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Smoothed Molecular Dynamics For Thermally Embedded Systems

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Abstract

This paper makes use of statistical mechanics in order to construct effective potentials for Molecular Dynamics for systems with nonstationary thermal embedding. The usual approach requires the computation of a statistical ensemble of trajectories. In the context of the new model the evaluation of only one single trajectory is sufficient for the determination of all interesting quantities, which leads to an enormous reduction of computational effort. This single trajectory is the solution to a corrected Hamiltonian system with a new potential $\tilde{V}$. It turns out that $\tilde{V}$ can be defined as spatial average of the original potential V. Therefore, the Hamiltonian dynamics defined by $\tilde{V}$ is smoother than that effected by V, i.e. a numerical integration of its evolution in time allows larger stepsizes. Thus, the presented approach introduces a Molecular Dynamics with smoothed trajectories originating from spatial averaging. This is deeply connected to time–averaging in Molecular Dynamics. These two types of *smoothed Molecular Dynamics* share advantages (gain in efficiency, reduction of error amplification, increased stability) and problems (necessity of closing relations and adaptive control schemes) which will be explained in detail.

Keywords: smoothed molecular dynamics, effective potentials, averaging, nonstationary heat bath embedding, expectation values, ensemble averages

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1 Introduction

In Molecular Dynamics (MD) we are interested in a description of the dynamical behaviour of a (macro)molecular system in the scope of classical mechanics. Therefore we are concerned with Hamiltonian functions of the form

$$H(q,p) \;=\; \frac{1}{2}p^T M^{-1} p + V(q) \;\geq\; 0 \tag{1.1}$$

which lead to the following Hamiltonian equations of motion:

$$\begin{aligned} \frac{d}{dt}q &= D_p H(q,p) &=& \; M^{-1}p \\ \frac{d}{dt}p &= -D_q H(q,p) &=& \; -DV(q), \end{aligned} \tag{1.2}$$

where D_p and $D = D_q$ are the differential operators with respect to $p \in \mathbb{R}^{3N}$ and $q \in \mathbb{R}^{3N}$, the momenta and space coordinates of the N atoms of the considered molecular system. We assume that the potential V is given, and that it is a "good classical model" for the system. Then, if adequate initial conditions

$$(q,p)(0) \;=\; (q_0, p_0) \tag{1.3}$$

are given, a solution of (1.2) describes *the motion of the molecular system without interaction with any other system.* Thus, we only have to care for an *efficient, accurate, and stable* numerical solution of (1.2).
This is the idealized situation. There are several serious problems. Three of them will be explained in the following. They make up the starting point for the considerations in this paper.

Problem 1: Even if we accept that the exact solution of (1.2) gave us the answers we are interested in, we are often not able to compute its numerical solution on a sufficiently large time scale. In the typical situation the potential V contains parts which stand for the bond interaction between bonded atoms in the molecule:

$$V(q) \;=\; U(q) + \frac{1}{2}\sum_{k=1}^{m} \lambda_k \, g_k(q) \tag{1.4}$$

with e.g. harmonic models for g_k for the $k = 1 \ldots m$ different bond-types:

$$g_k(q) \;=\; \sum_{i,j \in B} \left(\|q_i - q_j\| - L_k \right)^2 ,$$

where L_k is the equilibrium length of bond type k, $q_i \in \mathbb{R}^3$ the vector of the space coordinates of the ith atom, and the summation runs over all bonded pairs. This g–part of the potential V causes *highly oscillatory* motions of the bonded atoms. Because of the typical magnitude of the λ_k, these *bond vibrations* appear on a timescale of about 1 femtosecond and are the "fastest degrees of freedom" of the molecule. Careful investigations have shown that the bond vibrations are an essential part of the nonlinear dynamics of the molecule, i.e. they cannot simply be eliminated or modelled [3][8].
Thus, if we are interested in the *accuracy* of the numerical solution of (1.2), we have to resolve this timescale, i.e. we have to choose stepsizes $\tau \approx 1\,\mathrm{fs}$ in the time discretization. And even if accuracy is less important we have to use $\tau \approx 1\,\mathrm{fs}$ in order to ensure *numerical stability* for the iteration of the discretization (at least for all conventional explicit discretizations [1]; for most implicit methods similar stepsize bounds result from the requirement of unique convergence of the iterative solution of the nonlinear equations in each step).
The typical time length of an MD simulation is $t_{\mathrm{max}} \gg 1\,\mathrm{ps}$. Therefore we have to make a large number t_{max}/τ of time steps, i.e. only the large computational effort of a typical MD calculation strictly limits its time length. In Section 2 the idea of "smoothed dynamics" will be discussed as a proposal for reducing the effort of those computations.

