



Extended molecular dynamics: Seamless temporal coarse-graining and transition between deterministic and probabilistic paradigms

Ignacio Romero ^{a,b,*}, Michael Ortiz ^c

^a Universidad Politécnica de Madrid, Spain

^b IMDEA Materials Institute, Spain

^c California Institute of Technology, USA

ARTICLE INFO

Keywords:

Time multiscale
Molecular dynamics
Atomistic mechanics
Hamiltonian mechanics
Time resolution

ABSTRACT

This article explores the formulation of evolution equations for atomistic systems where the time resolution is controlled at will. Based on a time-rescaled version of Hamilton's equations of motion, the equations of motion of these systems are derived with adjustable time granularity. Also, using the Liouville formalism for Hamiltonian mechanics, the evolution equations are recast in probabilistic terms, opening the door to variational, Galerkin-type projections. The resulting approximation provides the governing equations for the average motion of the system as well as the evolution of a temperature-like variable that modulates the thermal, unresolved, vibrations of each particle. The balance between the resolved and unresolved motions is, by construction, adjustable at every instant and fully reversible. This kind of models can be used to study the behavior of atomistic systems at different time scales.

1. Introduction

The accurate modeling of atomistic systems, both solid and fluid, entails the representation of phenomena that take place at a wide range of spatial and temporal scales. This fundamental difficulty motivates the use of models that describe a given space/time scale of the system and knowingly replaces all the physics happening in the small and fast scales with effective quantities (Phillips, 2001; Tadmor and Miller, 2011; Van der Giessen, 2019). One could argue that the formulation and analysis of such models is one of the main goals of mechanics and physics.

Multiscale models that can encompass two or more space and time scales have been developed, with much success, by combining physical descriptions and numerical methods. Broadly speaking, these methods bridge separate scales with techniques that are able to up- and down-scale the information in a concurrent or sequential fashion (Tadmor and Miller, 2011). Naturally, this scale handshake demands additional efforts but, when effective, it provides a beneficial compromise between cost and accuracy.

Among all multiscale techniques, the methods that focus on the spatial scale bridging have been the most successful of all. For example, in solid mechanics, the so-called *FE² method* has been extensively employed for more than twenty years (Feyel, 1999, 2003; Schröder, 2014). This asynchronous method approximates the solution to the mechanical problem using the Galerkin projection at the global level

– using standard finite elements – and at every Gauss point of the large scale equations. Alternatively, the *quasicontinuum method* was proposed to resolve the large and small spatial scales concurrently by recourse to mesh refinement and special quadrature rules (Tadmor et al., 1996; Shenoy et al., 1998; Knap and Ortiz, 2001; Zhang and Ge, 2005; Beex et al., 2011). A third idea that has been equally applied in the solid and fluid mechanics fields is the *variational multiscale method* (Hughes et al., 1998). This general framework is designed to transfer subgrid scale information to the resolved scales, but only through effective values, hence respecting the simplicity of standard Galerkin methods.

Time multiscale methods have been developed to a lesser extent, arguably because dynamical problems in mechanics lack a minimization structure that can be exploited by Galerkin projections. Numerical approaches that have enabled solutions for relatively long interval of time include kinetic Monte Carlo methods (Fichthorn and Weinberg, 1991), accelerated molecular dynamics (Voter, 1997; Voter et al., 2002) and *metadynamics* (Laio and Parrinello, 2002; Branduardi et al., 2012; Dama et al., 2014; Khanjari et al., 2017; Eslami et al., 2017). In the first case, the precise evolution of the system is replaced with discrete events whose probability is calculated beforehand. The second type collects various numerical methods that perturb the energetic landscape of the atomistic system so as to increase its chance of escaping deep energy basins. Similarly, the third group collects numerical methods

* Correspondence to: ETS Ingenieros Industriales, José Gutiérrez Abascal, 2, Madrid 28006, Spain.

E-mail addresses: ignacio.romero@upm.es (I. Romero), ortiz@aero.caltech.edu (M. Ortiz).

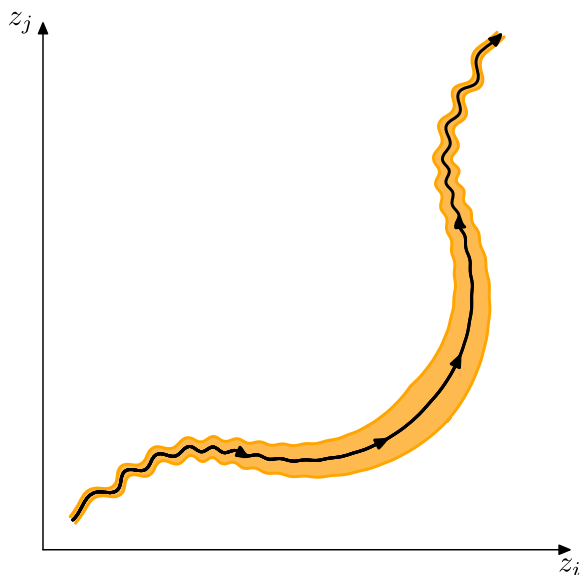


Fig. 1. Illustration of the xMD scale bridging process. The black line represents the mean trajectory in phase space and the colored region represents the region in which a fixed fraction (say 50%) of the Liouville probability is concentrated. As time progresses, the xMD theory is able to replace the high-frequency oscillations in the trajectory by a “wider” probability density function that accounts for these oscillations energetically. By reversing this process, the oscillatory response is recovered at the expense of the variance of the phase probability.

that modify the potential energy of particle systems, biasing the latter with trajectory-dependent Gaussians that, centered at the visited configurations, filling the energy wells and increasing the probability that the system escapes them. In these and related methods the objective is to bypass the stringent constraints on the time step size of explicit integrators employed in molecular dynamics (Allen and Tildesley, 1987; Tuckerman, 2010). However, none of these change the fundamental models that describe the physics of the systems, that is, the differential equations that govern their behavior, before any numerical discretization.

In contrast, in this work we wish to formulate models for the dynamic description of atomistic systems whose temporal resolution can be modulated in a controlled and continuous fashion. These *extended molecular dynamics* (xMD) models will provide the foundation for analyses and time discretizations that can be used to extract information from these systems at the desired time scales. In particular, when the time resolution employed is fine, the models we aim to obtain should coincide with those employed in standard molecular dynamics simulation. Conversely, when the selected time resolution is coarse, the models should approach thermodynamical descriptions of the systems in which one or several state variables will account for rapidly oscillating motions in a statistically representative manner.

The point of departure for our analysis is recognizing that the dynamical behavior of atomistic systems over short and long time intervals is fundamentally different. For instance, under reasonable growth assumptions on the potential energy, stationary trajectories are minimizers when restricted to sufficiently short intervals (Müller and Ortiz, 2004). By contrast, over long time intervals, trajectories may wander in phase space and become stochastic. Under the latter conditions, statistical descriptions of the system, such as derived, e. g., from ergodic theory, are more appropriate than deterministic descriptions focusing on individual trajectories. However, no theory appears to as yet exist that provides a bridge between the two limits of deterministic molecular dynamics and ergodic theory depending on the granularity of the temporal resolution of the model.

To further describe the motivation for the current work, consider the motion of an atomistic system described by a curve in phase space.

Most systems of this type follow trajectories that exhibit rapid and small oscillations arising from the complex energetic landscape created by the interatomic potential. The goal of this work is to formulate a theory that can model the mechanics of atomistic systems but accounting for the aforementioned oscillations in a stochastic manner, when so desired. Roughly speaking, we aim at devising a theory capable of systematically replacing the differential equations that describe the phase space trajectories with a dynamical system for a probability function that accounts for unresolved oscillations in a reversible fashion. As illustrated in Fig. 1, the theory should replace the wiggly dynamics of the atomistic system by a smoother, albeit uncertain, description of the configuration of the system that accounts for the energetic contributions of the smoothed oscillations. Such a substitution, to be completely useful, should be controllable and reversible, so that the level of mesodynamical modeling adapts to the physical phenomena taking place at every instant, or the goals of the analysis.

Hamiltonian mechanics provides the mathematical background for this work. More specifically, two ingredients of the theory will prove essential for the formulation of xMD. First, to uncover the role of time resolution in atomistic systems, we exploit the effects of a time reparameterization in Hamilton’s action. This avenue unveils a control function that can be used to modulate, as desired, the advance of time in the phase space. Second, the use of Liouville’s formalism of Hamiltonian mechanics (Arnold, 1989) will introduce the key concept of phase probability and will eventually allow to replace the precise description of the fast vibrations in the motion with statistical averages.

To complete our program, we will propose an approximation theory for the solution of reparametrized Hamiltonian mechanics in the Liouville picture, exploiting a variational reformulation of Liouville’s equations. Several alternative avenues will be identified, and we will complete the derivations for an approximation theory based on optimal representations. More specifically, and following previous results (Kulkarni et al., 2008; Ariza et al., 2012; Venturini et al., 2014), *maximum entropy* probability functions will be obtained and their corresponding mesodynamical equations will be derived. The latter will correspond to the molecular dynamics evolution equations, *extended* with the thermodynamic relations that describe the energetic effects not resolved by the optimal, yet coarse, probability.

The remainder of the article has the following structure. Section 2 reviews the Hamiltonian formalism as it applies to atomistic systems. Here, a time reparameterization of Hamilton’s action is introduced as the key idea to reveal the time granularity in the motion. Its reformulation in a probabilistic context is developed in Section 3, where the Liouville description is presented and then recast in variational form, opening the door to approximation theory. The latter is explored in Section 4, leading to mesodynamical evolution equations and further approximations for systems with complex interaction potentials. These concepts are validated with examples in Section 5 and the article is closed with some remarks in Section 6.

2. Hamiltonian formulation of molecular dynamics

Hamiltonian mechanics provides the basis for the statistical description systems of particles, including classical statistical mechanics and the Liouville equation. By virtue of this nexus, it also provides the appropriate framework – and point of departure – for the formulation of mesodynamical approximations of the motion. Hamiltonian mechanics can be formulated with great generality in – finite or infinite-dimensional – symplectic manifolds. However, this degree of generality is beyond the scope of this work, and we focus on system of particles in flat spaces.

2.1. Hamilton's equations

We specifically consider systems of particles whose instantaneous state is given by $z \equiv (z_i)_{i=1}^N \in P = \mathbb{R}^{dN} \times \mathbb{R}^{dN}$, where $z_i \equiv (q_i, p_i) \in \mathbb{R}^d \times \mathbb{R}^d$ is the position of particle i in the *phase space* P , $q_i \in \mathbb{R}^d$ is the position of particle i and $p_i \in \mathbb{R}^d$ its momentum and d denote the spatial dimension. The dynamical properties of the system are characterized by a – possibly time dependent – Hamiltonian $H = H(z, t)$, where time is $t \in [0, T]$. For instance, in applications we shall be concerned with Hamiltonians of the form

$$H(z, t) = \sum_{i=1}^N \frac{|p_i|^2}{2m_i} + V(q, t), \quad (1)$$

where m_i is the mass of particle i and $V(q, t)$ is the potential energy of the system of particles accounting for both the interatomic interactions and external fields, if any. Hamilton's equations

$$\dot{q}_i(t) = \frac{\partial H}{\partial p_i}(z(t), t), \quad \dot{p}_i(t) = -\frac{\partial H}{\partial q_i}(z(t), t), \quad (2)$$

then determine the trajectories of the system in phase space. Here, and below, a dot over any symbol denotes its time derivative. The ordinary differential equations (2) can be rewritten more succinctly as

$$\dot{z}(t) = X_H(z(t), t), \quad (3)$$

where

$$X_H = \left(\frac{\partial H}{\partial p}, -\frac{\partial H}{\partial q} \right) \quad (4)$$

is the Hamiltonian vector field (Arnold, 1989). In this setting, the trajectories $z(t)$ of the system are streamlines of X_H in phase space. An alternative statement of Hamilton's equations of motion can be given in terms of the *Poisson bracket*. We recall that the Poisson bracket of two differentiable functions $f, g : P \times [0, T] \rightarrow \mathbb{R}$ is defined as

$$\{f, g\} \equiv \frac{\partial f}{\partial q} \cdot \frac{\partial g}{\partial p} - \frac{\partial f}{\partial p} \cdot \frac{\partial g}{\partial q}, \quad (5)$$

which is obviously skew-symmetric. In terms of this Poisson bracket, Hamilton's equations can be written in the compact and convenient form

$$\dot{q} = \frac{\partial H}{\partial p} = \{q, H\}, \quad \dot{p} = -\frac{\partial H}{\partial q} = \{p, H\}. \quad (6)$$

In addition, the time derivative of a function $f(z, t)$ along trajectories follows as

$$\dot{f} = \frac{\partial f}{\partial t} + \frac{\partial f}{\partial q} \cdot \dot{q} + \frac{\partial f}{\partial p} \cdot \dot{p} = \frac{\partial f}{\partial t} + \{f, H\}. \quad (7)$$

In particular, we have

$$\dot{H} = \frac{\partial H}{\partial t} + \{H, H\} = \frac{\partial H}{\partial t}, \quad (8)$$

which shows that the Hamiltonian $H(z)$, or total energy, of an autonomous system is conserved along trajectories.

