



Variational methods for time-dependent classical many-particle systems



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ABSTRACT

A variational method for the classical Liouville equation is introduced that facilitates the development of theories for non-equilibrium classical systems. The method is based on the introduction of a complex-valued auxiliary quantity Ψ that is related to the classical position-momentum probability density ρ via $\rho = \Psi^*\Psi$. A functional of Ψ is developed whose extrema imply that ρ satisfies the Liouville equation. Multiscale methods are used to develop trial functions to be optimized by the variational principle. The present variational principle with multiscale trial functions can capture both the microscopic and the coarse-grained descriptions, thereby yielding theories that account for the two way exchange of information across multiple scales in space and time. Equations of the Smoluchowski form for the coarse-grained state probability density are obtained. Constraints on the initial state of the N -particle probability density for which the aforementioned equation is closed and conserves probability are presented. The methodology has applicability to a wide range of systems including macromolecular assemblies, ionic liquids, and nanoparticles.

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1. Introduction

Variational principles have been used in many areas of science and engineering [1]. Here, a classical nonequilibrium variational method is introduced to facilitate the analysis of the Liouville equation (LE). Its use is demonstrated in deriving stochastic equations for coarse-grained (CG) variables characterizing long-scale dynamics. A methodology based on multiscale perturbation analysis is provided for constructing trial functions to be optimized via the variational principle.

Variational approaches to quantum and classical systems include the following. The entropy maximum principle is used to construct the equilibrium probability [2]. For the stationary states of quantum systems, the energy-minimum principle is used [3,4]. The least-action principle is used for time-dependent pure-state quantum systems [5]. For nonequilibrium reacting systems described by a master equation, an evolution criterion has been discussed [6]. Variational approaches based on the maximum entropy production hypothesis have been presented [7–10]. For example, the Onsager–Machlup approach [10,11] is based on a phenomenological maximum entropy production principle; it appears to be appropriate for systems which are close to equilibrium.

A variational method for the LE was developed in the 1970s by Gross; it was cast in terms of the Laplace transform of the N -particle density ρ [12]. The functional considered is related to correlation functions of interest. The stationary values of the constructed functionals implied the LE exactly for ρ when no restrictions on the trial function are imposed. The trial functions used were taken in successive approximations as the sum of one-body, then two-body, etc., terms [13]. It was noted that there is a multiplicity of alternative variational functionals whose extrema satisfy the LE [12]. While this multiplicity of functionals raises the question of the physical motivation for choosing one over another, it suggests that this may enable one to gain experience in choosing functionals that yield results that are optimal for addressing a given problem, e.g., for constructing correlation functions of a given type. In the present formulation, a functional is introduced

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that involves a complex-valued quantity Ψ related to the N -particle density ρ via $\rho = \Psi^* \Psi$. The complex valuedness of the auxiliary function Ψ in effect introduces two N -particle densities, and provides a self-consistent way to construct both of them. In the Gross formulation, a second function in addition to the N -particle density is needed to formulate the variational principle. This function was chosen to be a specific modification of ρ (namely, a momentum reversed density). Here, the second function is simply the complex conjugate of the first, and the variational principle implies equations for both.

The Martin–Siggia–Rose method [14–16] starts with a coarse-grained statistical description that follows from renormalization group arguments. The present approach starts with a variational principle built on the original (not renormalized) LE. Trial functions are then used that are inspired by multiscale perturbation theory [17]. Such trial functions will be shown to account for the coupling of processes across scales in space and time that underlies the dissipative phenomena of interest in nonequilibrium systems.

The formulation proposed here is suggested by analogy with the quantum least-action principle. The quantum principle is based on a functional whose extrema correspond to the solutions of the time-dependent Schrödinger equation [5]. The quantum action takes the form of an expectation value of $i\hbar\partial/\partial t - H$, for Hamiltonian H . Here, a similar quadratic functional is constructed for the classical LE. To achieve this, a wave function-like quantity Ψ is introduced. It is an essential feature of the present variational method that this auxiliary function Ψ is complex-valued. In effect, $\text{Re } \Psi$ is found to serve as a test function [18] for $\text{Im } \Psi$, and conversely. The use of this variational principle in deriving stochastic equations of CG dynamics is discussed based on multiscale perturbation theory-inspired trial functions.

Multiscale perturbation methods [19,20] yield Smoluchowski or other equations for the stochastic dynamics of the probability density of a set of coarse-grained variables [20–23], the latter describing the larger-scale features of a classical N -particle system. These methods account for the coupling of processes across multiple scales in space and time. They follow a long tradition of multiple time and length scale approaches to many-particle quantum [24] and classical [19,21, 22,25,26] systems. Multiscale perturbation approaches for classical systems have been validated via, e.g., simulation of viral capsids [27,28], RNA [20], and virus-like particles [26,29]. A necessary condition for their validity is that correlation functions of the CG momenta do not display long-time tails [20]. The variational method presented here provides a framework to extend/utilize perturbation theory in a manner similar to that of other variational approaches.

A variety of CG variables have been used as a starting point of a multiscale perturbation approach [20,30–35]. It is hoped that reexamination of these results by using them to construct trial functions for the present variational method will facilitate the development of novel stochastic equations for CG dynamics. All methods based on the identification of slow modes must address the requirement for the existence of a timescale gap between the slow and fast modes of an N -particle system. One may proceed by assuming the existence of this gap between the fastest modes and the quasi-continuum of slower ones [36], and then justifying it *a posteriori*. The latter justification is achieved via comparison with experimental or computer molecular dynamics results, or through the identification of self-consistency criteria. Examples of the latter are as follows.

- CG momenta correlation functions should not have long-time tails since the latter indicate coupling to slow modes not included in the set considered.
- Emergence of large differences between the all-atom configuration generated coherently through the CG variables versus that from MD computations may be used to identify additional modes to be included [20]. In developing a multiscale approach to classical nanosystems, it was shown that certain CG variables could be introduced in a manner that enables the automated detection of key missing CG variables, and provides an explicit algorithm for relating these otherwise hidden variables to the underlying N -particle description [20].
- Straightforward use of multiscale perturbation theory may lead to non-conserving equations for a reduced probability density. Certainly, one does not expect that conserving equations should follow for an arbitrarily chosen set of slow variables given any initial statistical state. This is addressed in the context of the present variational principle by identifying initial statistical states which lead to a conserving equation for the reduced probability of the CG state.

These considerations can also be applied to the projection operator methods [19,21,25]. For example, if key CG variables are missing then memory functions have long time tails.

The variational principle introduced here has the following features (those indicated with * are unique to our approach).