Problem 2: Normally, we are not interested in *the motion of the molecular system without interaction with any other system.* It is frequently desirable to simulate a system under conditions of constant temperature T, since this is the condition under which most experiments are performed. Hence, we have to model the *heat bath embedding* of the considered molecular system, "simply" solving (1.2) is not enough. But "temperature" and "heat bath embedding" can only be defined in a *statistical* sense, i.e. for an *ensemble* of identically prepared systems or in a stochastic theory for the single system. In addition, we are *not* interested in the pure equilibrium theory but in the motions, reactions, and structural changes of the molecular system embedded in an environment with constant temperature. Hence Section 3 shortly presents the statistical formulation of (1.2) and a definition of an ensemble of molecular systems with *nonstationary* embedding in heat baths of temperature T, which in particular is different from the "canonical" equilibrium theory.

Problem 3: Another crucial point is the requirement for adequate initial conditions. The initial state of the molecular system is typically known from measurement. Therefore there is a fundamental uncertainty about the initial condition of (1.2) if they are adapted to experimental realizations. More precisely, the coordinates q can only be given with a (small) degree of uncertainty

$$q_k(0) \in \{x : |x - q_k^0| \leq \delta_k\} \qquad \forall k = 1 \dots 3N, \tag{1.5}$$

whereas the initial momenta p are typically not determined experimentally. As a consequence adequate initial condition can only be given in the framework of, again, an ensemble formulation. The statistical version of (1.2) (cf. Section 3) can be used for a concise definition of the "initial conditions", in particular for the initial momenta.

Problems 2 and 3 demand for a statistical formulation of (1.2). But the dynamical behaviour of the statistical ensemble is "rich", the computational effort for its full simulation is far too large. One main aspect of the following sections is the reduction of this effort. This is realized by reducing the rich ensemble–dynamics to the far simpler evolution of a single Hamiltonian system with a new Hamiltonian $\tilde{H}$. The other main aspect (construction of a smoothed MD) is deeply connected to this because the $\tilde{H}$-trajectories are smoother than the corresponding H-trajectories.

2 Smoothed MD and Averaging in Time

As stated above bond vibrations are the fastest motions in typical MD situations and lead to hard restrictions for the stepsize τ in (explicit) numerical integration methods. Mostly, we do not want to compute all these "unessential" oscillatory details. But we want to get *correct* information about the physically relevant dynamical behaviour of the considered system, i.e. we cannot ignore the bond dynamics.

2.1 Basic Ideas and Problems

The idea of *smoothed dynamics* is to compute only the "running average"

$$\begin{pmatrix} \overline{q}(t) \\ \overline{p}(t) \end{pmatrix} := \mathcal{A}_\alpha \begin{pmatrix} q \\ p \end{pmatrix}(t)$$

of the exact solution $(q,p)^T$ of (1.2). The average operator $\mathcal{A}_\alpha$ is given by

$$(\mathcal{A}_\alpha x)(t) := \frac{1}{\alpha} \int\limits_{\mathbb{R}} w\left(\frac{t-s}{\alpha}\right) x(s)\, ds$$

with an appropriate weight function w with $\lim_{t\to\infty} w(t) = 0$, e.g.

$$w(x) = \chi_{[-1/2,1/2]}(x) = \begin{cases} 1: & -1/2 \le x \le 1/2 \\ 0: & \text{otherwise} \end{cases} .$$

Another possibility may be to choose w in a way which makes $\mathcal{A}_\alpha$ a low pass filter with cut–off frequency $\mathcal{O}(1/\alpha)$. Now, the task is to deduce a differential equation for $(\overline{q},\overline{p})$ from (1.2). We can use the fact that

$$\frac{d}{dt}\mathcal{A}_\alpha\, x = \mathcal{A}_\alpha \frac{d}{dt} x, \qquad \forall x$$

to get using (1.2) that

$$\frac{d}{dt}\begin{pmatrix} \overline{q} \\ \overline{p} \end{pmatrix} = \begin{pmatrix} M^{-1}\overline{p} \\ -\overline{DV(q)} \end{pmatrix} \tag{2.1}$$

The trajectories of (2.1) would be *smooth*, if $\mathcal{A}_\alpha$ was chosen in a way which lets the "fastest oscillations" of $(\overline{q},\overline{p})$ occur on a time scale $\Delta t \gg 1\,\text{fs}$, i.e. that the numerical integration of (2.1) allows stepsizes $\tau \approx \Delta t \gg 1\,\text{fs}$ (cf. Figure 1).