2.2. Hamilton's principle of stationary action

For purposes of approximation, the variational form of Hamiltonian mechanics, namely, Hamilton's principle of stationary action, is of particular interest. In the framework of Hamiltonian mechanics, the action integral along a trajectory $z(t)$ of the system is defined as

$$A[z] = \int_0^T (p \cdot \dot{q} - H(z, t)) dt. \quad (9)$$

The first term in the integrand is referred to as the *canonical one-form*. Hamilton's principle of stationary action then states that the trajectories of the system render the action stationary, i. e.,

$$\delta A[z, \delta z] = 0, \quad (10)$$

for all admissible variations δz . We verify that this statement can be written as

$$\delta A[z, \delta z] = \int_0^T \left((\delta p \cdot \dot{q} + p \cdot \delta \dot{q}) - \left(\frac{\partial H}{\partial q}(z, t) \cdot \delta q + \frac{\partial H}{\partial p}(z, t) \cdot \delta p \right) \right) dt. \quad (11)$$

Integrating by parts and only considering variations that satisfy $\delta z(0) = \delta z(T) = 0$, we obtain

$$\delta A[z, \delta z] = \int_0^T \left((\delta p \cdot \dot{q} - \dot{p} \cdot \delta q) - \left(\frac{\partial H}{\partial q}(z, t) \cdot \delta q + \frac{\partial H}{\partial p}(z, t) \cdot \delta p \right) \right) dt. \quad (12)$$

The first term in the integrand is referred to as the *symplectic two-form*. Finally, the stationarity principle (10) returns Hamilton's equations (2), as advertised.

2.3. Time-energy principle

A fundamental question that pervades the present work concerns the interplay and trade-off between time resolution, energy and uncertainty. This resolution-uncertainty trade-off may be ascertained by considering the effect of perturbations of the form

$$A[z] \rightarrow \tilde{A}[\tilde{z}] = \int_0^T (\tilde{p} \cdot \dot{\tilde{q}} - f'(\tilde{t}) H(\tilde{z}, f(\tilde{t}))) d\tilde{t}, \quad (13)$$

corresponding to time reparameterizations

$$t = f(\tilde{t}), \quad \tilde{z}(\tilde{t}) = z(f(\tilde{t})), \quad (14)$$

with $f'(\tilde{t}) > 0$. We note that in Eq. (13) and below the derivative of scaled functions, e.g. $\dot{\tilde{q}}, \dot{\tilde{p}}$, now refers to the derivative with respect to the scaled time \tilde{t} .

The relationship between the time scales t and \tilde{t} is a key concept of the theory that follows. Since $f'(\tilde{t})$ determines their ratio, we observe that large values of this derivative correspond to high resolutions in the perturbed solution, and vice versa.

Stationarity of the perturbed action (13) demands

$$\dot{\tilde{q}}(\tilde{t}) = \frac{\partial \tilde{H}}{\partial \tilde{p}}(\tilde{z}(\tilde{t}), \tilde{t}), \quad (15a)$$

$$\dot{\tilde{p}}(\tilde{t}) = -\frac{\partial \tilde{H}}{\partial \tilde{q}}(\tilde{z}(\tilde{t}), \tilde{t}), \quad (15b)$$

with

$$\tilde{H}(\tilde{z}, \tilde{t}) = f'(\tilde{t}) H(\tilde{z}, f(\tilde{t})) \quad (16)$$

being the perturbed Hamiltonian. An application of identity (8) to the Hamiltonian (16) further gives

$$\dot{\tilde{H}}(\tilde{z}(\tilde{t}), \tilde{t}) = f'^2(\tilde{t}) \frac{\partial H}{\partial t}(\tilde{z}(\tilde{t}), f(\tilde{t})) + \frac{f''(\tilde{t})}{f'(\tilde{t})} \tilde{H}(\tilde{z}(\tilde{t}), f(\tilde{t})). \quad (17)$$

We observe from this identity that the perturbed motion is *attenuated*, $\dot{\tilde{H}} < 0$, (respect., *excited*, $\dot{\tilde{H}} > 0$), by a decrease, $f''(\tilde{t}) < 0$, (respect., increase, $f''(\tilde{t}) > 0$) in temporal resolution, which may be regarded as a *time-dissipation principle*. In the case of autonomous Hamiltonians, relation (17) reduces to

$$\dot{\tilde{H}}(\tilde{z}(\tilde{t}), \tilde{t}) = \frac{f''(\tilde{t})}{f'(\tilde{t})} \tilde{H}(\tilde{z}(\tilde{t}), f(\tilde{t})), \quad (18)$$

which is equivalent to

$$\frac{d}{d\tilde{t}} (\tilde{E}(\tilde{t}) \tau(\tilde{t})) = 0, \quad (19)$$

where we write

$$\tilde{E}(\tilde{t}) = \tilde{H}(\tilde{z}(\tilde{t}), \tilde{t}), \quad \tau(\tilde{t}) = \frac{1}{f'(\tilde{t})}. \quad (20)$$

Eq. (19) further implies

$$\tilde{E}(\tilde{t}) \tau(\tilde{t}) = \text{constant}, \quad (21)$$

which may be regarded as a *time-energy principle*. This principle gives shape to the trade-off between temporal coarseness, as measured by $\tau(\tilde{t})$ and energy. Specifically, an increase in time resolution (smaller τ) is accompanied by a concomitant increase in energy, while a reduction in resolution (larger τ) subtracts energy from the system.

The unperturbed trajectories are recovered by demanding stationarity of \tilde{A} with respect to the time reparameterization f . Thus, the corresponding Euler–Lagrange equation follows from (13) as

$$\frac{d}{d\tilde{t}} H(\tilde{z}(\tilde{t}), f(\tilde{t})) - f'(\tilde{t}) \frac{\partial H}{\partial \tilde{t}}(\tilde{z}(\tilde{t}), f(\tilde{t})) = 0. \quad (22)$$

Evidently, the choice $f'(\tilde{t}) = 1$ reduces Eqs. (15) and (22) to Eqs. (2) and (8), respectively. Moreover, if the Hamiltonian is autonomous, Eq. (22) shows that H is a constant of the motion. Hence, conservation of energy is the consequence of the invariance of the action with respect to time reparameterizations.

2.4. Relationship with time integration schemes

Variational time integration schemes are systematically obtained by approximating Hamilton's action (see, e.g. Marsden and West (2001), Lew et al. (2004)). For that, the time interval $[0, T]$ is first partitioned into disjoint subintervals $(t_k, t_{k+1}]$ with $0 = t_0 < t_1 < \dots < t_K = T$ of length $\tau_{k+1/2} \equiv t_{k+1} - t_k$. Then, the unknown trajectory $(q(t), p(t))$ is approximated by piecewise polynomials $(q_h(t), p_h(t))$ whose coefficients are inductively obtained by recourse to the principle of stationary action. By refining the time partition (i. e., when $\max \tau_{k+1/2} \rightarrow 0$), the sequence $z_h(t) = (q_h(t), p_h(t))$ can be shown to converge, under certain conditions, to the exact trajectory in phase space.

For concreteness, let us assume that the position and momentum in the interval $(t_k, t_{k+1}]$ are approximated as

$$q_h(t) = \frac{t - t_k}{\tau_{k+1/2}} q_{k+1} + \frac{t_{k+1} - t}{\tau_{k+1/2}} q_k, \quad (23)$$

$$p_h(t) = p_{k+1/2},$$

with $q_k, p_{k+1/2}$ constant coefficients. Then, replacing these expressions in the action integral (9), and approximating the energy integral with a midpoint quadrature, we obtain

$$A[z_h] = \sum_{k=1}^{K-1} [p_{k+1/2} (q_{k+1} - q_k) - H_{k+1/2} \tau_{k+1/2}] \quad (24)$$

with

$$H_{k+1/2} = \sum_i \frac{|p_{i,k+1/2}|^2}{2m_i} + V(q_h(t_{k+1/2}), t_{k+1/2}). \quad (25)$$

The *discrete Euler–Lagrange* equations of the action (24) provide the update map $(q_k, p_{k+1/2}) \mapsto (q_{k+1}, p_{k+1/2})$ corresponding to the time integration algorithm.

Exploring an apparently unrelated argument, let us now consider a time reparameterization of the action of the type described in Section 2.3. Specifically, let us select a map f of the form

$$f(\tilde{t}) = \tilde{t}_k, \quad \text{for } \tilde{t} \in (\tilde{t}_k, \tilde{t}_{k+1}]. \quad (26)$$

See Fig. 2 for an illustration of this piecewise constant function. Under reasonable assumptions for the smoothness of the potential energy (it is sufficient for it to be continuous) the action \tilde{A} of Eq. (13) integrates exactly to

$$\tilde{A}[\tilde{z}] = \sum_{k=0}^K [p_{k+1/2} (q_{k+1} - q_k) - H_{k+1/2} \tau_{k+1/2}] \quad (27)$$

where now $p_{k+1/2}$ is the value of the momentum in the interval $(t_k, t_{k+1}]$, which is constant, and $H_{k+1/2}$ is precisely given by Eq. (25).

The foregoing argument sheds new light on the origin and interpretation of variational time integration schemes. As shown above for one example, the solutions of some variational integrators are the *exact* trajectories of reparametrized Hamiltonian systems, an insight that opens the door to new proofs for convergence of these methods, among other things.

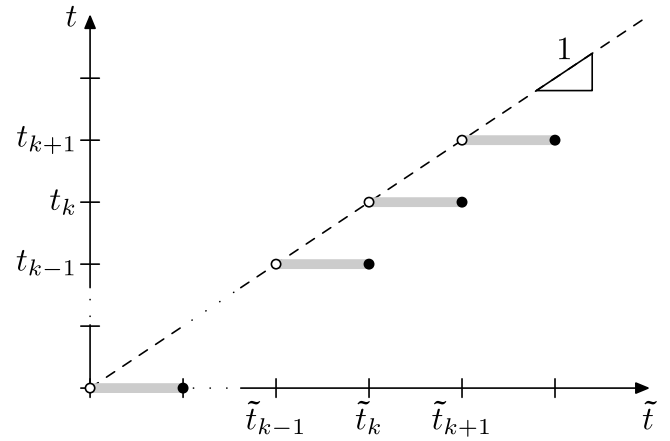


Fig. 2. Graph of the function (26) defining a piecewise constant time reparameterization.

3. Probabilistic reformulation: Liouville equation

In this section we continue to study Hamiltonian mechanics for systems of particles but shifting the point of view, in search for a variational statement of the latter that paves the way to approximation theory. This will be accomplished by relying on Liouville mechanics, a reformulation of the Hamiltonian formalism in terms of measures (see, e.g., Abraham and Marsden (1978)). The approximation schemes will be derived by restricting the Liouville equation to conveniently parameterized spaces of measures.

3.1. The Liouville equation

An alternative description of Hamiltonian flows is obtained by using measures. To this end, let $\rho(z, t)$ denote the probability that the mechanical system be in state $z \in P$ at time t . Then, ρ evolves according to the Liouville equation

$$\frac{\partial \rho}{\partial t} = -\text{div}(\rho X_H), \quad (28)$$

where div stands for the divergence operator in phase space. Equivalently,

$$\frac{\partial \rho}{\partial t} = -\{\rho, H\}, \quad (29)$$

where we have used the incompressibility of the Hamiltonian vector field, namely,

$$\text{div} X_H = 0. \quad (30)$$

Eq. (28) is simply the transport equation for the scalar measure $\rho(z, t)$ corresponding to the Hamiltonian vector field (4). It defines a flow in the space of probability measures, with the usual Riemannian manifold structure.