- * A quadratic functional of a complex-valued quantity is introduced in analogy with the quantum least-action principle and has symmetry properties that greatly facilitate variational calculations.
- Extrema of the proposed functional satisfy the LE.
- * A remote time factor is introduced to ensure that the operator $\partial/\partial t$ is skew Hermitian.
- * Multiscale perturbation theory is used to inspire trial functions.
- * Intuitive arguments starting with multiscale mean-field functions provide a way to develop novel kinetic theories of nonequilibrium classical systems. These properties will be explored via several illustrative examples.

Closure has been a long standing issue, e.g., for the BBGKY hierarchy [37]. A method for discovering a closed equation for the probability of the CG state is presented. It follows from a detailed examination of the initial statistical state's influence on the dynamics of the N -particle probability density. A variational principle is used to generate an approximation for the N -particle density.

The proposed variational method is formulated and demonstrated via simple Vlasov approximation, which describes the inertia-dominated, frictionless dynamics of N identical particles (Section 2). A multiscale perturbation scheme for generating

trial functions is presented (Section 3). A Smoluchowski equation for a set of coarse-grained variables is derived via the variational principle, and conditions on the initial N -particle statistical state for its validity are obtained (Section 4). The presentation is concluded with a prospective on the use of the variational approach for deriving kinetic equations for nonequilibrium classical systems via the use of perturbation theory-inspired trial functions (Section 5).

2. The variational principle: definitions, properties, and simple illustration

2.1. Formulation

The LE for a classical N -particle system $\partial\rho/\partial t = \mathcal{L}\rho$ yields the evolution of the position-momentum density ρ , and the Liouville operator \mathcal{L} is given by

$$\mathcal{L} = - \sum_{\ell=1}^N \left[\frac{\vec{P}_{\ell}}{M_{\ell}} \cdot \frac{\partial}{\partial \vec{r}_{\ell}} + \vec{F}_{\ell} \cdot \frac{\partial}{\partial \vec{P}_{\ell}} \right]. \quad (1)$$

Analysis of this equation is challenging due to the complexity of the structure of ρ since it subsumes a range of phenomena from continuous processes like diffusion to discontinuous ones like shock waves. The objective here is to develop a variational approach that facilitates the analysis of the LE based on approximations inspired by intuition and perturbation methods.

The first step in the development is to introduce a complex-valued auxiliary quantity Ψ related to ρ via

$$\rho = \Psi^* \Psi. \quad (2)$$

Introduction of ψ enables the construction of a quadratic functional $C(\Psi^*, \Psi)$ which has a similar form to the action of quantum theory [5]. By design, the structure of this functional is chosen such that its extrema occur at Ψ that imply the classical LE for ρ , and which has convenient symmetry properties.

Consider the functional C defined such that

$$C = i \int dt d\Gamma e^{-\eta t^2} \Psi^* [\partial/\partial t - \mathcal{L}] \Psi. \quad (3)$$

Here, Γ is a point in $6N$ -dimensional particle position-momentum space, η is a positive infinitesimal constant, the range of t goes from the remote past to the remote future, while the range of Γ is determined by constraints on the system (e.g., a closed volume). The factor $e^{-\eta t^2}$ ensures that after integration by parts of a $\partial/\partial t$ term, the boundary values at $t \rightarrow \pm\infty$ are zero; this remote-time repression factor ensures that $\partial/\partial t$ is skew Hermitian. With this, C is found to be real and nonnegative.

Finding extrema of C with respect to the complex function Ψ is equivalent to doing so simultaneously for the real and imaginary parts of Ψ . This is also equivalent to minimizing C with respect to Ψ and Ψ^* themselves, as pointed out in the 1930s in the context of the quantum least-action principle [12,38]. Such symmetry is built in the variational principle discussed below. With this, one may compute the functional derivative $\delta C/\delta\Psi^*$ to arrive at an equation for Ψ , and similarly for taking the functional derivative with respect to Ψ to obtain an equation for Ψ^* . With this, the variational equation $\delta C/\delta\Psi^* = 0$ implies the LE for Ψ ,

$$\partial\Psi/\partial t = \mathcal{L}\Psi. \quad (4)$$

Recalling that $\rho = \Psi^*\Psi$, the dynamical equation for Ψ (and a similar one for Ψ^*) imply that ρ satisfies the LE. This is an advantage over other approaches which start with the renormalized coarse-grained equations [14–16], and not with the full LE. The complex auxiliary function formulation has advantages over other approaches [12,13] where a second probability density is introduced that is arbitrarily taken to be a time-reversed solution of the LE. In the present formulation no such assumption is needed, – a factor that has particular advantages when constructing and using trial functions for optimization (as in Section 4).

2.2. Necessity of complex-valuedness of the auxiliary function

The above development does not yet clarify the importance of introducing Ψ as a complex-valued function. To do so, consider finding the extrema of C . If the auxiliary function Ψ is real, the variational equation $\delta C/\delta\Psi(\Gamma, t) = 0$ based on (3) yields no information, as follows. If Ψ equals the real-valued function A , it follows that

$$C = \frac{i}{2} \int dt d\Gamma e^{-\eta t^2} [\partial/\partial t - \mathcal{L}] A^2. \quad (5)$$

The fact that \mathcal{L} only involves first-order derivatives with respect to Γ , and that A vanishes at the boundaries in Γ -space, imply the integrated $\mathcal{L}A^2$ term of (5) is zero. Since $\int d\Gamma A^2$ can be shown to be constant, it follows that $\int d\Gamma \frac{\partial}{\partial t} A^2 = 0$. Thus, seeking the extrema of C when Ψ is real yields no information. However, since Ψ is complex-valued, the extrema of C are nontrivial, as follows.

Let $\Psi = A + iB$ for independent real functions $A(\Gamma, t)$ and $B(\Gamma, t)$. With this, C can be thought of as a functional of A and B . Letting $\Omega = \partial/\partial t - \mathcal{L}$, one obtains

$$C(A, B) = \int dt d\Gamma e^{-\eta t^2} [i(A\Omega A + B\Omega B) - B\Omega A + A\Omega B]. \quad (6)$$

The $A\Omega A$ and $B\Omega B$ terms yield no information when seeking extrema of C with respect to A or B , as can be shown using arguments similar to the case when Ψ is real. The $-B\Omega A$ term is equal to the $A\Omega B$ term, as can be shown using integration by parts and the fact that AB vanishes at the boundaries of the Γ domain. With this, one finds that $\delta C/\delta A = 0$ implies that B obeys the LE. Similarly, setting $\delta C/\delta B$ to zero implies that A satisfies the LE. Thus, when Ψ is complex-valued the variational principle yields nontrivial results. A similar conclusion can be derived using a polar representation (see [Appendix](#)).