Unfortunately, we have to know the solution $q(t)$ of (1.2) to compute the right hand side $\overline{DV(q)}$ of (2.1), because the *nonlinear* function $DV(q)$ and $\mathcal{A}_\alpha$ do not commute:

$$\overline{DV(q)} = \mathcal{A}_\alpha\, DV(q) \ne DV(\mathcal{A}_\alpha q) = DV(\overline{q}). \tag{2.2}$$

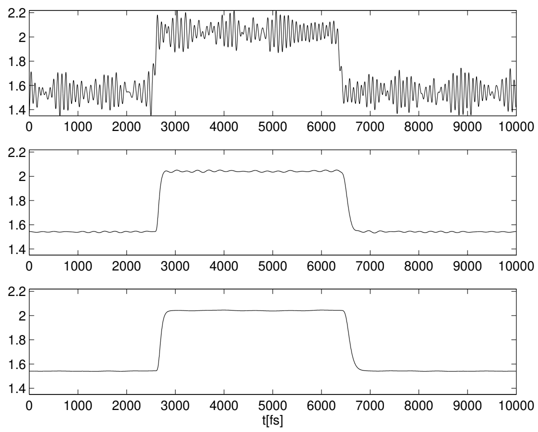

FIG. 1. Typical dynamics with bond vibrations (top) and its running average with averaging on different time scales.

And worse, up to now there is no way to *deduce* a function v with

$$\overline{DV(q)} \;=\; v(\overline{q}) \tag{2.3}$$

using mathematical means only. Thus, we have to look for a physical alternative: we may *construct* v by using additional physical insight in the dynamics, e.g. in form of additional postulates. [9] and [10] may be taken as examples for this approach. In [9] , a result from statistical mechanics (equipartition of energy for ergodic systems embedded in a heat bath of fixed temperature) is used as such a postulate. Then, it is shown that v can be written as $v = D\tilde{V}$ with a corrected potential $\tilde{V}$, if the parameters λ_k in (1.4) are large enough in comparison to all changes in the forces effected by U (gap condition):

$$\lambda_k \;\gg\; \max_t \; D^2U(q(t)).$$

In the new potential $\tilde{V}$ the bond interaction part $V - U$ is cancelled and a "smoother" correction term occurs, which models the influence of the bond motions on the "rest" of the motions. Conclusively, a statistical postulate allows to construct a smoother potential which models the influence of bond dynamics instead of containing it explicitly. How can such a smoother potential be constructed directly using a statistical formulation of (1.2)? Section 4 gives an answer to this question.

2.2 Reduction of Error Amplification

Potentials with steep gradients can lead to a strong amplification of numerical errors along the trajectories of the corresponding Hamiltonian system. For highly oscillatory trajectories a "successful smoothing" can effect an essential reduction of this error amplification. This should become clear if one considers the following 4-dimensional test system:

$$H(q_1, q_2, p_1, p_2) \;=\; \frac{1}{2}\left(\frac{p_1^2}{2} + \frac{p_2^2}{2} + \omega^2\,(q_2 - q_1)^2\right) \;+\; V(q_1) \tag{2.4}$$

with a strong harmonic part ($\omega \gg 1$) and the morse potential (cf. Figure 2)

$$V(q) \;=\; \frac{1}{2}(1 - \exp(-a\,q))^L \qquad \text{with } a > 0 \text{ and } L \in \mathbb{N}. \tag{2.5}$$

It can be shown (using perturbation analysis or the results of [9]) that for $\omega \gg a$ (gap condition) and time intervals not too large the smoothed evolution of (2.4) is approximately given by the solution of the 2d–Hamiltonian system with

$$H(q,p) \;=\; \frac{1}{2}p^2 \;+\; V(q).$$

This allows us to compare the *error propagation* in the two systems: Assume that we have made an (numerical) error ϵ for the state (q,p) of a system at $t = 0$. How strong will it be amplified by the evolution of the system? Let Φ^t be the phase flow of (2.4), i.e. $\Phi^t x_0$ is the solution of (2.4) with initial conditions $x_0 = (q,p)(0) = (q_0, p_0)$. Then we are interested in the *interval condition number*

$$\kappa[0,t] \;:=\; \max_{s\in[0,t]}\;\sup_{\epsilon}\;\frac{\|\Phi^t(x_0+\epsilon) \,-\, \Phi^t x_0\|}{\|\epsilon\|}, \tag{2.6}$$

in an arbitrary norm $\|\cdot\|$ (for the theoretical background of this concept see [2]). Figure 3 shows the evolution of $\kappa[0,t]$ in time t for the original and for the smoothed system. We observe that, firstly, the amplification of errors can be strong for collision potentials like (2.5) and that, secondly, this *amplification can be reduced by smoothing the dynamics.* Thus, smoothing techniques will not only help to increase stepsize and efficiency but also allow accurate MD integration on larger time intervals.