3.2. Variational and Hamiltonian structure of the Liouville equation

In order to cast the equations of motion variationally, we begin by expressing the Liouville equation (28) in weak form as

$$\int_0^T \int (\dot{\rho} + \text{div}(\rho X_H)) \delta \pi \, dz \, dt = 0, \quad (31)$$

where $\delta \pi$ is an admissible variation and we write, here and henceforth,

$$\dot{\rho}(z, t) = \frac{\partial \rho}{\partial t}(z, t). \quad (32)$$

Evidently, the left-hand side of Eq. (31) is the variation of the functional

$$\mathcal{A}[\mathcal{Z}] = \int_0^T \int (\dot{\rho} + \operatorname{div}(\rho X_H)) \pi \, dz \, dt, \quad (33)$$

with respect to π , where we write $\mathcal{Z} = (\rho, \pi)$. We refer to $\mathcal{A}[\mathcal{Z}]$ as the *Liouville action*. Integrating (33) by parts in time and applying Stoke's theorem, we obtain

$$\mathcal{A}[\mathcal{Z}] = \int_0^T \int \left(\pi \dot{\rho} - \sum_{i=1}^N \left(\frac{\partial \rho}{\partial q_i} \cdot \frac{\partial \pi}{\partial p_i} - \frac{\partial \pi}{\partial q_i} \cdot \frac{\partial \rho}{\partial p_i} \right) H \right) dz \, dt, \quad (34)$$

or, in terms of the Poisson bracket (5),

$$\mathcal{A}[\mathcal{Z}] = \int_0^T \int (\pi \dot{\rho} - \{\rho, \pi\} H(z, t)) \, dz \, dt. \quad (35)$$

We observe that this action is in analogy with (9), provided we identify ρ with the configuration of the Liouville system, π with the Liouville momentum, $\mathcal{Z} = (\rho, \pi)$ with a generic point in the – infinite-dimensional – Liouville phase space, and

$$H(\mathcal{Z}, t) = \int \{\rho, \pi\} H(z, t) \, dz \quad (36)$$

with the *Liouville Hamiltonian*. In addition, the first term in the action integral (35) may be identified as the *Liouville one-form*. Taking variations in the action (35) and integrating by parts in time gives

$$\delta \mathcal{A}[\mathcal{Z}, \delta \mathcal{Z}] = \int_0^T \int \left((\dot{\rho} \delta \pi - \dot{\pi} \delta \rho) - (\{\delta \rho, \pi\} + \{\rho, \delta \pi\}) H(z, t) \right) dz \, dt, \quad (37)$$

where the first term in the time integral may be regarded as a *Liouville symplectic two-form*. The principle of stationary action then gives the Euler–Lagrange equations

$$\dot{\rho} + \operatorname{div}(\rho X_H) = 0, \quad (38a)$$

$$\dot{\pi} + \operatorname{div}(\pi X_H) = 0, \quad (38b)$$

which may be identified with *Hamilton's equations for the Liouville system*. We note that both the probability density ρ and the Liouville momentum π are transported along trajectories of the system, i. e., they satisfy the Liouville transport equation corresponding to the Hamiltonian vector field X_H . We also note that, if $\rho(t)$ satisfies (38a), then

$$\pi(t) = -\log \rho(t) \quad (39)$$

satisfies (38b). We may thus identify the space of Liouville momenta with the space of *free entropies*. From Eqs. (36) and (38), along trajectories we have

$$\begin{aligned} \dot{\mathcal{H}} &= \int \{\dot{\rho}, \pi\} H(z, t) \, dz + \int \{\rho, \dot{\pi}\} H(z, t) \, dz + \int \{\rho, \pi\} \frac{\partial H}{\partial t}(z, t) \, dz \\ &= \int \{\rho, \pi\} \frac{\partial H}{\partial t}(z, t) \, dz. \end{aligned} \quad (40)$$

In particular, it follows that for autonomous Hamiltonians $H(z)$ the Liouville energy \mathcal{H} is conserved along trajectories.

In the Liouville formalism, the entropy of the system is the functional

$$S = - \int \rho \log \rho \, dz. \quad (41)$$

Using (38a), we note that

$$\dot{S} = - \frac{d}{dt} \int \rho \log \rho \, dz = \int \operatorname{div}(\rho X_H) \log \rho \, dz = \int X_H \cdot \nabla \rho \, dz = 0, \quad (42)$$

by Stoke's theorem. We thus recover the expected result that the entropy of a closed system remains constant along trajectories.

3.3. Time-energy and uncertainty principles

As in Section 2.3, we consider perturbed actions of the form (13) resulting from the time rescaling (14). In this case, the Liouville action becomes

$$\tilde{\mathcal{A}}[\tilde{\mathcal{Z}}] = \int_0^T \int (\tilde{\pi} \dot{\tilde{\rho}} - \{\tilde{\rho}, \tilde{\pi}\} \tilde{H}(\tilde{z}, \tilde{t})) \, d\tilde{z} \, d\tilde{t}, \quad (43)$$

and the corresponding Liouville-Hamiltonian is

$$\tilde{H}(\tilde{\mathcal{Z}}, \tilde{t}) = \int \{\tilde{\rho}, \tilde{\pi}\} \tilde{H}(\tilde{z}, \tilde{t}) \, d\tilde{z}. \quad (44)$$

As in identity (40), we have for the perturbed Hamiltonian that

$$\begin{aligned} \dot{\tilde{H}}(\tilde{\mathcal{Z}}(\tilde{t}), \tilde{t}) &= \int \{\tilde{\rho}, \tilde{\pi}\} \left(f''(\tilde{t}) H(\tilde{z}(\tilde{t}), f(\tilde{t})) + f'^2(\tilde{t}) \frac{\partial H}{\partial t}(\tilde{z}(\tilde{t}), f(\tilde{t})) \right) d\tilde{z} \\ &= \frac{f''(\tilde{t})}{f'(\tilde{t})} \tilde{H}(\tilde{\mathcal{Z}}(\tilde{t}), \tilde{t}) + f'(\tilde{t}) \int \{\tilde{\rho}, \tilde{\pi}\} \frac{\partial H}{\partial t}(\tilde{z}(\tilde{t}), f(\tilde{t})) \, d\tilde{z}. \end{aligned} \quad (45)$$

In particular, for autonomous Hamiltonians $H(z)$, this identity reduces to

$$\dot{\tilde{H}}(\tilde{\mathcal{Z}}(\tilde{t}), \tilde{t}) = \frac{f''(\tilde{t})}{f'(\tilde{t})} \tilde{H}(\tilde{\mathcal{Z}}(\tilde{t}), \tilde{t}), \quad (46)$$

which is equivalent to

$$\frac{d}{d\tilde{t}} \left(\tilde{\mathcal{E}}(\tilde{t}) \tau(\tilde{t}) \right) = 0, \quad (47)$$

where we write

$$\tilde{\mathcal{E}}(\tilde{t}) \equiv \tilde{H}(\tilde{\mathcal{Z}}(\tilde{t}), \tilde{t}), \quad \tau(\tilde{t}) = \frac{1}{f'(\tilde{t})}. \quad (48)$$

Eq. (47) further implies

$$\tilde{\mathcal{E}}(\tilde{t}) \tau(\tilde{t}) = \text{constant}, \quad (49)$$

which may be regarded as a *time-energy principle* analogous to (21) and expressing a trade-off between temporal resolution, as measured by the inverse of $\tau(\tilde{t})$, and energy.

Following an analogous argument, we can define the perturbed entropy to be

$$\tilde{S}(\tilde{\mathcal{Z}}, \tilde{t}) = - \frac{1}{f'(\tilde{t})} \int \tilde{\rho} \log \tilde{\rho} \, d\tilde{z} \quad (50)$$

Then, its time derivative satisfies

$$\dot{\tilde{S}}(\tilde{\mathcal{Z}}, \tilde{t}) = - \frac{f''(\tilde{t})}{f'(\tilde{t})} \tilde{S}(\tilde{\mathcal{Z}}, \tilde{t}). \quad (51)$$

This identity is equivalent to

$$\frac{d}{d\tilde{t}} \left(\frac{\tilde{\mathcal{N}}(\tilde{t})}{\tau(\tilde{t})} \right) = 0, \quad (52)$$

where we write

$$\tilde{\mathcal{N}}(\tilde{t}) \equiv \tilde{S}(\tilde{\mathcal{Z}}(\tilde{t}), \tilde{t}), \quad (53)$$

and $\tau(\tilde{t})$ is defined in Eq. (48). Eq. (52) then implies that

$$\frac{\tilde{\mathcal{N}}(\tilde{t})}{\tau(\tilde{t})} = \text{constant}, \quad (54)$$

which may be regarded as an *uncertainty principle*. Indeed, by virtue of this principle, an increase (respect., decrease) in temporal resolution, as measured by $1/\tau(\tilde{t})$, is accompanied by a concomitant decrease (respect., increase) in uncertainty, as measured by the entropy $\tilde{\mathcal{N}}$.

3.4. Variational approximation of the perturbed Liouville equation

Approximation schemes for the perturbed Liouville equation can be systematically formulated by restricting the Liouville action (43) to sequences of special trajectories $\tilde{\mathcal{Z}}_h(\tilde{t})$. Specifically, we may consider parameterized densities of the form

$$\tilde{\rho}_h(\tilde{z}, \tilde{t}) = \varphi_h(\tilde{z}, \xi_h(\tilde{t})), \quad (55a)$$

$$\tilde{\pi}_h(\tilde{z}, \tilde{t}) = v_h(\tilde{z}, \xi_h(\tilde{t})) \cdot \eta_h(\tilde{t}), \quad (55b)$$

where (ξ_h, η_h) are parameters. By differentiation with respect to \tilde{t} , we have

$$\dot{\tilde{\pi}}_h(\tilde{z}, \tilde{t}) = \partial_{\xi_h} \varphi_h(\tilde{z}, \xi_h(\tilde{t})) \cdot \dot{\xi}_h(\tilde{t}) \equiv \varphi_h(\tilde{z}, \xi_h(\tilde{t})) u_h(\tilde{z}, \xi_h(\tilde{t})) \cdot \dot{\xi}_h(\tilde{t}), \quad (56)$$

where

$$u_h(\tilde{z}, \xi_h) = \frac{\partial_{\xi_h} \varphi_h(\tilde{z}, \xi_h)}{\varphi_h(\tilde{z}, \xi_h)} = \partial_{\xi_h} \log \varphi_h(\tilde{z}, \xi_h) \quad (57)$$

may be regarded as tangent basis functions. Inserting the *ansatz* (55) in the perturbed Liouville action (43), we obtain the restricted action

$$\tilde{\mathcal{A}}[\tilde{\mathcal{Z}}_h] = \int_a^b \int \left(\tilde{\pi}_h \dot{\tilde{\pi}}_h - \{ \tilde{\pi}_h, \tilde{\pi}_h \} f'(\tilde{t}) \tilde{H}(\tilde{z}, \tilde{t}) \right) d\tilde{z} d\tilde{t}, \quad (58)$$

or, in parameter space

$$\tilde{\mathcal{A}}[\tilde{\mathcal{Z}}_h] = \int_a^b \left(\eta_h \cdot A_h(\xi_h(\tilde{t})) \dot{\xi}_h - H_h(\xi_h, \eta_h, \tilde{t}) \right) d\tilde{t}, \quad (59)$$

where

$$A_h(\xi_h) = \int v_h(\tilde{z}, \xi_h) \otimes u_h(\tilde{z}, \xi_h) \varphi_h(\tilde{z}, \xi_h) d\tilde{z}, \quad (60a)$$

$$H_h(\xi_h, \eta_h, \tilde{t}) = \int \{ \varphi_h(\tilde{z}, \xi_h), v_h(\tilde{z}, \xi_h) \cdot \eta_h \} f'(\tilde{t}) \tilde{H}(\tilde{z}, \tilde{t}) d\tilde{z}. \quad (60b)$$

Evidently, the matrix $A_h(\xi_h)$ is rendered symmetric by the choice

$$v_h(\tilde{z}, \xi_h) = u_h(\tilde{z}, \xi_h). \quad (61)$$

The reduced action (59) then defines a Hamiltonian system on the Riemannian manifold of parameters ξ_h metrized by the Fisher information metric $A_h(\xi_h)$.

Enforcing stationarity of the action (59) with respect to η_h , we obtain

$$A_h(\xi_h(\tilde{t})) \dot{\xi}_h(\tilde{t}) - B_h(\xi_h(\tilde{t}), \tilde{t}) = 0, \quad (62)$$

where

$$B_h(\xi_h, \tilde{t}) = \int \{ \varphi_h(\tilde{z}, \xi_h), v_h \} \tilde{H}(\tilde{z}, \tilde{t}) d\tilde{z} \quad (63)$$

defines a reduced Hamiltonian vector field. As a particular case, we might consider the trivial time scaling $f(\tilde{t}) = \tilde{t}$. Then, the former variational projection defines evolution equations in the unperturbed system.

We note that Eqs. (62) are still Hamiltonian. This has important consequences in the qualitative behavior of their solution, including the existence of first integrals of the motion and, in particular, conservation of energy.

4. Mesodynamical approximations of the Liouville equation

We exploit next the variational structure of Liouville's equation of time-scaled systems to propose approximations that enforce the granularity of the solution. Indeed, the results of Section 3.4 leave open the definition of the trial densities φ_h , and several alternative expressions can be suggested.

4.1. Maximum-entropy ansatz

We seek to represent the mean or mesoscopic flow deterministically and the fluctuations probabilistically. In this representation, the mean flow and the fluctuations take on, respectively, the additional significance of *resolved* and *unresolved* parts of the flow.

To this end, let $g(\tilde{q}, \tilde{p}, \tilde{t})$ be a time-dependent function of the position and momentum of the system and let us assume that there exists a probability density function $\tilde{\rho}(\tilde{q}, \tilde{p}, \tilde{t})$, also time-dependent, giving the probability of the system having the state (\tilde{q}, \tilde{p}) at time \tilde{t} . Assuming

ergodicity, the time average of any phase function g , denoted as \bar{g} , coincides with the ensemble average, that is,

$$\bar{g} = \langle g \rangle \equiv \int g(\tilde{q}, \tilde{p}, \tilde{t}) \tilde{\rho}(\tilde{q}, \tilde{p}, \tilde{t}) d\tilde{q} d\tilde{p}. \quad (64)$$

Proceeding again formally, we postulate now that the probability density function $\tilde{\rho}$ obeys the principle of maximum entropy (Jaynes, 1957; Venturini et al., 2014) and thus

$$\{S(\tilde{\rho}) = -k_B \langle \log \tilde{\rho} \rangle : \{\text{constraints}\}\} \rightarrow \max!, \quad (65)$$

i. e., $\tilde{\rho}$ maximizes the information-theoretical entropy of the local ensemble of particles subject to constraints to be introduced. In Eq. (65), k_B is the Boltzmann constant. By this normalization, $S(\tilde{\rho})$ reduces to the Boltzmann entropy at equilibrium.