2.3. Relation to the Gross formulation

Consider a reformulation of the functional C into Fourier representation. The Fourier transform $\bar{\Psi}$ is related to Ψ via

$$\Psi(\Gamma, t) = \frac{1}{2\pi} \int d\omega e^{i\omega t} \bar{\Psi}(\Gamma, \omega). \quad (7)$$

With this, C (3) can be written as a functional of $\bar{\Psi}$:

$$C = \frac{i}{(2\pi)^2} \int d\omega d\omega' dt d\Gamma e^{-\eta t^2} e^{i(\omega-\omega')t} \bar{\Psi}^*(\Gamma, \omega') [i\omega - \mathcal{L}] \bar{\Psi}(\Gamma, \omega). \quad (8)$$

For infinitesimal η

$$\frac{1}{2\pi} \int dt e^{-\eta t^2} e^{i(\omega-\omega')t} = \delta(\omega - \omega'), \quad (9)$$

and hence

$$C = \frac{i}{2\pi} \int d\omega d\Gamma \bar{\Psi}^* [i\omega - \mathcal{L}] \bar{\Psi}. \quad (10)$$

This functional looks similar to that of Gross except that here (1) the objective is to construct both the $\text{Re } \bar{\Psi}$ and $\text{Im } \bar{\Psi}$ via a unified approach, i.e., finding the extrema of C with respect to $\text{Re } \bar{\Psi}$ and $\text{Im } \bar{\Psi}$ rather than focusing on the N -particle density and its momentum-reversed image, and (2) the integration over ω is not considered in the Gross formulation and the present representation is in Fourier and not Laplace transform. However, the results of Sections 3 and 4 suggest that it is convenient to adopt a time-domain formulation when using multiscale perturbation methods to generate trial functions. Finally, the time-domain ρ is related to Ψ via the product rule ($\rho = \Psi^* \Psi$), while for the Fourier transform $\bar{\rho} \neq \bar{\Psi}^* \bar{\Psi}$ but is related to $\bar{\Psi}$ via a convolution. Again, this suggests the convenience of working in the time-domain. These advantages are illustrated more specifically in Sections 3 and 4.

To further explore the relation of the present approach to that of Gross, first let \underline{r} and \underline{p} be the set of particle positions and momenta, respectively. The method of Gross is equivalent to the present one when $\text{Im } \bar{\Psi}(\underline{r}, \underline{p}; t) = \text{Re } \Psi(\underline{r}, -\underline{p}; -t)$. If this $\text{Re } \Psi$ is a solution of the LE then so is $\text{Im } \Psi$. In contrast, the present formulation is less restricted, i.e., the only criterion is that $\text{Re } \Psi$ and $\text{Im } \Psi$ may not be simply related via constant of proportionality. The assumption that $\text{Im } \Psi$ is the momentum-time reversed $\text{Re } \Psi$ is restrictive when, e.g., developing a trial function for optimization by the present variational method.

2.4. Simple mean-field trial function: the Vlasov equation

To illustrate that the variational procedure of Section 2.1 allows one to recover a familiar result, consider a mean-field approximation for a collection of N identical particles interacting with pairwise forces. Stating the classic mean-field approximation in the present notation, $\Psi(\Gamma, t)$ is postulated to be a product of single-particle functions $\psi(\vec{r}, \vec{p}, t)$. In this case, the trial function, denoted T , is given by

$$T = \prod_{\ell=1}^N \psi(\vec{r}_{\ell}, \vec{p}_{\ell}, t). \quad (11)$$

With this, the functional C (3) takes the form

$$C = i \int dt d\Gamma e^{-\eta t^2} \prod_{\ell=1}^N \psi^*(\vec{r}_{\ell}, \vec{p}_{\ell}, t) [\partial/\partial t - \mathcal{L}] \prod_{\ell'=1}^N \psi(\vec{r}_{\ell'}, \vec{p}_{\ell'}, t). \quad (12)$$

A dynamical equation for ψ is then obtained from the extremum condition

$$\delta C / \delta \psi^*(\vec{r}, \vec{p}, t) = 0. \quad (13)$$

The result is

$$\frac{\partial \psi}{\partial t} = -\frac{\vec{p}}{m} \cdot \frac{\partial \psi}{\partial \vec{r}} - \vec{F} \cdot \frac{\partial \psi}{\partial \vec{p}}. \quad (14)$$

The mean-field force \vec{F} is given by

$$\vec{F}(\vec{r}, t) = -\frac{(N-1)}{\vartheta} \frac{\partial}{\partial \vec{r}} \int d^3 r' d^3 p' |\psi(\vec{r}', \vec{p}', t)|^2 u(\vec{r}, \vec{r}'), \quad (15)$$

where $u(\vec{r}, \vec{r}')$ is the pair potential and

$$\vartheta = \int d^3 r d^3 p |\psi(\vec{r}, \vec{p}, t)|^2. \quad (16)$$

The norm ϑ can be shown to be independent of time for finite systems assuming that $\psi = 0$ at the boundaries of \vec{r}, \vec{p} space.

The kinetic equation (14), rewritten for the single-particle density $|\psi|^2$, is the Vlasov equation from plasma theory [39]. The only damping is of the Landau type and is, therefore, not appropriate for liquids.

3. Multiscale perturbation theory-inspired trial functions for dissipative phenomena

The mean-field trial function used in Section 2.4 generated the Vlasov equation upon use of the variational principle. However, the Vlasov equation does not provide a realistic account of dissipative phenomena in a condensed system. Here, multiscale perturbation theory is used to generate trial functions which are rich enough to capture dissipative effects that dominate most phenomena in classical liquids. A further advantage of using trial functions inspired by multiscale perturbation theory is that they incorporate a degree of physical intuition into a formulation via the specific choice of CG variables used.

There is often a smallness parameter ε that naturally emerges when computing the rate of change of CG variables. Typically, ε is a dimensionless ratio of characteristic masses, lengths, or force constants. For simplicity, it is assumed that there is a regular progression of times $t_n = \varepsilon^n t$ that characterize all the relevant timescales displayed by a system of interest. These timescales are $O(\varepsilon^{-n})$ ($n = 0, 1, \dots$). Consider a set Φ of CG variables which, by construction, evolve on timescales much greater than that for individual particle collisions/vibrations [20,40]. With this, the multiscale ansatz is made

$$\Psi = \Psi(\Gamma, \Phi; t_0, \underline{t}; \varepsilon), \quad (17)$$

where $\underline{t} = \{t_1, t_2, \dots\}$ is the set of long time variables. Using the LE for Ψ (4), the ansatz (17), and the chain rule, one obtains

$$\sum_{n=0} \varepsilon^n \partial \Psi / \partial t_n = (\mathcal{L}_0 + \varepsilon \mathcal{L}_1 + \dots) \Psi. \quad (18)$$

The operators \mathcal{L}_n follow from \mathcal{L} and the Γ -dependence of the N_{CG} CG variables Φ . Specifically, \mathcal{L}_0 has the same form as \mathcal{L} but the Γ -derivatives are at constant Φ , while the \mathcal{L}_n ($n > 0$) involve Φ -derivatives at constant Γ . This framework is not a violation of the number of degrees of freedom; rather, it simply reflects the ansatz (17) on the multiple dependencies of Ψ on Γ [20,41]. The resulting formulation allows for the construction of these dependencies via a perturbation scheme valid when ε is small.

