1(x)}{k_B}\right\} \delta(\Pi(x)-y) dx. \quad (21)$$

In practical applications, the integral in Eq. (21) might be dominated by states x near the maximum of the integrand; the saddle-point approximation would then be useful for evaluating the coarse-grained entropy.

For the L matrix one can verify the transformation behavior

$$L_2(y) = \int \exp\left\{\frac{S_1(x)-S_2(y)}{k_B}\right\} \times \frac{\delta \Pi(x)}{\delta x} L_1(x) \frac{\delta \Pi(x)}{\delta x} \delta(\Pi(x)-y) dx. \quad (22)$$

While the above three relations involve only static properties, the time evolution comes in when coarse graining the M matrix. In order to find a tractable expression for that matrix we rewrite the matrix $M_2(y)$ of Eq. (11) in the equivalent form

$$M_2(y) = \frac{1}{k_B} \int_0^{\tau_2} dt \int \exp\left\{\frac{S_1(x) - S_2(y)}{k_B}\right\} \delta(\Pi(x) - y) \times [(\dot{y}_0(z)\dot{y}_0(z(t)))_x^0 - \dot{y}_2(y)\dot{y}_2(y)] dx, \quad (23)$$

where $\langle \rangle_x^0$ is the flat average (the normalized integral) over all z with $\Pi_1(z) = x$,

$$\dot{y}_0(z(t)) = \frac{d}{dt} \Pi[\Pi_1(z(t))], \quad (24)$$

and

$$\dot{y}_2(y) = L_2(y) \frac{\delta E_2(y)}{\delta y}. \quad (25)$$

[This notation is consistent with Eqs. (12) and (16).]

We now assume that $x(t) = \Pi_1(z(t))$ is represented by GENERIC on level 1 where, for evaluating correlations, it is obviously important to consider the GENERIC with fluctuations (corresponding to variations of the microscopic state variables on time scales shorter than τ_1). According to the stochastic differential equation of GENERIC with fluctuations and Itô calculus [11], there is a white-noise (δ -correlated) contribution to $d\Pi(x(t))/dt$, which leads to

$$M_2'(y) = \int \exp\left\{\frac{S_1(x) - S_2(y)}{k_B}\right\} \times \frac{\delta\Pi(x)}{\delta x} M_1(x) \frac{\delta\Pi(x)}{\delta x} \delta(\Pi(x) - y) dx. \quad (26)$$

While this contribution accounts for the fluctuations resulting from the fast time evolution of z compared to x (faster than τ_1), we still need to account for the fluctuations of x on the time scale τ_2 on which y remains constant. We replace $\dot{y}_0(z(t))$ by the mean forward time derivative of the stochastic process $\Pi(x(t))$ (as the best possible estimate for the future time-evolution of y ; see p. 80 of [17]),

$$D\Pi(x(t)) = \frac{\delta\Pi}{\delta x} \left(L_1 \frac{\delta E_1}{\delta x} + M_1 \frac{\delta S_1}{\delta x} + k_B \frac{\delta M_1}{\delta x} \right) + k_B M_1 \frac{\delta^2 \Pi}{\delta x \delta x}, \quad (27)$$

evaluated at $x = x(t)$. In order to preserve the proper symmetry of the microscopic time-evolution, which is related to the symmetry of the friction matrix $M_2(y)$, we replace $\dot{y}_0(z(0))$ by the mean backward time derivative (see p. 95 of [17]),

$$D_* \Pi(x(0)) = \frac{\delta\Pi}{\delta x} \left(L_1 \frac{\delta E_1}{\delta x} - M_1 \frac{\delta S_1}{\delta x} - k_B \frac{\delta M_1}{\delta x} \right) - k_B M_1 \frac{\delta^2 \Pi}{\delta x \delta x}, \quad (28)$$

evaluated at $x = x(0)$. We then obtain the final result $M_2(y) = M_2'(y) + M_2''(y)$ with

$$M_2''(y) = \frac{1}{k_B} \int_0^{\tau_2} dt \int \exp\left\{\frac{S_1(x) - S_2(y)}{k_B}\right\} \delta(\Pi(x) - y) \times [\langle D_* \Pi(x(0)) D \Pi(x(t)) \rangle_x - \dot{y}_2(y)\dot{y}_2(y)] dx, \quad (29)$$

where $\langle \rangle_x$ is the ensemble average over the trajectories obtained by solving the fluctuating GENERIC on level 1 with $x(0) = x$. Compared to Eq. (23), the microscopic level is now completely eliminated. The expressions (26) and (29) for the coarse-grained friction matrix agree with the result of a direct projection [16] from level 1 to level 2 after adapting it to a microcanonical ensemble.

The two contributions (26) and (29) to $M_2(y)$ thus correspond to fluctuations resulting from the fast time evolution of z compared to x and from the fast time evolution of x compared to y , respectively. If the step from level 1 to level 2 involves coarse graining then we expect $M_2'' \neq 0$. There may be reductions in the number of state variables for which $M_2'' = 0$; the passage from level 1 to level 2 may then be considered as a ‘‘solution’’ of the level 1 model rather than a coarse graining.

For determining M_2 by numerical simulations on level 1 one generally needs Brownian dynamics simulations because $x(t)$ is obtained as the solution of a stochastic differential equation. The situation is different when one determines the friction matrix from the most microscopic level, where molecular dynamics simulations of Hamilton’s equations are required.

V. CONCLUSIONS

It is amazing that the entire GENERIC structure previously obtained from many examples of nonequilibrium systems and from an abstract consideration of different levels of description can be derived in such a simple way from projection operator techniques. While the actual derivation is completely based on standard calculations, the proper identification of the building blocks, their individual properties, and the mutual degeneracy requirements make the previous results much more valuable. In practical applications, the importance of molecular and Brownian dynamics simulations for coarse graining the friction matrix M is obvious. The developments of this paper provide a theoretical background for these different types of simulations for nonequilibrium systems.

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