An appropriate set of constraints can be formulated as follows. First, we would like the probability function to be such that the average of the phase coordinates coincides with their known mean values, that is,

$$\langle \tilde{q}_i \rangle = \bar{q}_i \quad \langle \tilde{p}_i \rangle = \bar{p}_i. \quad (66)$$

Also, we would like to control the size of the fluctuations in position and momentum and relate the latter with the time resolution. For that, we start by defining a, possibly time-dependent, *particle potential* $W_i = W_i(\tilde{q}_i; \tilde{t})$ and the *energy norm* of particle i to be

$$\tilde{e}_i(\tilde{q}_i, \tilde{p}_i, \tilde{t}) = \tau_i(\tilde{t}) \left(\frac{1}{2m_i} |\tilde{p}_i|^2 + W_i(\tilde{q}_i; \tilde{t}) \right), \quad (67)$$

where $\tau_i(\tilde{t})$ is a particle, dimensionless time granularity. To close the max-ent problem we append to (66) an energy constraint for each particle, that is, we impose

$$\langle \tilde{e}_i \rangle = \bar{e}_i. \quad (68)$$

Hence, the sought probability distribution maximizes the entropy (65) subject to the constraints (66) and (68). We may enforce these constraints by recourse to Lagrange multipliers. To this end, we introduce the Lagrangian

$$\frac{1}{k_B} L(\tilde{\rho}; \alpha, \beta, \gamma, \delta) = -\langle \log \tilde{\rho} \rangle - \alpha \langle 1 \rangle - \sum_{i=1}^N (\gamma_i \langle \tilde{q}_i \rangle + \delta_i \langle \tilde{p}_i \rangle + \beta_i \langle \tilde{e}_i \rangle), \quad (69)$$

where α , β_i , γ_i , and δ_i are Lagrange multipliers.

The optimality conditions for program (65) are (cf., e. g., Rockafellar (1970))

$$\frac{\partial L}{\partial \tilde{\rho}} = 0, \quad \frac{\partial L}{\partial \alpha} = 0, \quad \frac{\partial L}{\partial \beta_i} = 0, \quad \frac{\partial L}{\partial \gamma_i} = 0, \quad \frac{\partial L}{\partial \delta_i} = 0, \quad (70)$$

giving a probability function that must be of the form

$$\tilde{\rho}(\tilde{q}, \tilde{p}; \beta, \gamma, \delta) = \frac{1}{Z} \exp \left[- \sum_i (\beta_i \tilde{e}_i + \gamma_i \tilde{q}_i + \delta_i \tilde{p}_i) \right], \quad (71)$$

with partition function

$$Z = \int \exp \left[- \sum_i (\beta_i \tilde{e}_i + \gamma_i \tilde{q}_i + \delta_i \tilde{p}_i) \right] d\tilde{q} d\tilde{p}. \quad (72)$$

We note that, in order for this integral to be well-defined, the particle energy needs to satisfy certain growth conditions on $|\tilde{q}_i|$. For example, if W_i is a polynomial on \tilde{q}_i , it would need to have order 2 or higher. From the partition function the following equilibrium relations are obtained directly:

$$-\frac{\partial \log Z}{\partial \gamma_i} = \bar{q}_i, \quad -\frac{\partial \log Z}{\partial \delta_i} = \bar{p}_i, \quad -\frac{\partial \log Z}{\partial \beta_i} = \bar{e}_i. \quad (73)$$

The probability (71), as a function of the parameters β, γ, δ , provides a *canonical* description of the stochastic behavior of the system. The identities (73) can be used to reformulate the probability in terms of the *micro-canonical* parameters $\bar{e}, \bar{q}, \bar{p}$. More generally, mixed descriptions can be contemplated that involve a subset of the imposed quantities and a subset of the Lagrange multipliers. In all cases, the evolution of the parameterized probabilities can be obtained from (62).

4.2. Mesodynamical equations of motion

The mesodynamical equations of motion for the max-ent approximation follow as a special case of the general treatment put forth in Section 3.4. In what follows, we would like to obtain evolution equations for \bar{q} , \bar{p} and β while controlling the value of the mesodynamical resolution τ .

From Eqs. (55a) and (57) we can obtain explicit expressions for the tangent basis functions. Using the family of probabilities (71), the weighting functions in the variational principle must be

$$\begin{aligned} u_{\gamma_i} &= \frac{\partial \log \bar{\rho}}{\partial \gamma_i} = \bar{q}_i - \tilde{q}_i, \\ u_{\delta_i} &= \frac{\partial \log \bar{\rho}}{\partial \delta_i} = \bar{p}_i - \tilde{p}_i, \\ u_{\beta_i} &= \frac{\partial \log \bar{\rho}}{\partial \beta_i} = \bar{e}_i - \tilde{e}_i. \end{aligned} \quad (74)$$

These identities, when replaced in Eq. (62), give, after some simple manipulations, the three mesodynamical equations

$$\dot{\bar{q}}_i = \left\langle \frac{\partial \tilde{H}}{\partial \bar{p}_i} \right\rangle, \quad (75a)$$

$$\dot{\bar{p}}_i = -\left\langle \frac{\partial \tilde{H}}{\partial \bar{q}_i} \right\rangle, \quad (75b)$$

$$\dot{\bar{e}}_i - \langle \tilde{e}_i \rangle = \langle X_{\tilde{H}} \cdot \nabla \tilde{e}_i \rangle, \quad (75c)$$

which can be further simplified to

$$\dot{\bar{q}}_i = f' \frac{\bar{p}_i}{m_i}, \quad (76a)$$

$$\dot{\bar{p}}_i = -f' \left\langle \frac{\partial V}{\partial \bar{q}_i} \right\rangle, \quad (76b)$$

$$\dot{\bar{e}}_i - \langle \tilde{e}_i \rangle = \tau_i \left\langle \frac{\partial W_i}{\partial \bar{q}_i} - \frac{\partial V}{\partial \bar{q}_i} \right\rangle \bar{q}_i. \quad (76c)$$

4.3. Harmonic ansatz

Let us note that the procedure outlined before is completely general. The, possibly complex, energy interactions among all the particles in the system are accounted for by the potential V . The particle potential W_i , in turn, is only employed to give shape to the parameterized probabilities.

Each *ansatz* for W_i gives, as a result, a different mesodynamical approximation. For practical purposes, however, not every potential can be employed because the partition function (72) needs to be calculated in closed form so as to eliminate the Lagrange multipliers γ_i, δ_i in favor of the variables \bar{q}_i and \bar{p}_i . A convenient choice is the harmonic function

$$W_i(\bar{q}_i; t) \equiv \frac{1}{2} m_i \omega_i^2 |\bar{q}_i|^2, \quad (77)$$

where ω_i is a characteristic particle frequency. This choice for the particle potential yields a Gaussian probability function. Moreover, using the equilibrium equations (73), the Lagrange multipliers can be found in closed form to be

$$\gamma_i = -\beta_i \tau_i m_i \omega_i^2 \bar{q}_i, \quad \delta_i = -\beta_i \tau_i \frac{\bar{p}_i}{m_i}. \quad (78)$$

Hence, the mixed canonical/micro-canonical probability function takes the form

$$\rho(\bar{q}, \bar{p}; \bar{q}, \bar{p}, \beta) = \frac{1}{Z} \exp \left[-\sum_i \beta_i \tilde{e}_i(\bar{q}_i - \bar{q}_i, \bar{p}_i - \bar{p}_i) \right], \quad (79)$$

in terms of the desired model variables $(\bar{q}, \bar{p}, \beta)$, and the partition function is

$$Z = \prod_i \left(\frac{2\pi}{\beta_i \omega_i \tau_i} \right)^d. \quad (80)$$

Let us note that we could have chosen to express the probability function in any set of complete variables. In this case, we select \bar{q}, \bar{p}, β because they admit the physical interpretation of mean position, momentum and inverse temperature.

For the harmonic particle potential, the mesodynamical equation (75c) can be explicitly evaluated to be

$$0 = \frac{d}{dt} (\beta_i \tau_i) \quad (81)$$

and the average energy norm simplifies to

$$\bar{e}_i = \langle \tilde{e}_i(\bar{q}_i, \bar{p}_i) \rangle = \langle \tilde{e}_i(\bar{q}_i - \bar{q}_i, \bar{p}_i - \bar{p}_i) \rangle + \tilde{e}_i(\bar{q}_i, \bar{p}_i) = \frac{d}{\beta_i} + \tilde{e}_i(\bar{q}_i, \bar{p}_i). \quad (82)$$

Here we can identify the average energy norm of the fluctuations

$$\langle \tilde{e}_i(\bar{q}_i - \bar{q}_i, \bar{p}_i - \bar{p}_i) \rangle = \frac{d}{\beta_i}. \quad (83)$$

The mesodynamical equation (81) it is thus equivalent to

$$0 = \frac{d}{dt} \left(\langle \tilde{e}_i(\bar{q}_i - \bar{q}_i, \bar{p}_i - \bar{p}_i) \rangle \frac{1}{\tau_i} \right) = \frac{d}{dt} \langle \tilde{e}_i(\bar{q}_i - \bar{q}_i, \bar{p}_i - \bar{p}_i) \rangle \frac{1}{\tau_i}. \quad (84)$$

This result is a *time-energy* principle for the unresolved part of the motion. According to it, a high resolution (small τ_i) will be concomitant to a reduction of the energy \tilde{e} of the perturbations, and vice-versa.

4.3.1. Optimal mean-field particle potential

The choice of particle frequencies ω_i in the norm (67) is arbitrary, up to a certain extent, and motivated by the convenience of working with simple Gaussian probabilities whose partition function can be calculated in closed form. These frequencies can, alternatively, be selected in an optimal fashion by recourse to variational mean-field theory, thus providing a rational criterion for the selection of an optimal norm.

Following Venturini et al. (2014), we can consider probabilities of the type (79) where now the particle frequency, denoted $\bar{\omega}_i$, is not known *a priori*, but rather obtained as the minimizers of a certain functional. To define it, consider the particle potential energy

$$V_i(\bar{q}_i; t) = \int \frac{\partial V}{\partial \bar{q}_i}(\bar{q}_1(\bar{t}), \bar{q}_2(\bar{t}), \dots, \bar{q}_N(\bar{t})) d\bar{q}_i, \quad (85)$$

that satisfies

$$\frac{\partial V_i}{\partial \bar{q}_i}(\bar{q}_i(t); t) = \frac{\partial V}{\partial \bar{q}_i}(\bar{q}(t)). \quad (86)$$

The function V_i expresses the potential energy of the i -th particle when the positions of the remaining ones are known. We note that the calculation of the potential V_i only involves the position of particle i and those that interact with it. Also, definition (85) is completely general and does not assume an additive structure of the potential V .

Next, let us define the particle energy

$$\tilde{e}_i(\bar{q}, \bar{p}) \equiv \tau_i \left(\frac{|p_i|^2}{2m_i} + V_i(\bar{q}_i; t) \right), \quad (87)$$

the assumed particle energy

$$\tilde{e}_{i0}(\bar{q}, \bar{p}; \bar{q}, \bar{p}, \bar{\omega}) \equiv \tau_i \left(\frac{|\bar{p}_i - \bar{p}_i|^2}{2m_i} + \frac{1}{2} m_i \bar{\omega}_i^2 |\bar{q}_i - \bar{q}_i|^2 \right), \quad (88)$$

and study probability functions of the form

$$\rho_0(\bar{q}, \bar{p}; \bar{q}, \bar{p}, \bar{\omega}, \beta) = \frac{1}{Z_0} \exp \left[-\sum_i \beta_i \tilde{e}_{i0} \right], \quad (89)$$

with partition function

$$Z_0 = \prod_i \left(\frac{2\pi}{\beta_i \tau_i \bar{\omega}_i} \right)^d. \quad (90)$$

Such probabilities define a new average operator on any function g defined on phase space as

$$\langle g \rangle_0 \equiv \int \rho_0(\bar{q}, \bar{p}; \bar{q}, \bar{p}, \bar{\omega}, \beta) g(\bar{q}, \bar{p}) d\bar{q} d\bar{p}. \quad (91)$$

To find the optimal frequencies, let us define the Bogoliubov functional (Callen, 1985; Yeomans, 1992)

$$F(\bar{\omega}; \bar{q}, \bar{p}, \beta) \equiv \sum_i \beta_i \langle \tilde{e}_i - \tilde{e}_{i0} \rangle_0 - \log Z_0. \quad (92)$$

Then, for known values of \bar{q}, \bar{p}, β , the optimal particle frequencies are the minimizers

$$\bar{\omega} = \arg \min_{\xi} F(\xi; \bar{q}, \bar{p}, \beta). \quad (93)$$

See Venturini et al. (2014). This meanfield approximation introduces an implicit coupling among all the degrees of freedom of the system through the particle frequencies in Eq. (87), activating thus anharmonic effects in the approximation. This improvement relative to the simple harmonic ansatz entails a greater complexity derived from the minimization (93).