To be more specific, consider the set Φ of CG variables introduced earlier [41]. Assuming all these CG variables evolve on about the same timescale, then the form of the multiscale LE (18) holds with

$$\mathcal{L}_1 = -\Pi \cdot \frac{\partial}{\partial \Phi}, \quad (19)$$

where the notation

$$A \cdot B \equiv \sum_{k=1}^{N_{CG}} A_k B_k. \quad (20)$$

Note that \mathcal{L}_0 and \mathcal{L}_1 operate on the space of functions that depend on both Γ and Φ , and k labels the CG variables. The CG variable velocity Π_k is given by

$$\Pi_k = -\mathcal{L} \Phi_k. \quad (21)$$

Next, the smallness of ε is used to construct Ψ as a perturbation expansion

$$\Psi = \Psi_0 + \varepsilon\Psi_1 + \dots \tag{22}$$

Placing this expansion in (18), and collecting terms to each order in ε , equations for the coefficients Ψ_n of the expansion are obtained.

As with the analysis of the N -particle probability density ρ as earlier [20,27,32–35,41–43], one may construct Ψ_0 under conditions where it evolves slowly (i.e., is independent of t_0). Thus, to lowest order,

$$\mathcal{L}_0\Psi_0 = 0. \tag{23}$$

This equation admits the solution

$$\Psi_0 = \hat{\Psi}(\Gamma, \Phi)\Upsilon(\Phi, \underline{t}). \tag{24}$$

Since $\hat{\Psi}^*\hat{\Psi}$ is the conditional probability for Γ given Φ (in analogy with earlier studies [20,27,32–35,41–43]), $\hat{\Psi}$ is determined via the entropy maximum principle. For isothermal conditions, this implies

$$\hat{\Psi} = e^{-\beta H/2}/Q^{1/2}, Q = \int d\tilde{\Gamma} \Delta(\Phi - \tilde{\Phi}(\Gamma)) e^{-\beta\tilde{H}}. \tag{25}$$

Here, \sim indicates evaluation at $\tilde{\Gamma}$ over which integration is taken. The factor Δ is a product of Gaussian-like functions (one for each of the N_{CG} CG variables in the set Φ) that favors states $\tilde{\Gamma}$ for which the CG variables have values near Φ . Since $\hat{\Psi}^*\hat{\Psi}$, and not $\hat{\Psi}$, is a probability, the entropy maximization principle was used to construct $\hat{\Psi}^*\hat{\Psi}$, and not $\hat{\Psi}$ itself.

Next, one collects terms to first order in ε in (18) to find

$$[\partial/\partial t_0 - \mathcal{L}_0]\Psi_1 = \mathcal{L}_1\Psi_0. \tag{26}$$

Removal of secular behavior [44] in Ψ_1 implies $\partial\Upsilon/\partial t_1 = 0$; this results in the absence of a $\partial\Psi_0/\partial t_1$ term in (26). Collecting the above results yields

$$\Psi_1 = e^{\mathcal{L}_0 t_0} \Psi_1^o(\Gamma, \Phi, \underline{t}) + \hat{\Psi} \int_{-t_0}^0 dt'_0 e^{-\mathcal{L}_0 t'_0} \sum_{k=1}^{N_{CG}} \Pi_k \left\{ \frac{\beta}{2} f_k \Upsilon - \frac{\partial \Upsilon}{\partial \Phi_k} \right\}. \tag{27}$$

Here f_k is the thermal-average force:

$$f_k(\Phi) = -\partial F/\partial \Phi_k. \tag{28}$$

The Helmholtz free energy F is related to the partition function Q via

$$Q(\Phi) = e^{-\beta F}. \tag{29}$$

The value of Ψ_1 at $t_0 = 0$ is denoted Ψ_1^o .

The integral term in Ψ_1 contains the timecourse of a fluctuating microscopic variable, i.e., the momentum Π_k (21) conjugate to the CG variable Φ_k . The exchange of information between particle-like and CG variables contained in Ψ_1 is the source of dissipative effects. Thus, including them in a trial function for condensed systems should overcome some of the shortcomings of the Vlasov equation (Section 2.4) as developed in the next section.

4. Equations for stochastic CG dynamics derived from the variational principle

4.1. General considerations

The variational principle of Section 2 opens the way to use the multiscale perturbation theory of Section 3 to generate trial functions and then optimize them. This allows one to go beyond perturbation methods by constructing trial functions such as those involving mean-field approximations. In this section this theme is developed by taking the $O(\varepsilon)$ results from Section 3 as the trial function to be optimized. First consider some general issues.

Let T be a trial function. Then the functional (3) takes the form

$$C(T, T^*) = i \int dt d\Gamma e^{-\eta t^2} T^* [\partial/\partial t - \mathcal{L}] T = -i \int dt d\Gamma e^{-\eta t^2} T [\partial/\partial t - \mathcal{L}] T^*. \tag{30}$$

The second result is implied by the first upon using integration by parts and the fact that the positive infinitesimal η removes the remote time boundary terms. These expressions for C show that $\delta C/\delta T^*$ and $\delta C/\delta T$ are related via

$$\delta C(T, T^*)/\delta T = -\delta C(T^*, T)/\delta T^*. \quad (31)$$

This symmetry rule enables one to avoid computing derivatives with respect to both T and T^* , thereby reducing the number of calculations. This is a consequence of the present complex formulation of the variational principle. This result is used to facilitate obtaining the kinetic equation for a CG probability density in Section 4.5.

Note that when T is an exact solution of the LE, $C(T, T^*) = 0$. In this way, the closeness of C to zero provides an assessment of the quality of a variational solution.

4.2. Multiscale trial functions

Consider trial functions with the multiscale dependence $T(\Gamma, \Phi; t_0, t_2; \varepsilon)$ as suggested by the $O(\varepsilon)$ multiscale development of Section 3. This is to suggest that T depends on Γ both directly and, via a set of CG variables Φ , indirectly. Using the chain rule and introducing an expression for the CG variables as functions of Γ (denoted $\tilde{\Phi}(\Gamma)$), one has $\mathcal{L}T = \mathcal{L}_0T + \varepsilon\mathcal{L}_1T$, where \mathcal{L}_0 and \mathcal{L}_1 , as in Section 3, act on quantities which are functions of both Γ and Φ . With the above, the action C for multiscale trial functions may be written in the convenient form

$$C(T, T^*) = i \int dt dt_0 dt_2 d\Gamma d\Phi e^{-\eta t^2} \Delta(\Phi - \tilde{\Phi}(\Gamma)) \delta(t_0 - t) \delta(t_2 - \varepsilon^2 t) T^* [\partial/\partial t_0 + \varepsilon^2 \partial/\partial t_2 - \mathcal{L}_0 - \varepsilon\mathcal{L}_1] T, \quad (32)$$

where Δ is defined above, after Eq. (25); $\delta(t_n - \varepsilon^n t)$ indicates the Dirac delta function. In the above, the dependence of T and T^* on Γ , Φ , t_0 , t_2 , and ε is implied.