4.3.2. The averaged potential

Phase probabilities such as (79) and (89) are of the form $\rho = \rho(\bar{q}, \bar{p}; \bar{q}, \bar{p}, \Gamma)$, for some set of approximation parameters Γ , and verify the relation

$$\frac{\partial \rho}{\partial \bar{q}}(\bar{q}, \bar{p}; \bar{q}, \bar{p}, \Gamma) = -\frac{\partial \rho}{\partial \bar{q}}(\bar{q}, \bar{p}; \bar{q}, \bar{p}, \Gamma). \quad (94)$$

Then, exploiting the decay at infinity of the probability, we have that

$$\begin{aligned} \langle \frac{\partial V}{\partial \bar{q}_i} \rangle &= \int \frac{\partial V}{\partial \bar{q}_i}(\bar{q}) \rho(\bar{q}, \bar{p}; \bar{q}, \bar{p}, \Gamma) d\bar{q} d\bar{p} \\ &= - \int V(\bar{q}) \frac{\partial \rho}{\partial \bar{q}_i}(\bar{q}, \bar{p}; \bar{q}, \bar{p}, \Gamma) d\bar{q} d\bar{p} \\ &= \frac{\partial}{\partial \bar{q}_i} \int V(\bar{q}) \rho(\bar{q}, \bar{p}; \bar{q}, \bar{p}, \Gamma) d\bar{q} d\bar{p} \\ &= \frac{\partial}{\partial \bar{q}_i} \bar{V}(\bar{q}; \Gamma), \end{aligned} \quad (95)$$

where we write

$$\bar{V}(\bar{q}; \Gamma) \equiv \int V(\bar{q}) \rho(\bar{q}, \bar{p}; \bar{q}, \bar{p}, \Gamma) d\bar{q} d\bar{p}. \quad (96)$$

Using the averaged potential \bar{V} , the mesodynamical equations of motion (75) further simplify to

$$\dot{\bar{q}}_i = \frac{1}{\tau_i} \frac{\bar{p}_i}{m_i}, \quad (97a)$$

$$\dot{\bar{p}}_i = -\frac{1}{\tau_i} \frac{\partial \bar{V}}{\partial \bar{q}_i}(\bar{q}; \Gamma), \quad (97b)$$

$$\dot{\bar{e}}_i - \langle \dot{\bar{e}}_i \rangle = \langle X_{\bar{H}} \cdot \nabla \bar{e}_i \rangle. \quad (97c)$$

Eq. (97b) shows that for probability distributions verifying (94), the mean motion of the particles is governed by an averaged potential. These mesodynamical equations can be further simplified by noting that an average particle can be defined as

$$\bar{V}_i(\bar{q}_i; t) = \int V_i(\bar{q}_i; t) \rho(\bar{q}, \bar{p}; \bar{q}, \bar{p}, \Gamma) d\bar{q} d\bar{p}. \quad (98)$$

therefore allowing to replace Eq. (97b) with

$$\dot{\bar{p}}_i = -\frac{1}{\tau_i} \frac{\partial \bar{V}_i}{\partial \bar{q}_i}(\bar{q}_i; \Gamma), \quad (99)$$

4.3.3. Mesodynamical averaging

To investigate further the effects of the mesodynamical modeling, consider now a particle moving on the real line under a general potential $V = V(q)$ and denote as $\hat{V}(\xi)$ its Fourier transform, with ξ the wave number. The max-ent probability for the position of the particle is

$$\rho_1(\bar{q}; \bar{q}, \beta) = \int \rho(\bar{q}, \bar{p}; \bar{q}, \bar{p}, \beta) d\bar{p} = \frac{\beta \omega \tau}{2\pi} \exp[-\beta \tau \frac{m \omega^2}{2} |\bar{q} - \bar{q}|^2]. \quad (100)$$

The function $\rho_1(\bar{q}; 0, \beta)$ has itself the Fourier transform

$$\hat{\rho}(\xi; \beta) = \frac{1}{\sqrt{2\pi}} \exp[-\frac{\xi^2}{2m\omega^2\beta\tau}]. \quad (101)$$

Hence, the effective potential (96) for this particle is obtained with the convolution

$$\bar{V}(\bar{q}; \beta) = \int V(\bar{q}) \rho_1(\bar{q}; \bar{q}, \beta) d\bar{q} = \int V(\bar{q}) \rho_1(\bar{q} - \bar{q}; 0, \beta) d\bar{q}. \quad (102)$$

Its Fourier transform is therefore

$$\hat{\bar{V}}(\xi; \beta) = \hat{V}(\xi; \beta) \hat{\rho}(\xi; \beta) = \frac{\hat{V}(\xi; \beta)}{\sqrt{2\pi}} \exp[-\frac{\xi^2}{2m\omega^2\beta\tau}]. \quad (103)$$

We observe that the Fourier transform of the effective potential is a filtered version of the standard potential $\hat{V}(\xi)$, where high wave numbers ($|\xi| \gg 1$) are attenuated. This effect is, however, modulated by the time resolution: large values of $\beta\tau$ reduce the attenuation throughout the spectrum.

The mesodynamical equation of motion (97b) defines the effective force on a particle as a function of the filtered potential. Using normal modes, complex potentials can always be expressed as Taylor series of increasingly oscillatory components (Ziman, 1960). Hence, the previous argument suggests that, even in these cases, the mesodynamical modeling will reduce the high oscillatory components of the energetic interactions, without the explicit need to calculate them.

4.4. Quadratic energy ansatz

The fundamental idea of the max-ent approximation developed before is to select as trial probability the most unbiased one that verifies the constraints (66) and (67). The first two constraints link the probability and the mesodynamical phase coordinates, while the third one introduces the (inverse) temperature variable as a controllable measure of the statistical averaging. The energy norm (67) with the potential (77) is the simplest one that ensures the control over position and momentum, while being analytically tractable.

We consider now a more general energy norm. For that, let us introduce the $(2d) \times (2d)$ matrix

$$C_i = \begin{bmatrix} C_i^{qq} I & C_i^{qp} I \\ C_i^{pq} I & C_i^{pp} I \end{bmatrix}, \quad (104)$$

with the scalars $C_i^{qq}, C_i^{qp}, C_i^{pp} = C_i^{pq}$ possibly depending on time \bar{t} and I denoting the $d \times d$ identity matrix. If C_i is positive definite, we can define the Mahalanobis distance

$$d_i(\bar{z}_i, \bar{z}_i) = ((\bar{z}_i - \bar{z}_i)^T C_i (\bar{z}_i - \bar{z}_i))^{1/2}, \quad (105)$$

with $\bar{z}_i = (\bar{q}_i, \bar{p}_i)$, $\bar{z}_i = (\bar{q}_i, \bar{p}_i)$. Then, if we redefine the energy norm (67) as

$$\bar{e}_i = \frac{1}{2} \bar{z}_i^T C_i \bar{z}_i, \quad (106)$$

the maximum entropy probability function that satisfies (66) and (106) is

$$\rho_Q(\bar{q}, \bar{p}; \bar{q}, \bar{p}, \beta) = \frac{1}{Z_Q} \exp \left[- \sum_i \frac{\beta_i}{2} d_i^2(\bar{z}_i, \bar{z}_i) \right], \quad (107)$$

with

$$Z_Q = \prod_i \frac{(2\pi)^d}{\beta_i |C_i|^{1/2}}. \quad (108)$$

Here $|C_i|$ is the determinant of the matrix C_i , itself being the covariance of the Gaussian probability (107). The mesodynamical equations corresponding to this ansatz are (75), which can be evaluated to

$$\dot{\bar{q}}_i = f' \frac{\bar{p}_i}{m_i}, \quad (109a)$$

$$\dot{\bar{p}}_i = -f' \langle \frac{\partial V}{\partial \bar{q}_i} \rangle, \quad (109b)$$

$$\begin{aligned} \frac{\dot{\beta}_i}{\beta_i^2} d + \frac{d}{2\beta_i} \frac{C_i^{qq} C_i^{pp} - 2C_i^{qp} C_i^{pq} + C_i^{pp} C_i^{qq}}{C_i^{qq} C_i^{pp} - (C_i^{qp})^2} \\ = f' C_i^{qp} \langle \bar{q}_i \frac{\partial V}{\partial \bar{q}_i} \rangle - f' \frac{C_i^{qp}}{m_i \beta_i} \frac{d C_i^{qq}}{C_i^{qq} C_i^{pp} - (C_i^{qp})^2}. \end{aligned} \quad (109c)$$

We examine with more detail the last mesodynamical equation which gives the evolution of the inverse temperature. To simplify Eq. (109c), and motivated by the harmonic expression of the energy norm, we select $\tau_i = 1/f'$ and

$$C_i^{qq} = \tau_i m_i \omega_i^2, \quad C_i^{qp} = C_i^{pq} = \frac{\tau_i \omega_i}{\sqrt{2}}, \quad C_i^{pp} = \frac{\tau_i}{m_i}, \quad (110)$$

upon which (109c) becomes

$$\frac{\dot{\beta}_i}{\beta_i} + \frac{\dot{\tau}_i}{\tau_i} = \frac{\omega_i \beta_i}{\sqrt{2d}} \langle \bar{q}_i \frac{\partial V}{\partial \bar{q}_i} \rangle - \frac{\sqrt{2} \omega_i}{\tau_i}. \quad (111)$$

This result should be compared with Eq. (81). In the latter, the evolution of the inverse temperature in each particle is dictated, exclusively, by the time resolution τ_i . In the quadratic model, however, the mean work $\langle \bar{q}_i \frac{\partial V}{\partial \bar{q}_i} \rangle$ on each particle can modify its temperature, even for fixed τ_i .

We note that the choice (110) is not canonical, so others could be considered. The main result, however, is that in order to account for the dynamics into the evolution of β_i is to employ a covariance with nonzero coupling terms between the position and momentum.

4.5. Other trial probabilities

The max-ent class of functions described in Sections 4.1–4.4 furnishes one template for constructing a finite dimensional space of probabilities that can be used in the approximating theory of Section 3.4. This theory, however, is completely general and other trial spaces could be envisioned. We briefly present two alternatives to illustrate the idea, but we do not pursue them in this work.

4.5.1. Probability functions based on Hermite polynomials

The Hermite polynomials over \mathbb{R} are defined as

$$H_n(x) = (-1)^n e^{x^2} \frac{d^n}{dx^n} e^{-x^2}, \quad (112)$$

and satisfy

$$\int_{\mathbb{R}} H_n^2(x) e^{-x^2} dx = \sqrt{\pi} n! 2^n. \quad (113)$$

Their extension to \mathbb{R}^N is

$$H_n(x) = e^{|\mathbf{x}|^2} D^n e^{-|\mathbf{x}|^2}, \quad (114)$$

where now $n = n_1, n_2, \dots, n_N \in \mathbb{N}^N$ is a multi-index and $D^n = \partial_1^{n_1} \cdot \partial_N^{n_N}$ is the corresponding differential operator. The analogue of Eq. (113) is the result

$$\int_{\mathbb{R}^N} e^{-|\mathbf{x}|^2} H_n^2(x) dx = \prod_{i=1}^N 2^{n_i} n_i! \sqrt{\pi} \equiv \eta_n. \quad (115)$$

Hermite polynomials can be used as follows to construct a hierarchy of probability distributions. First, a non-negative probability distribution is defined as

$$\rho(z, t) = |\psi(z, t)|^2, \quad (116)$$

where an order h wave function is proposed to be of the form

$$\psi_h(z, t) = \sqrt{|S(t)|} e^{-\frac{|\mathbf{z}|^2}{2}} P_h(x), \quad (117)$$

with

$$x(z, t) = S(t)(z - \bar{z}(t)), \quad P_h(x) = \sum_{|n| \leq h} c_n(t) H_n(x), \quad (118)$$

$|n| = \max_i n_i$, $\{c_n(t), |n| \leq h\}$ time-dependent coefficients, $S(t) \in \mathbb{R}^{N \times N}$ a time-dependent matrix with determinant $|S(t)|$, and $\bar{z}(t) \in \mathbb{R}^N$ a time-dependent vector of central values of the distribution. We note that $\psi_h(z, t)$ is a linear combination of Cartesian products of polynomials of

degree less or equal to h in each of the components of $x = S(t)(z - \bar{z}(t))$. By the orthogonality property (115) we have that

$$\int \rho_h(z, t) dz = \int |\psi_h(z, t)|^2 dz = \sum_{|n| \leq h} \eta_n |c_n(t)|^2 = 1. \quad (119)$$

Hence, the sequence $\{\rho_h\}_{h=1}^\infty$ includes increasingly rich trial probabilities that can be used in the formalism of Section 4 to approximate the Liouville probability with the desired accuracy.

4.5.2. Max-ent with alternative constraints

In Section 4.1, trial probabilities were constructed that maximized the information entropy under average and energy constraints, namely, Eqs. (66) and (67). Again, as an illustration, we show next how different constraints lead to alternative trial probabilities.

A reasonable option is to consider the sequence of probabilities

$$\rho_k(z; \Gamma) \in \arg \max \{ -\langle \log \rho \rangle, \langle z^\alpha \rangle = \bar{z}_\alpha, 0 \leq |\alpha| \leq k \}, \quad (120)$$

where $\alpha \in \mathbb{N}^N$ is a multi-index, $|\alpha| = \alpha_1 + \alpha_2 + \dots + \alpha_N$ is its degree and we write

$$z^\alpha = z_1^{\alpha_1} \dots z_N^{\alpha_N}. \quad (121)$$

In the definition of $\rho_k(z, \Gamma)$, thus, we control the moments of degree less or equal to k , whose values are $\Gamma = \{\bar{z}_\alpha, 0 \leq |\alpha| \leq k\}$, providing again, an increasingly rich sequence of trial probabilities depending on k parameters. To ensure that ρ_k is integrable over \mathbb{R}^N , k must be larger or equal to 2. See Gupta et al. (2021) for an application.

5. Examples

5.1. Time rescaled, deterministic solution of the harmonic oscillator

First, and in order to gain insight on the effects of time rescaling, we study the motion of the harmonic oscillator when formulated in a time-rescaled formalism. For that, consider an oscillator of mass m and potential energy

$$V(q) = \frac{m\omega^2}{2} q^2, \quad (122)$$

where ω is the frequency of vibration of the oscillator. The kinetic energy also has a quadratic form, namely,

$$K(p) = \frac{1}{2m} p^2. \quad (123)$$

The motion of the oscillator in phase space is the curve $z(t) = (q(t), p(t))$ with $t \in [0, T]$ that solves Hamilton's equations of motion (2) with $H(q, p) = V(q) + K(p)$.

Next, let us consider a time rescaling $t = f(\tilde{t})$ as in Section 2.3 defining new phase space variables (\tilde{q}, \tilde{p}) that solve Eqs. (15), namely,

$$\dot{\tilde{q}} = f' \frac{\tilde{p}}{m}, \quad \dot{\tilde{p}} = -f' m \omega^2 \tilde{q}. \quad (124)$$

By eliminating the momentum, these two equations lead to the equation of motion

$$\ddot{\tilde{q}} - \frac{f''}{f'} \tilde{q} + (f')^2 \omega^2 \tilde{q} = 0, \quad (125)$$

whose closed-form solution is

$$\tilde{q}(\tilde{t}) = q_0 \cos(\omega f(\tilde{t})) + \frac{p_0}{m\omega} \sin(\omega f(\tilde{t})), \quad (126)$$

where q_0, p_0 are the initial position and momentum of the oscillator. Naturally, when there is no time rescaling (i.e., $f(\tilde{t}) = \tilde{t}$), the solution in the transformed phase space (Eq. (126)) coincides with the standard solution of the harmonic oscillator.

From Eq. (126) we can calculate \tilde{p} using the expression

$$\tilde{p}(\tilde{t}) = m \frac{d}{d\tilde{t}} (\tilde{q} \circ f^{-1}) \circ f(\tilde{t}) = p_0 \cos(\omega f(\tilde{t})) - m\omega q_0 \sin(\omega f(\tilde{t})). \quad (127)$$

The rescaled solution thus has exactly the same trajectory in phase space as the standard harmonic oscillator, but reparametrized in time. As a result, the perturbed Hamiltonian

$$\tilde{H}(\tilde{q}, \tilde{p}, \tilde{t}) = \tilde{K}(\tilde{p}, \tilde{t}) + \tilde{V}(\tilde{q}, \tilde{t}) \quad (128)$$

with

$$\tilde{K}(\tilde{p}, \tilde{t}) = \frac{1}{2\tilde{m}}|\tilde{p}|^2, \quad \tilde{V}(\tilde{q}, \tilde{t}) = \frac{\tilde{m}\tilde{\omega}^2}{2}|\tilde{q}|^2, \quad (129)$$

and $\tilde{m} = m/f'$, $\tilde{\omega} = f'\omega$, is not a first integral of motion. As proven in Eq. (21), the value of this Hamiltonian is proportional f' .

5.2. The harmonic oscillator with variable time resolution

We study now the harmonic oscillator using a probabilistic description of the type described in Section 3. We consider again the mechanical system of Section 5.1 and we analyze the evolution of the phase probability in time-rescaled space. The *max-ent* approximation of this measure is, according to Eq. (79), the Gaussian probability

$$\rho(\tilde{q}, \tilde{p}; \tilde{q}, \tilde{p}, \beta) = \frac{1}{Z} \exp \left[-\beta \tau \left(\frac{|\tilde{p} - \bar{p}|^2}{2m} + \frac{m\omega^2|\tilde{q} - \bar{q}|^2}{2} \right) \right], \quad Z = \frac{2\pi}{\beta\omega\tau}. \quad (130)$$

The average values of the potential and kinetic energy of the oscillator are, respectively,

$$\begin{aligned} \bar{V}(\tilde{q}; \beta) &= \langle V(\tilde{q}) \rangle = \frac{m\omega^2}{2}|\tilde{q}|^2 + \frac{1}{2\beta\tau}, \\ \bar{K}(\tilde{p}; \beta) &= \langle K(\tilde{p}) \rangle = \frac{1}{2m}|\tilde{p}|^2 + \frac{1}{2\beta\tau}, \end{aligned} \quad (131)$$

and thus the mesodynamical equations of the motion for the oscillator are

$$\dot{\tilde{q}} = \frac{1}{\tau} \frac{\bar{p}}{m}, \quad \dot{\tilde{p}} = -\frac{1}{\tau} m\omega^2 \tilde{q}, \quad \frac{d}{dt}(\beta\tau) = 0. \quad (132)$$

The first two equations are identical to Eqs. (124), interpreting the phase coordinates as their mean values. The last equation can be used to solve exactly for the Lagrange multiplier, i.e.,

$$\beta(\tilde{t}) = \frac{\beta_0 \tau_0}{\tau(\tilde{t})}, \quad (133)$$

where β_0, τ_0 are the initial values of the multiplier and the time resolution, respectively. The probabilistic description of the oscillator furnishes additional information about the dynamics of the motion, more precisely, the size of the unresolved phase motion (see Eq. (83)). In particular, based on the definition (67) of the energy norm, we can introduce the following uncertainty measures for the two phase coordinates

$$\sigma_q \equiv \frac{1}{\omega\sqrt{m}} \langle \tilde{q}(\tilde{q} - \bar{q}, 0) \rangle^{1/2}, \quad \sigma_p \equiv \sqrt{m} \langle \tilde{p}(\tilde{p} - \bar{p}, 0) \rangle^{1/2}, \quad (134)$$

whose values for the oscillator are, respectively,

$$\sigma_q = \frac{1}{\omega\sqrt{2m\beta}}, \quad \sigma_p = \sqrt{\frac{m}{2\beta}}. \quad (135)$$

We consider the specific example of a time rescaling function of the form

$$f(\tilde{t}) = \tilde{t} + \frac{8\pi}{5\omega} \left(1 - \cos\left(\frac{\omega\tilde{t}}{2\pi}\right) \right), \quad (136)$$

shown in Fig. 3. The time rescaling function is selected so that the time granularity $\tau = 1/f'$ satisfies $\tau(0) = \tau_0 = 1$, and shifts between fine and coarse values. See Fig. 4. The oscillator is initially at rest with position $q(0) = q_0$.

Figs. 5 and 6 show the values of the normalized phase coordinates in the mesodynamic solution when the initial value for the Lagrange multiplier is

$$\beta_0 = \frac{m\omega^2 q_0^2}{2\tau_0}. \quad (137)$$

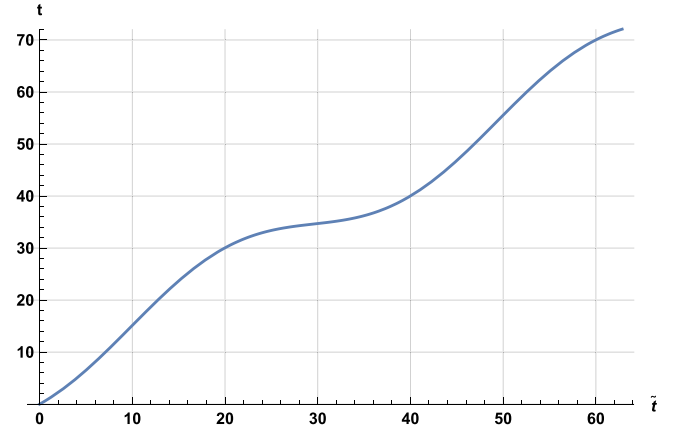


Fig. 3. Time rescaling function $f(\tilde{t})$ for Example 5.2.

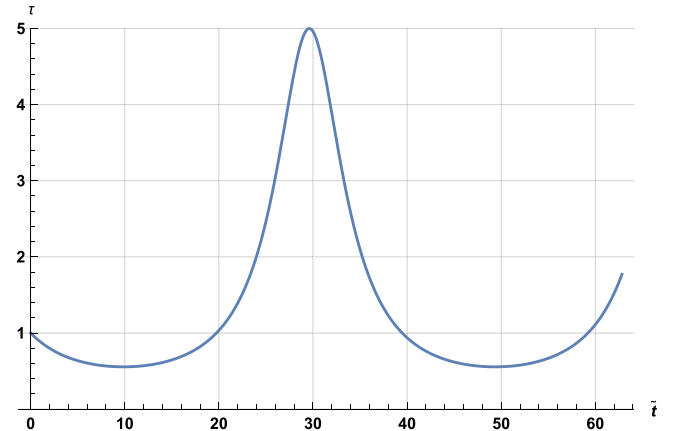


Fig. 4. Time granularity $\tau = 1/f'$ in Example 5.2.

These two figures show that the first and last parts of the solution, which are obtained with a fine time granularity, give an oscillating trajectory that is well resolved. When the time is coarsened, in the middle part of the solution, the resolution in both the position and momentum is reduced. Concomitant to the coarsening of the time scale, there is an increase in the uncertainty of the solution as measured by σ_q and σ_p .

Next, we solve again the harmonic oscillator problem, now using a initial value of the Lagrange multiplier that is

$$\beta_0 = 10 \frac{m\omega^2 q_0^2}{2\tau_0}. \quad (138)$$

This corresponds to a “colder” system in which the phase trajectory wanders close to the mean values of the phase coordinates. As seen in Figs. 7 and 8, the coarsening in the time variable has the same effect as in the first solution, namely, increasing the uncertainty in the description of the motion. We note that a completely deterministic description of the motion, i.e. $\beta \rightarrow \infty$, would result in vanishing variances for the position and momenta. In this case, the uncertainty bands in Figs. 7 would disappear and the normalized variables would remain within the classical interval $[-1, +1]$.

5.3. The harmonic and anharmonic monoatomic chain

We study next a chain of N identical atoms, each of them of mass m and phase space coordinates (q_i, p_i) with $i = 1, 2, \dots, N$. Interatomic forces are modeled with a pair potential $U = \tilde{U}(\beta)$, where β is the

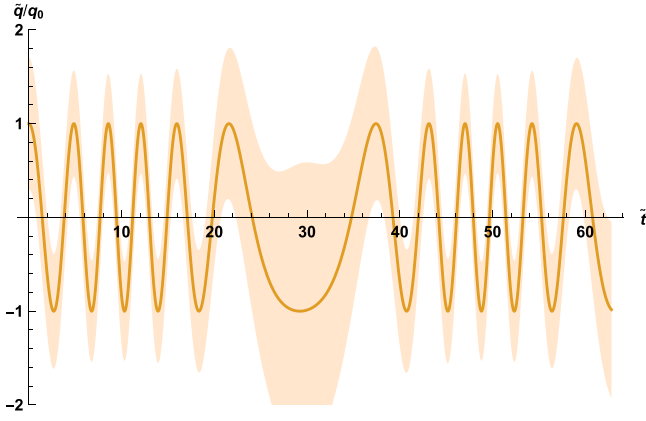


Fig. 5. Normalized position in the stochastic solution of the harmonic oscillator with β_0 given by (137). Color bands indicate the normalized $[-\sigma_q, \sigma_q]$ uncertainty interval of the solution.

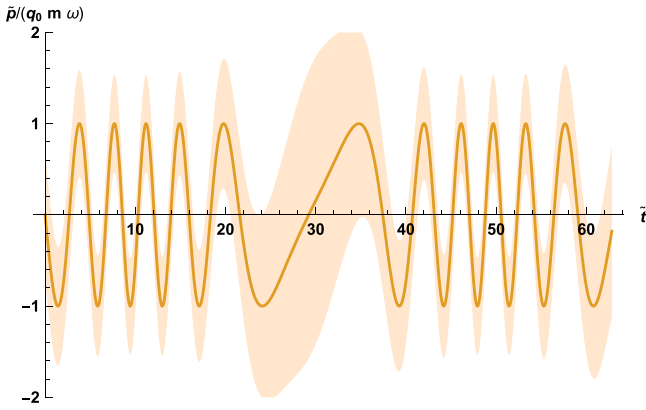


Fig. 6. Normalized momentum in the stochastic solution of the harmonic oscillator with β_0 given by (137). Color bands indicate the normalized $[-\sigma_p, \sigma_p]$ uncertainty interval of the solution.

distance between atoms. If the first and last point masses are held fixed, then the total potential energy of the chain is

$$V(q) = \sum_{i=1}^{N-1} U(|q_{i+1} - q_i|), \quad (139)$$

and the particle potential follows as

$$V_i(q_i; t) = U(|q_{i+1}(t) - q_i|) + U(|q_i - q_{i-1}(t)|). \quad (140)$$

for $i = 2, \dots, N-1$. Irrespective of the expression for U , the mesodynamic equations of evolution (97) can be simplified to

$$\dot{q}_i = \frac{1}{\tau} \frac{\bar{p}_i}{m}, \quad \dot{\bar{p}}_i = \frac{-1}{\tau} \frac{\partial \bar{V}_i}{\partial \bar{q}_i}(\bar{q}_i; \bar{t}) \quad \frac{d}{d\bar{t}}(\beta_i \tau) = 0. \quad (141)$$

We look with more detail into two specific situations. In the first one, the interatomic potential under consideration is quadratic, i.e.,

$$U = U_2(\beta) = \frac{1}{2} m \omega^2 \beta^2, \quad (142)$$

for some constant frequency ω . In this case the average particle potential can be evaluated as

$$\bar{V}_i(\bar{q}_i; t) = \frac{1}{2} m \omega^2 (q_{i+1}(t) - \bar{q}_i)^2 + \frac{1}{2} m \omega^2 (\bar{q}_i - q_{i-1}(t))^2 + \frac{1}{\beta_i \tau} = V_i(\bar{q}_i; t) + \frac{1}{\beta_i \tau}. \quad (143)$$

For each particle, the phase probability is of the form

$$\rho_i(\bar{q}_i, \bar{p}_i; \bar{q}_i, \bar{p}_i, \beta_i) = \frac{\omega_i \beta_i \tau}{2\pi} \exp \left[-\beta_i \bar{q}_i (\bar{q}_i - \bar{q}_i, \bar{p} - \bar{p}) \right], \quad (144)$$

a Gaussian whose variance will be constant. Hence, fluctuations in one particle will not have any impact on neighboring particles, precluding all types of heat transfer, as expected, since this is an anharmonic phenomenon. A similar analysis carried out using normal modes will lead to the conclusion that each of them will evolve independently, possibly even if resolved with different time granularity.