Take the trial function T to be given by the series (22) truncated to a given order in ε . If the truncation is to $O(\varepsilon)$, then the CG factors are Υ and Υ^* (see (22), (24) and (27)). With this, one can use the variational principle to find a pair of equations to determine Υ and Υ^* , i.e., $\delta C/\delta \Upsilon^* = 0$, $\delta C/\delta \Upsilon = 0$. These two equations obey a symmetry rule analogous to (31).

For the choice $T = \Psi_0$ of (24) one has $\mathcal{L}_0T = 0$ as in (23). This implies that

$$C(\Upsilon, \Upsilon^*) = -i\varepsilon \int dt dt_0 dt_2 d\Gamma d\Phi e^{-\eta t^2} \Delta(\Phi - \tilde{\Phi}(\Gamma)) \delta(t_0 - t) \delta(t_2 - \varepsilon^2 t) \hat{\Psi} \Upsilon^* \mathcal{L}_1(\hat{\Psi} \Upsilon). \quad (33)$$

The following facts can be used to simplify the expression for $C(T, T^*)$: (1) $\hat{\Psi}$ is even in the particle momenta; (2) the CG momenta Π_k (see (19) and (21)) are odd in the individual particle momenta; and (3) Υ is independent of the particle momenta. As in Section 3, $\partial\Psi_0/\partial t_0 = 0$; thus, for the choice $T = \Psi_0$ from (26) it follows that $C = 0$ and there is no useful information for optimizing Υ with this choice of trial function. Hence, a higher-order trial function is now considered.

Next, take the trial function to be the series (22) truncated to $O(\varepsilon)$:

$$T = \Psi_0 + \varepsilon\Psi_1. \quad (34)$$

The Υ and Υ^* dependence of T is embedded in Ψ_1^0 or explicitly provided as in (27). Since Ψ_1 obeys (26), it is seen that $[\partial/\partial t_0 - \mathcal{L}_0]\Psi_1 - \mathcal{L}_1\Psi_0$ term does not contribute to C . Assuming $\partial\Psi_1^0/\partial t_1 = 0$ (which is found to be self-consistent *a posteriori*), for the trial function (34) C takes the form

$$C(\Upsilon, \Upsilon^*) = i\varepsilon^2 \int dt dt_0 dt_2 d\Gamma d\Phi e^{-\eta t^2} \Delta(\Phi - \tilde{\Phi}(\Gamma)) \delta(t_0 - t) \delta(t_2 - \varepsilon^2 t) \Psi_0^* \{\partial\Psi_0/\partial t_2 - \mathcal{L}_1\Psi_1\}. \quad (35)$$

4.3. Reduced probability density

The main objective of the remainder of this section is to develop an approximate equation for the reduced probability $W(\Phi, t)$. By definition,

$$W(\Phi, t) = \int d\Gamma \Delta(\Phi - \tilde{\Phi}(\Gamma)) \rho. \quad (36)$$

To lowest order in the multiscale perturbation scheme, $\rho \rightarrow \hat{\Psi}^2 \Upsilon^* \Upsilon$, since $\hat{\Psi}$ can be taken to be real-valued. With this, $W \rightarrow \Upsilon^* \Upsilon$ as $\varepsilon \rightarrow 0$. Hence, to lowest order, W is a function of t_2 and thus

$$\partial W/\partial t_2 = \Upsilon^* \partial \Upsilon/\partial t_2 + \Upsilon \partial \Upsilon^*/\partial t_2. \quad (37)$$

With this and an approximate equation for Υ , one can construct a kinetic equation for W , as follows.

4.4. Variational calculus for multiscale trial functions

To facilitate the use of multiscale perturbation theory-inspired trial functions to construct a kinetic equation for W , consider the following device. Define a quantity U which is a typical term encountered when constructing C during optimization of trial functions derived from multiscale perturbation theory:

$$U(\gamma, \gamma^*) = \int dt dt_0 dt_2 d\Gamma d\Phi e^{-\eta t^2} \Delta(\Phi - \tilde{\Phi}) \delta(t_0 - t) \delta(t_2 - \varepsilon^2 t) \gamma^* X(\Gamma, \Phi, t_0, t_2; \gamma), \quad (38)$$

where X is a function of Γ, Φ, t_0 and t_2 , and is a functional of $\gamma(\Phi, t_2)$. The goal is to compute the functional derivative of U with respect to $\gamma^*(\Phi, t_2)$. First carry out the straightforward integration with respect to t , leaving only t_0 and t_2 time integrations. The remote time factor $e^{-\eta t^2}$ requires special attention since it will be most convenient to express the integrand of (38) only in terms of t_2 . To this end, rewrite it as $e^{-\eta t_2^2/\varepsilon^4}$. Since η is smaller than the square of the longest inverse time, and this time is $O(\varepsilon^{-2})$, then it is convenient to write $\eta = \varepsilon^4 \eta'$. With this,

$$U(\gamma, \gamma^*) = \int dt_2 d\Phi \gamma^* e^{-\eta' t_2^2} \tilde{U}(\Phi, t_2; \gamma), \quad (39)$$

$$\tilde{U}(\Phi, t_2; \gamma) = \int dt_0 d\Gamma \Delta(\Phi - \tilde{\Phi}) \delta(t_2 - \varepsilon^2 t_0) X(\Gamma, \Phi, t_0, t_2; \gamma).$$

Thereby, t_0 and Γ integrations can be folded into the surviving Φ, t_2 integrations so that the remaining functional dependence on γ^* becomes transparent, as follows. Since X in (38) is independent of γ^* , then the functional derivative of U with respect to γ^* follows by inspection:

$$\delta U / \delta \gamma^* = e^{-\eta' t_2^2} \tilde{U}(\Phi, t_2; \gamma). \quad (40)$$