Consider next a simple anharmonic case, where now the interatomic potential has a high-order contribution, i.e.,

$$U(\beta) = U_2(\beta) + U_4(\beta), \quad U_4(\beta) = \frac{1}{12} \eta \beta^{24}, \quad (145)$$

where $\eta = m \omega^2 / a^2$ and a is a constant with dimensions of length. The particle potential has the expression (140) and a simple derivation gives its effective value

$$\bar{V}_i(\bar{q}_i; t) = V_i(\bar{q}_i; t) + \frac{1}{\beta_i \tau} + \frac{1}{2 m \omega^2 a^2 \beta_i^2 \tau^2} + \frac{(\bar{q}_i - \bar{q}_{i-1})^2 + (\bar{q}_i - \bar{q}_{i+1})^2}{2 a^2 \beta_i \tau}. \quad (146)$$

When compared with Eq. (143), we notice that both effective potential energies consist of the sum of the mechanical energy plus terms that accounts for the statistical averaging. There is, however, a critical difference between the two. In the harmonic model, the effective force on the particle, namely,

$$\bar{f}_i(\bar{q}_i; t) \equiv \frac{-1}{\tau} \frac{\partial \bar{V}_i}{\partial \bar{q}_i}(\bar{q}_i; t) \quad (147)$$

does not depend on the multiplier β_i because the following relationship holds

$$\frac{\partial \bar{V}_i}{\partial \bar{q}_i}(\bar{q}_i; t) = \frac{\partial V_i}{\partial \bar{q}_i}(\bar{q}_i; t) \quad (148)$$

due to the fact that no term in the effective potential couples the mechanical variables (\bar{q}, \bar{p}) and the thermodynamic gauge β . In the anharmonic model, in contrast, the effective force (147)

$$\bar{f}_i(\bar{q}_i; t) = \frac{-1}{\tau} \frac{\partial V_i}{\partial \bar{q}_i}(\bar{q}_i; t) - \frac{1}{\tau} \frac{2\bar{q}_i - q_{i-1}(t) - q_{i+1}(t)}{2 a^2 \beta_i \tau} \quad (149)$$

possesses a coupling contribution. This term suggests that the mesodynamic averaging of an anharmonic model will not only accommodate the time rescaling, but modulate the strength of the interatomic forces. See more on this conclusion in Section 5.4.

5.4. Particle under a wiggly potential

We study next the effects of the mesodynamical averaging when the potential energy is non convex and possesses multiple local energy minima. This is a common situation in practical atomistic problems, where the energy landscape has ripples that critically affect the dynamics of the system, when it is analyzed with full resolution, but are irrelevant when only the global equilibria are sought. As we will verify next, the framework of Section 4 leads to the definition of the averaged potential (96) which can be used to seamlessly model the transition between fine and coarse time granularities.

For this, we consider a mass m under a wiggly potential of the form

$$V(q) = \frac{1}{2} m \omega^2 \left(q^2 + b^2 \sin^2 \left(\frac{q}{a} \right) \right), \quad (150)$$

where, as in previous examples, m stands for the mass, ω is a frequency, and a, b are two constants with dimensions of length (see Fig. 9). This is a nonlinear, nonconvex potential where the amplitude of the oscillations is modulated by b and their lengthscale by a . The relatively simple expression of the potential (150) allows the closed-form calculation of the effective potential (96), namely,

$$\bar{V}(\bar{q}; \beta) = \frac{1}{2} m \omega^2 \bar{q}^2 + \frac{1}{2 \beta \tau} + \frac{b^2 m \omega^2}{4} \left(1 - \cos \left(\frac{2\bar{q}}{a} \right) \exp \left[-\frac{2}{a^2 \beta \tau m \omega^2} \right] \right).$$

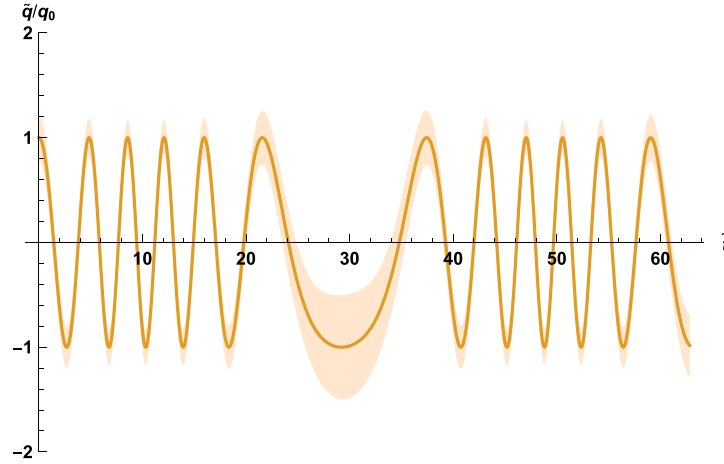


Fig. 7. Normalized position in the stochastic solution of the harmonic oscillator with β_0 given by (138). Color bands indicate the normalized $[-\sigma_q, \sigma_q]$ uncertainty interval of the solution.

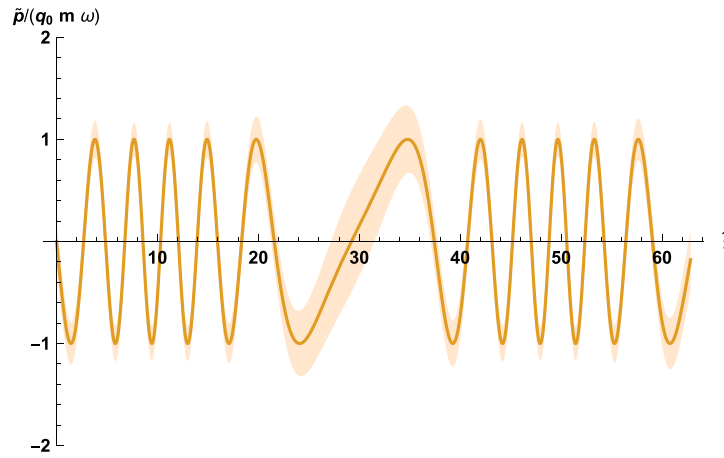


Fig. 8. Normalized momentum in the stochastic solution of the harmonic oscillator with β_0 given by (138). Color bands indicate the normalized $[-\sigma_p, \sigma_p]$ uncertainty interval of the solution.

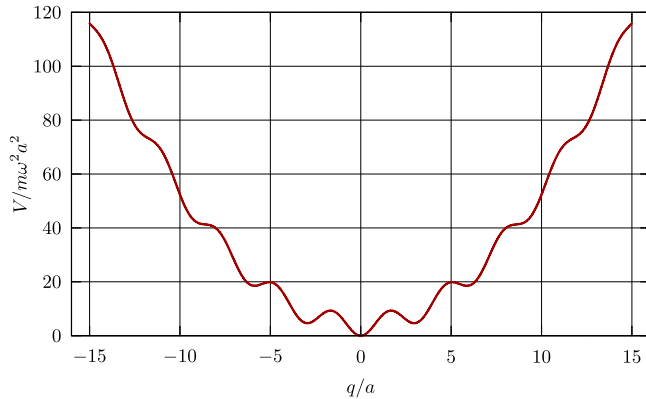


Fig. 9. Wiggly potential with $b = 4a$.

(151)

This function is the sum of three contributions. The first one is a quadratic term, identical to the quadratic part of the wiggly potential. The second term is purely stochastic, suggesting that $\beta\tau$ is the inverse of the temperature, as in statistic thermodynamics (up to Boltzmann's constant). The last term is a oscillatory term that vanishes in the high temperature limit $\beta\tau \rightarrow 0$.

Fig. 10 shows a contour map of the normalized effective potential energy as a function of the particle mean position and the inverse temperature $\beta\tau$. The contours verify that oscillations in the energy appear only for cold temperatures (large values of $\beta\tau$), progressively disappearing as the temperature increases (small values of $\beta\tau$) and fluctuations are accounted for thermodynamically. In the coarse time resolution limit, i.e. when $\beta\tau \rightarrow 0$, the quadratic potential is recovered and all the wiggles disappear, although their energy is accounted for in the stochastic constant of the potential. See Eq. (151).

5.5. Particle over an infinite atomic plane

We extend the results of Section 5.4 by considering now a single atom that can move while keeping constant its distance to a plane where an infinite and periodic array of atoms are placed. More specifically, let us assume that an infinite number of atoms are placed on a square lattice of side a and that another atom can move on a plane at a certain distance from the lattice in such a way that its potential energy, in terms of its two-dimensional Cartesian coordinates is

$$V(q_1, q_2) = \frac{1}{2} m \omega^2 \left(\cos \frac{2\pi q_1}{a} + \sin \frac{2\pi q_2}{a} \right), \quad (152)$$

where ω is a characteristic frequency and m is the mass of the moving atom. Fig. 11 shows a contour plot of the (normalized) potential energy in the plane where the motion takes place. The potential is clearly periodic, with maxima above the fixed atoms, minima at the centers

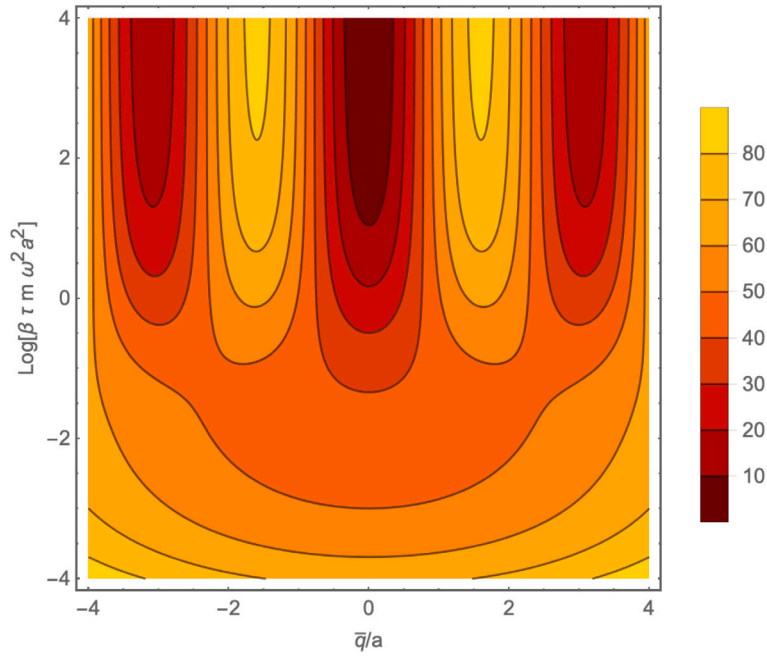


Fig. 10. Contour plot for the normalized effective potential ($V_{eff}/(m\omega^2 a^2)$) of a particle under a wiggly potential energy ($b = 4a, \beta\tau = 1$).

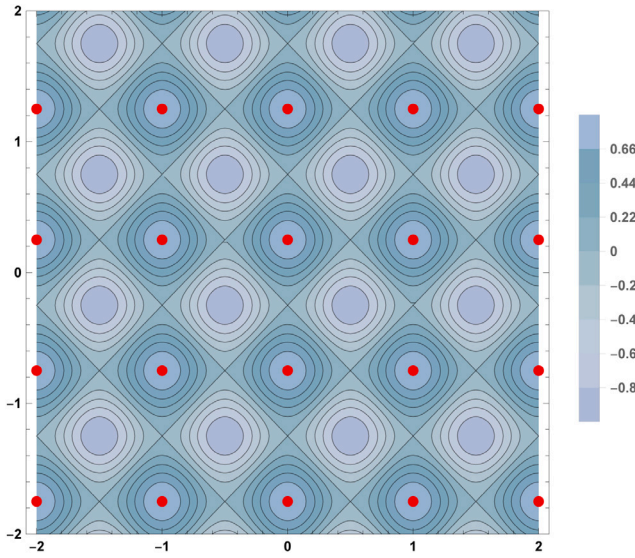


Fig. 11. Contour plot of the normalized potential $V/(m\omega^2)$ in example 5.5. The locations of the fixed atoms that create the potential are marked with red dots. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

of the unit square cell, and saddle points half-way between any pair of neighboring atoms.