4.5. Kinetic equations

Using the trial function (34) and the technique of Section 4.4, a kinetic equation for γ is implied by the extrema of C , as follows from setting the functional derivative of C with respect to γ^* to zero. In light of Section 4.2 and the expression for action (35), the variational problem can be cast in terms of the analysis of Section 4.4 with X of (38) given by

$$X(\Gamma, \Phi, t_0, t_2; \gamma) = i\varepsilon^2 \hat{\Psi}^* \{ \partial \Psi_0 / \partial t_2 - \mathcal{L}_1 \Psi_1 \}, \quad (41)$$

with Ψ_0 and Ψ_1 as in (24) and (27), and the operator \mathcal{L}_1 as in (19). Since $\varepsilon \ll 1$, the lower limit of the integration in (27) can be set to $-\infty$ and the kinetic equation for γ becomes

$$\frac{\partial \gamma}{\partial t_2} = \sum_{k, k'} D_{kk'} \left[\frac{\partial}{\partial \Phi_k} - \frac{\beta}{2} f_k \right] \left[\frac{\partial}{\partial \Phi_{k'}} - \frac{\beta}{2} f_{k'} \right] \gamma - \frac{\delta Z}{\delta \gamma^*}, \quad (42)$$

$$Z(\gamma) = \sum_k \int d\Phi dt_2 e^{-\eta' t_2^2} \gamma^* \int d\Gamma \Delta(\Phi - \tilde{\Phi}) \hat{\Psi}^* \Pi_k \frac{\partial \Psi_1^0(\Gamma, \Phi; \gamma)}{\partial \Phi_k}. \quad (43)$$

In obtaining (42) the following was used:

$$\frac{\partial \hat{\Psi}}{\partial \Phi_k} = -\frac{\beta}{2} f_k \hat{\Psi}. \quad (44)$$

The thermal-average force f_k is given by (28). The diffusivities $D_{kk'}$ are related to correlation functions of the momenta conjugate to Φ via

$$D_{kk'} = \int_{-\infty}^0 dt'_0 \int d\Gamma \Delta(\Phi - \tilde{\Phi}) \hat{\Psi}^2 \Pi_k e^{\mathcal{L}_0 t'_0} \Pi_{k'} = \int_{-\infty}^0 dt'_0 \left\langle \Pi_k e^{\mathcal{L}_0 t'_0} \Pi_{k'} \right\rangle. \quad (45)$$

The notation $\langle \dots \rangle$ implies a $\hat{\Psi}^2$ -weighted, Φ -constrained phase space average:

$$\langle \dots \rangle = \int d\Gamma \Delta(\Phi - \tilde{\Phi}) \hat{\Psi}^2 (\dots). \quad (46)$$

The initial term Ψ_1^0 is folded into the Z term. In the above, it was assumed Ψ_1^0 is independent of γ^* and lies in the null space of \mathcal{L}_0 , as is shown below.

Using the symmetry rule (31), one may obtain a dynamical equation for Υ^* as the complex conjugate of (42). Inserting the equations for Υ and Υ^* in (37) yields

$$\frac{\partial W}{\partial t_2} = \Upsilon \frac{\delta Z}{\delta \Upsilon} - \Upsilon^* \frac{\delta Z}{\delta \Upsilon^*} - \sum_{k,k'} \left(\frac{\partial}{\partial \Phi_k} \left(\frac{\beta}{2} f_{k'} \{D_{kk'} + D_{k'k}\} W \right) + \Upsilon \frac{\partial^2 (D_{kk'} \Upsilon^*)}{\partial \Phi_k \partial \Phi_{k'}} - D_{kk'} \Upsilon^* \frac{\partial^2 \Upsilon}{\partial \Phi_k \partial \Phi_{k'}} \right), \quad (47)$$

a kinetic equation for the CG probability density W . Defining G such that,

$$\Psi_1^o = \hat{\Psi} G(\Phi; \Upsilon), \quad (48)$$

yields

$$Z = \sum_k \int d\Phi dt_2 e^{-\eta' t_2^2} \Upsilon^* \left\langle \Pi_k \frac{\partial G}{\partial \Phi_k} \right\rangle. \quad (49)$$

4.6. Closure of the kinetic equation for W : identifying initial statistical states leading to Smoluchowski behavior

For a closed system, the N -particle position-momentum density ρ maintains normalization, as can be verified via integration of the LE over all Γ . This does not guarantee that conservation is maintained for the reduced density W of (36). It is shown here that a closed, conserving equation for W does exist under appropriate restrictions on the initial statistical state. Earlier, a conserving and closed equation of the Smoluchowski form was derived for stochastic CG dynamics starting with the LE and using a multiscale perturbation method [20,32,33,41]. Here, we investigate the emergence of the Smoluchowski equation for W that follows from a particular class of initial data Ψ_1^o .

Consider a condition on the initial statistical state for which W (36) displays Smoluchowski behavior. In the multiscale framework, this state (denoted ρ^o) is given by

$$\rho^o(\Gamma) = \rho(\Gamma, \tilde{\Phi}(\Gamma); t_n = 0 \text{ with } n = 0, 1, \dots; \varepsilon). \quad (50)$$

To $O(\varepsilon)$, the initial state of the associated auxiliary function is given by

$$\Psi^o = \hat{\Psi} \Upsilon(\Phi(\Gamma), t_2 = 0) + \varepsilon \Psi_1^o(\Gamma, \Phi(\Gamma), t_2 = 0). \quad (51)$$

With this, the initial statistical state question reduces to a consideration of Ψ_1^o for which W satisfies a Smoluchowski equation.

The rate equation for W (47) can be reduced to Smoluchowski form for a specific choice of the initial term Ψ_1^o . In the present notation, the Smoluchowski equation has the form

$$\frac{\partial W}{\partial t_2} = \sum_{k,k'} \frac{\partial}{\partial \Phi_k} \left(D_{kk'} \left[\frac{\partial}{\partial \Phi_{k'}} - \beta f_{k'} \right] W \right). \quad (52)$$

From the comparison of (47) and (52) one obtains the following condition on the initial term

$$\begin{aligned} & \Upsilon \frac{\delta Z}{\delta \Upsilon} - \Upsilon^* \frac{\delta Z}{\delta \Upsilon^*} \\ &= \sum_{k,k'} \left(\frac{\partial}{\partial \Phi_k} \left(\left[\frac{\partial}{\partial \Phi_{k'}} - \frac{\beta}{2} f_{k'} \right] (D_{kk'} W) + \Upsilon D_{kk'} \frac{\partial \Upsilon^*}{\partial \Phi_{k'}} \right) + \frac{\partial}{\partial \Phi_{k'}} \left(\frac{\beta}{2} f_{k'} D_{kk'} W - \Upsilon^* D_{kk'} \frac{\partial \Upsilon}{\partial \Phi_{k'}} \right) \right). \end{aligned} \quad (53)$$

Since the LHS of (53) involves an integral over Γ , there is a rich class of initial statistical states Ψ_1^o satisfying this restriction. The above development opens the way to understanding the relationship between the initial statistical state and the closure of a reduced description. Non-closure of the kinetic equation for W arises due to the incompleteness of a chosen set of CG variables. The existence of slow variables not included in the description would manifest itself in long-time behaviors of the correlation functions underlying the diffusion coefficients (45).

That this result was also obtained using multiscale perturbation theory [45], provides a validation for the variational approach. The above demonstrates how the variational approach can yield closed conserving equations for the probability of the CG state.