The max-ent probability for this system is given by Eq. (79) with partition function (80). As in the previous example, the relatively simple expression for the potential allows to determine the effective potential in closed form

$$\bar{V}(\bar{q}_1, \bar{q}_2; \beta) = \exp \left[-\frac{\pi^2}{m\omega^2 \beta \tau} \right] V(\bar{q}_1, \bar{q}_2). \quad (153)$$

Fig. 12 illustrates the changes in the effective potential (151) when the mesodynamic granularity is varied. In the well-resolved limit (large values of $\beta\tau$, on the top-left of the figure), the effective potential resembles the exact potential (150). As the resolution is decreased,

i.e., when $\beta\tau$ is reduced, ripples in the effective potential are smeared. In the coarsest description (bottom right), the fluctuations in the effective potential have almost disappeared, leading to an approximately constant potential.

When comparing the effective potentials (151) and (153), or their illustrations in Figs. 10 and 12, respectively, the same behavior is observed: large values of the mesodynamical granularity $\beta\tau$ lead to effective potential that differ little from the original potential of each problem. In contrast, small values of $\beta\tau$ are concomitant to smoothed potentials that are appropriate to model the motion with large uncertainty.

6. Concluding remarks

This work has introduced a general framework for the formulation of extended models that can be employed in the description of molecular dynamics. Using the Liouville formalism for a reparametrized version of Hamilton's principle of stationary action, we have proposed stochastic evolution equations for atomistic systems where the unresolved part of the motion is accounted for energetically. Remarkably, a control variable has been identified that allows to modulate qualitatively the contributions of the resolved and unresolved fluctuations to the motion.

The proposed framework allows to formulate sequences of mechanical models with a continuous control of their temporal resolution. In particular, the limits of the models obtained correspond, on the one hand, to the fully resolved equations of motion of the system (Hamilton's equations) and to averaged effective equations where all the thermal fluctuations are accounted for statistically and only the slow, mean motion is described.

As discussed, the time resolution of an extended molecular dynamics model can be increased or reduced to suit the needs of a given analysis. Hence, the framework introduced in this article could be exploited by numerical schemes – not presented herein – that employ adaptivity to adjust their time step size to the relevant phenomena at each instant of a simulation. For example, in mass diffusion phenomena, large time step sizes can be used most of the time, while small ones could be selected to follow closely atomic hops when expected. Remarkably, and in contrast with existing time integration schemes, thermal vibrations, whose

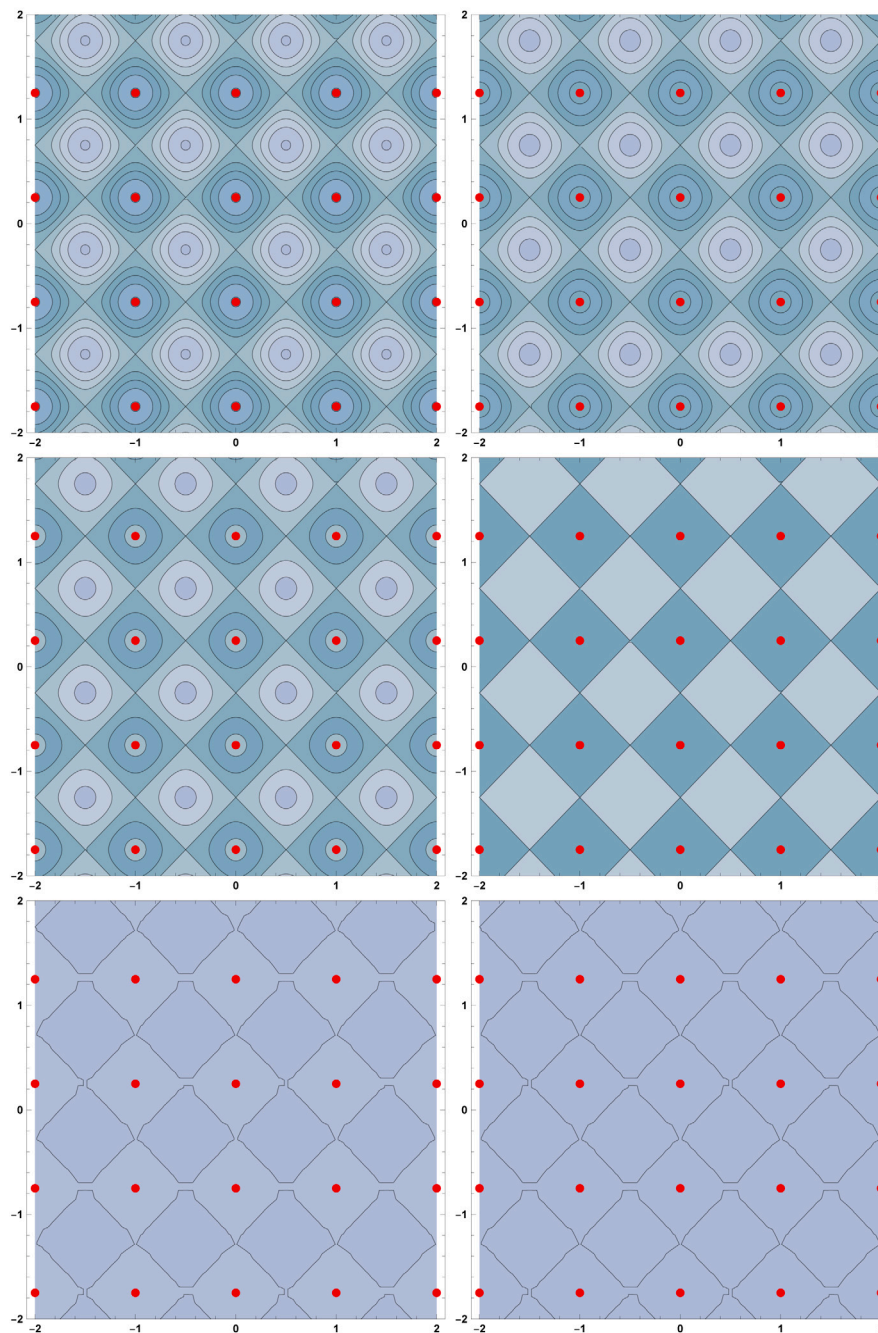


Fig. 12. Contour plots for the (normalized) effective potential (153) with parameters $\beta\tau = \frac{5\pi^2}{k}$ with $k = 1, 2, \dots, 6$. Colors refer to the same values as in Fig. 11.

characteristic times are very short, will be accounted for statistically when not fully resolved.

The findings of this work lead to mesodynamical equations of motion for systems of particles based on *effective potentials* that account for the time coarsening. We note that such functions can only be obtained in closed form in relatively simple situations. For large realistic systems, these potentials and their derivatives would have to be computed by recourse to quadrature.

Let us note, in closing, that in addition to the intrinsic interest of this family of models with adjustable time granularity, the results of this article can be used to understand the foundations of variational time integration methods. These discretizations naturally introduce a time scale – the time step size – whose effect in the resolved motion can be understood in light of the equations derived in this work.

CRediT authorship contribution statement

Ignacio Romero: Methodology, Software, Formal analysis, Writing – original draft, Writing – review & editing. **Michael Ortiz:** Conceptualization, Methodology, Formal analysis, Writing – original draft, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

References

- Abraham, R., Marsden, J.E., 1978. Foundations of Mechanics, second ed. Addison-Wesley.
- Allen, M.P., Tildesley, D.J., 1987. Computer Simulation of Liquids. Oxford Science Publications.
- Ariza, M.P., Romero, I., Ponga, M., Ortiz, M., 2012. HotQC simulation of nanovoid growth under tension in copper. *Int. J. Fract.* 174, 75–85.
- Arnold, V.I., 1989. Mathematical Methods of Classical Mechanics. Springer.
- Beex, L.A.A., Peerlings, R.H.J., Geers, M.G.D., 2011. A quasicontinuum methodology for multiscale analyses of discrete microstructural models. *Internat. J. Numer. Methods Engrg.* 87 (7), 701–718.
- Branduardi, D., Bussi, G., Parrinello, M., 2012. Metadynamics with adaptive Gaussians. *J. Chem. Theory Comput.* 8 (7), 2247–2254.
- Callen, H.B., 1985. Thermodynamics and an Introduction To Thermostatistics, second ed. Wiley, United States.
- Dama, J.F., Rotskoff, G., Parrinello, M., Voth, G.A., 2014. Transition-tempered metadynamics: Robust, convergent metadynamics via on-the-fly transition barrier estimation. *J. Chem. Theory Comput.* 10 (9), 3626–3633.
- Eslami, H., Khanjari, N., Müller-Plathe, F., 2017. A local order parameter-based method for simulation of free energy barriers in crystal nucleation. *J. Chem. Theory Comput.* 13 (3), 1307–1316.
- Feyel, F., 1999. Multiscale FE^2 elastoviscoplastic analysis of composite structures. *Comput. Mater. Sci.* 16 (1–4), 344–354.
- Feyel, F., 2003. A multilevel finite element method (FE^2) to describe the response of highly non-linear structures using generalized continua. *Comput. Methods Appl. Mech. Engrg.* 192 (28–30), 3233–3244.
- Fichtorn, K.A., Weinberg, W.H., 1991. Theoretical foundations of dynamical Monte Carlo simulations. *J. Chem. Phys.* 95 (2), 1090–1096.
- Gupta, P., Ortiz, M., Kochmann, D., 2021. Nonequilibrium thermomechanics of Gaussian phase packet crystals: Application to the quasistatic quasicontinuum method. *J. Mech. Phys. Solids* 153, 104495.
- Hughes, T.J.R., Feijoo, G.R., Mazzei, L., Quincy, J.-B., 1998. The variational multiscale method — A paradigm for computational mechanics. *Comput. Methods Appl. Mech. Engrg.* 166, 3–24.
- Jaynes, E.T., 1957. Information theory and statistical mechanics. *Phys. Rev.* 106 (4), 620–630.
- Khanjari, N., Eslami, H., Müller-Plathe, F., 2017. Adaptive-numerical-bias metadynamics. *J. Comput. Chem.* 38 (31), 2721–2729.
- Knap, J., Ortiz, M., 2001. An analysis of the quasicontinuum method. *J. Mech. Phys. Solids* 49 (9), 1899–1923.
- Kulkarni, Y., Knap, J., Ortiz, M., 2008. A variational approach to coarse graining of equilibrium and non-equilibrium atomistic description at finite temperature. *J. Mech. Phys. Solids* 56, 1417–1449.
- Laio, A., Parrinello, M., 2002. Escaping free-energy minima. *Proc. Natl. Acad. Sci.* 99 (20), 12562–12566.
- Lew, A., Marsden, J.E., Ortiz, M., West, M., 2004. Variational time integrators. *Internat. J. Numer. Methods Engrg.* 60, 153–212.
- Marsden, J.E., West, M., 2001. Discrete mechanics and variational integrators. *Acta Numer.* 10, 357–514.
- Müller, S., Ortiz, M., 2004. On the Γ -convergence of discrete dynamics and variational integrators. *J. Nonlinear Sci.* 14 (3), 279–296.
- Phillips, R.B., 2001. Crystals, Defects and Microstructures: Modeling Across Scales. Cambridge University Press.
- Rockafellar, R.T., 1970. Convex Analysis. Vol. 28, Princeton University Press, Princeton, N.J..
- Schröder, J., 2014. Plasticity and beyond: microstructures, crystal-plasticity and phase transitions. In: CISM International Centre for Mechanical Sciences Courses and Lectures, Vol. 550, Springer, Wien, pp. 1–64.
- Shenoy, V., Miller, R., Tadmor, E., Phillips, R., Ortiz, M., 1998. Quasicontinuum models of interfacial structure and deformation. *Phys. Rev. Lett.* 80 (4), 742–745.
- Tadmor, E.B., Miller, R.E., 2011. Modeling Materials: Continuum, Atomistic and Multiscale Techniques. Cambridge University Press.
- Tadmor, E.B., Ortiz, M., Phillips, R., 1996. Quasicontinuum analysis of defects in solids. *Phil. Mag. A* 73 (6), 1529–1563.
- Tuckerman, M., 2010. Statistical Mechanics: Theory and Molecular Simulation. OUP Oxford.
- Van der Giessen, E., 2019. Micromechanics & emergence in time. *Eur. J. Mech. A Solids* 75, 277–283.
- Venturini, G., Wang, K., Romero, I., Ariza, M.P., Ortiz, M., 2014. Atomistic long-term simulation of heat and mass transport. *J. Mech. Phys. Solids* 73, 242–268.
- Voter, A.F., 1997. A method for accelerating the molecular dynamics simulation of infrequent events. *J. Chem. Phys.* 106 (11), 4665–4677.
- Voter, A.F., Montalenti, F., Germann, T.C., 2002. Extending the time scale in atomistic simulation of materials. *Annu. Rev. Mater. Res.* 32 (1), 321–346.
- Yeomans, J.M., 1992. Statistical Mechanics of Phase Transitions. Oxford Science Publications, Oxford, UK.
- Zhang, Z., Ge, X., 2005. A new quasi-continuum constitutive model for crack growth in an isotropic solid. *Eur. J. Mech. A Solids* 24 (2), 243–252.
- Ziman, J.M., 1960. Electrons and Phonons. In: The International Series of Monographs on Physics, Oxford University Press.