5. Conclusions

A variational approach for time-dependent classical many-particle systems is presented and shown to imply the LE. This variational approach can be used to optimize trial functions generated, e.g., via intuitive arguments or perturbation theory.

The key to the variational approach is an auxiliary function Ψ that depends on the $6N$ particle positions and momenta. The approach is based on a quadratic functional in Ψ and has a form similar to that of the quantum least-action principle. It is only when Ψ is complex-valued that the variational principle yields non-trivial results, i.e., enables the derivation of approximations for nonequilibrium many-particle systems.

There are many functionals whose extrema satisfy the LE. That presented here is expressed in terms of Ψ and its complex conjugate. It has a number of interesting properties. First, it yields known results such as the Vlasov and Smoluchowski equations when appropriate trial functions are used. The question remains as to whether the form (12) is, in some sense, more fundamental than others, or does it simply have technical advantages in deriving approximate solutions to the LE? Its analogy with the quantum least-action principle does not necessarily indicate that it is fundamental. However, both the LE and the Schrödinger equation are linear so that there may be merit in casting variational approaches in terms of bilinear functionals. To accomplish this, we introduce Ψ for which $|\Psi|^2$ is the N -particle position-momentum probability density ρ , further continuing the analogy with the quantum least-action principle. The multiscale character of many-particle systems suggests that ρ , and hence the auxiliary function Ψ , has multiscale structure. It was shown in Sections 3 and 4 that the multiscale perturbation method facilitates the development of trial functions to be optimized by the variational principle. A method to facilitate the use of multiscale trial functions was presented.

Results show that the variational principle can lead to an equation for the reduced probability of CG variables that is not conservative, unless restrictions are placed on the initial statistical state of the system. One of the origins of this non-conservation is the existence of additional CG variables not included in the model, but which couple to those which are included. The question of probability conservation is shown to be related to the initial statistical state of the system. For example, if the system was initialized with a shock wave, then inertial behavior would be important and therefore a non-inertial Smoluchowski dynamics would be inappropriate. A specific example of these restrictions is given which leads to the conserving Smoluchowski equation for a set of CG variables.

The introduction of the specific variational functional, integration with multiscale perturbation theory, and mean-field or other intuitive arguments makes the present variational approach of great potential value for deriving approximate solutions to nonequilibrium problems in many-particle classical systems.

If Ψ is an exact solution to the LE, then the variational functional is zero. Thus, the value of the variational functional provides an assessment of the quality of an approximation based on an optimized trial function. This measure can be used via a sequence of trial functions to determine if there is a sense of convergence, e.g., for trial functions based on multiscale perturbation theory of various orders in the perturbation parameter.

The trial functions proposed here are based on multiscale perturbation theory. Such trial functions lead naturally to a mean-field argument at the CG, and not at the single-particle scale. Coarse-grained mean-field approximations account for realistic damping, and not that of Landau [46]. This is seen for the calculations of Section 3 via the appearance of the diffusion factors in the expression for ψ_1 (27) provided in (45) (Section 4.5).

As an example, consider a mean-field approximation for the coarse-grained factor Υ of Sections 3 and 4. In particular, take the CG variables Φ to be the scaled positions of each atom in a liquid argon droplet. This scaled position variable is defined so that it undergoes a unit displacement as the atom traverses the million-atom droplet. Thus, the dependence of Υ on scaled atom position describes the long space-time dynamics of the droplet. On these long scales, each particle has ample time, and traverses sufficiently long distances, to interact with many others. This suggests that, to good approximation, Υ can be written as a product of factors, one for each atom. Unlike for the N -particle density directly, it is arguable that each particle interacts with an average environment, the “mean field”. Thus, based on this mean-field coarse-grained picture one may use the variational approach to derive an equation for the density of a viscous many-atom droplet. It is concluded here that the variational approach with multiscale trial functions holds great promise for arriving at novel equations describing the kinetics of nonequilibrium condensed classical systems.

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Appendix

Consider the effect of complex-valuedness of Ψ in the polar representation, i.e., $\Psi = R \exp(i\Theta)$ for Γ , t -dependent factors R and Θ . Using the same arguments as in Section 2.2, one obtains

$$C(R, \Theta) = i \int dt d\Gamma e^{-\eta t^2} R \exp(-i\Theta) \Omega R \exp(i\Theta) = - \int dt d\Gamma e^{-\eta t^2} R^2 \Omega \Theta. \quad (\text{A.1})$$

Thus, $\delta C / \delta R = 0$ leads to the LE for the phase.

Using integration by parts and the fact that R vanishes at the boundaries of Γ space, (A.1) can be rewritten in the form

$$C(R, \Theta) = - \int dt d\Gamma e^{-\eta t^2} \left[\frac{\partial}{\partial t} (R^2 \Theta) - \Theta \Omega R^2 \right]. \quad (\text{A.2})$$

The first term in (A.2) does not contribute as can be seen after its integration over t by parts. Thus, $\delta C / \delta \Theta = 0$ leads to the LE for R .

References

- [1] V.L. Berdichevsky, *Variational Principles of Continuum Mechanics*, Springer, 2009.
- [2] E.T. Jaynes, Information theory and statistical mechanics, *Phys. Rev.* 106 (1957) 620–630.
- [3] A. Raab, On the Dirac–Frenkel/McLachlan variational principle, *Chem. Phys. Lett.* 319 (2000) 674–678.
- [4] E. Deumens, Y. Öhrn, Complete electron nuclear dynamics, *J. Phys. Chem. A* 105 (2001) 2660–2667.
- [5] R.P. Feynman, Space-time approach to non-relativistic quantum mechanics, *Rev. Modern Phys.* 20 (1948) 367–387.
- [6] G. Nicolis, Equality governing nonequilibrium fluctuations and its information theory and thermodynamic interpretations, *Phys. Rev. E* 79 (2009) 011106.
- [7] L.M. Martyushev, V.D. Seleznev, Maximum entropy production principle in physics, chemistry and biology, *Phys. Rep.* 426 (2006) 1–45.
- [8] A. Kleidon, Life, hierarchy, and the thermodynamic machinery of planet earth, *Phys. Life Rev.* 7 (2010) 424–460.
- [9] C. Nicolis, G. Nicolis, Stability, complexity and the maximum dissipation conjecture, *Q. J. R. Meteorol. Soc.* 136 (2010) 1161–1169.
- [10] L. Onsager, S. Machlup, Fluctuations and irreversible processes, *Phys. Rev.* 91 (1953) 1505–1512.
- [11] A.B. Adib, Stochastic actions for diffusive dynamics: reweighting, sampling, and minimization, *J. Phys. Chem. B* 112 (2007) 5910–5916.
- [12] E.P. Gross, Approximate solutions of the Liouville equation. II. Stationary variational principles, *J. Stat. Phys.* 9 (1973) 275–295.
- [13] E.P. Gross, Approximate solutions of the Liouville equation II. A truncation scheme for distribution functions, *Ann. Physics* 69 (1972) 42–55.
- [14] P.C. Martin, E.D. Siggia, H.A. Rose, Statistical dynamics of classical systems, *Phys. Rev. A* 8 (1973) 423–437.
- [15] R.V. Jensen, Functional integral approach to classical statistical dynamics, *J. Stat. Phys.* 25 (1981) 183–210.
- [16] H.C. Andersen, Functional and graphical methods for classical statistical dynamics. I. A formulation of the Martin–Siggia–Rose method, *J. Math. Phys.* 41 (2000) 1979–2020.
- [17] J. Kevorkian, J.D. Cole, *Multiple Scale and Singular Perturbation Methods*, Springer, 1996.
- [18] C. Fox, *An Introduction to the Calculus of Variations*, Oxford University Press, London, 1950.
- [19] J.M. Deutch, I. Oppenheim, The Concept of Brownian Motion in Modern Statistical Mechanics, in: *Faraday Discuss. Chem. Soc. London*, 1987, pp. 1–20.
- [20] A. Singharoy, S. Chelvaraja, P.J. Ortoleva, Order parameters for macromolecules: application to multiscale simulation, *J. Chem. Phys.* 134 (2011) 044104.
- [21] J.E. Shea, I. Oppenheim, Fokker–Planck equation and Langevin equation for one Brownian particle in a nonequilibrium bath, *J. Phys. Chem.* 100 (1996) 19035–19042.
- [22] J.E. Shea, I. Oppenheim, Fokker–Planck and non-linear hydrodynamic equations of an inelastic system of several Brownian particles in a non-equilibrium bath, *Physica A* 250 (1998) 265–294.
- [23] M.H. Peters, Fokker–Planck equation and the grand molecular friction tensor for coupled rotational and translational motions of structured Brownian particles near structured surfaces, *J. Chem. Phys.* 110 (1999) 528–538.
- [24] R.I. Cukier, J.M. Deutch, Spin relaxation: the multiple-time-scale point of view, *J. Chem. Phys.* 50 (1969) 36–41.
- [25] J.E. Shea, I. Oppenheim, Fokker–Planck equation and non-linear hydrodynamic equations of a system of several Brownian particles in a non-equilibrium bath, *Physica A* 247 (1997) 417–443.
- [26] H. Joshi, A.B. Singharoy, Y.V. Sereida, S.C. Chelvaraja, P.J. Ortoleva, Multiscale simulation of microbe structure and dynamics, *Prog. Biophys. Mol. Biol.* 107 (2011) 200–217.
- [27] Y. Miao, P.J. Ortoleva, Molecular dynamics/order parameter eXtrapolation (MD/OPX) for bionanosystem simulations, *J. Comput. Chem.* 30 (2009) 423–437.
- [28] Y. Miao, J.E. Johnson, P.J. Ortoleva, All-atom multiscale simulation of cowpea chlorotic mottle virus capsid swelling, *J. Phys. Chem. B* 114 (2010) 11181–11195.
- [29] H. Joshi, S. Chelvaraja, E. Somogyi, D.R. Brown, P.J. Ortoleva, A molecular dynamics study of loop fluctuation in human papillomavirus type 16 virus-like particles: a possible indicator of immunogenicity, *Vaccine* 29 (2011) 9423–9430.
- [30] Z. Shreif, S. Pankavich, P.J. Ortoleva, Liquid–crystal transitions: a first-principles multiscale approach, *Phys. Rev. E* 80 (2009) 031703.
- [31] Z. Shreif, P.J. Ortoleva, Multiscale approach to nanocapsule design, in: *Technical Proceedings of the 2008 NSTI Nanotechnology Conference and Trade Show*, 3, 2008, pp. 741–744.
- [32] S. Chelvaraja, P. Ortoleva, Thermal nanostructure: an order parameter/multiscale ensemble approach, *J. Chem. Phys.* 132 (2010) 075102.
- [33] P.J. Ortoleva, Nanoparticle dynamics: a multiscale analysis of the Liouville equation, *J. Phys. Chem. B* 109 (2005) 21258–21266.
- [34] Z. Shreif, P. Ortoleva, Curvilinear all-atom multiscale (CAM) theory of macromolecular dynamics, *J. Stat. Phys.* 130 (2008) 669–685.
- [35] Z. Shreif, P. Ortoleva, Scaling behavior of quantum nanosystems: emergence of quasi-particles, collective modes, and mixed exchange symmetry states, *J. Chem. Phys.* 134 (2011) 104106.
- [36] S. Pankavich, P. Ortoleva, Multiscaling for systems with a broad continuum of characteristic lengths and times: structural transitions in nanocomposites, *J. Math. Phys.* 51 (2010) 063303–063316.
- [37] R. Dobbartin, On functional relations between reduced distribution functions and entropy production by non-Hamiltonian perturbations, *Phys. Scr.* 14 (1976) 85–88.
- [38] J. Frenkel, *Wave Mechanics; Advanced General Theory*, Oxford University Press, 1934.
- [39] A.A. Vlasov, The vibrational properties of an electron gas, *Soviet Phys. Uspekhi* 10 (1968) 721–733.
- [40] A. Singharoy, Y.V. Sereida, P.J. Ortoleva, Hierarchical order parameters for macromolecular assembly simulations. I. Construction and dynamical properties of order parameters, *J. Chem. Theoret. Comput.* 8 (2012) 1379–1392.
- [41] S. Pankavich, Y. Miao, J. Ortoleva, Z. Shreif, P.J. Ortoleva, Stochastic dynamics of bionanosystems: multiscale analysis and specialized ensembles, *J. Chem. Phys.* 128 (2008) 234908–234920.
- [42] S. Pankavich, Z. Shreif, Y. Miao, P.J. Ortoleva, Self-assembly of nanocomponents into composite structures: derivation and simulation of Langevin equations, *Chem. Phys.* 130 (2009) 194115–194124.
- [43] Z. Shreif, P.J. Ortoleva, Multiscale derivation of an augmented Smoluchowski equation, *Physica A* 388 (2009) 593–600.
- [44] A.H. Nayfeh, B. Balachandran, *Applied Nonlinear Dynamics: Analytical, Computational, and Experimental Methods*, John Wiley and Sons, 1995.
- [45] S. Pankavich, Z. Shreif, P.J. Ortoleva, Multiscaling for classical nanosystems: derivation of Smoluchowski and Fokker–Planck equations, *Physica A* 387 (2008) 4053–4069.
- [46] R. Zwanzig, Approximate eigenfunctions of the Liouville operator in classical many-body systems, *Phys. Rev.* 144 (1966) 170–177.