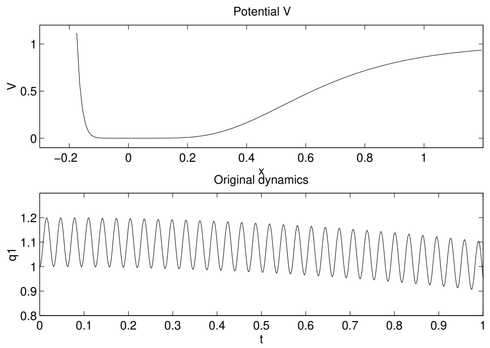

FIG. 2. Potential V from (2.5) for $a = 4$ and $L = 8$ and corresponding initial dynamics with resolution of the fast oscillations.

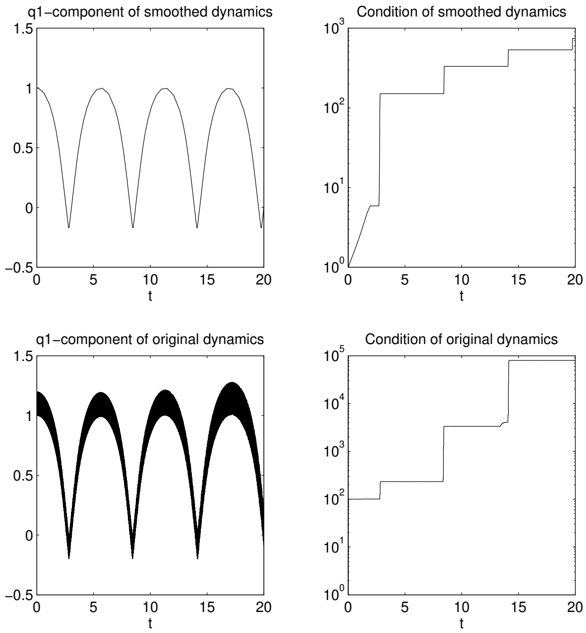

FIG. 3. Interval condition numbers $\kappa[0,t]$ and q_1–components of the original (bottom) and the smoothed (top) dynamics of (2.4) with $\omega = 100$, $a = 4$, and $L = 8$. Fast oscillations of original dynamics graphically not resolved (cf. Fig.2). Note that $\kappa[0,t]$ is 100 times larger for the original system.

2.3 Adaptation of Stepsizes

Figure 3 shows another important aspect of the smoothed dynamics: For the original, highly oscillatory solution and for each discretization scheme there is a fixed stepsize τ_0 which is overall optimal with respect to efficiency (τ = a fixed fraction of the average period of the oscillation), i.e. stepsize control cannot increase efficiency. For the corresponding solution of the smoothed dynamics this is *not* the case, because the oscillations are "cancelled" (cf. Figure 1: you can make large timesteps except in the region of the two jumps). Thus, in order to be efficient, smoothed MD requires stepsize control schemes. Up to now, it has not become clear how to solve this problem most efficiently: in the scope of explicit, symmetric extrapolation schemes (cf. [4] or [2]) or by use of symplectic discretizations [5][6].

3 Statistical formulation of Molecular Dynamics

This Section is concerned with the question of how to give an ensemble formulation of (1.2) and of the additional heat bath embedding of the molecular system.

3.1 Probability Density and Expectation Values

We consider a statistical ensemble of identically prepared molecular systems which are described by the Hamiltonian H from (1.1). The basic concept of the formulation is the introduction of a (phase space) probability density

$$f : \mathbb{R}^{3N} \times \mathbb{R}^{3N} \times \mathbb{R} \;\rightarrow\; [0,1].$$

for this ensemble. $f(q,p,t)$ must be interpreted as the relative frequency of systems in the ensemble which occupy state (q,p) at time t. The equation of motion for f is the well–known *Liouville equation*

$$\begin{aligned} \partial_t f &= [H\,,\,f] \\ &= D_q H \cdot D_p f \;-\; D_p H \cdot D_q f \\ &= DV(q) \cdot D_p f \;-\; D_q f \cdot M^{-1}\,p \end{aligned} \tag{3.1}$$

with the Poisson brackets $[\cdot,\cdot]$. Let us assume that a normalized initial density

$$f(\cdot,\cdot,0) \;=\; f_0 \;:\; \mathbb{R}^{3N}\times\mathbb{R}^{3N} \;\to\; [0,1] \qquad \text{with} \qquad \int\limits_{\mathbb{R}^{6N}} f_0(q,p)\,dq\,dp \;=\; 1$$

is given (see Section 3.3). Let Φ^t again be the phase flow of (1.2), i.e. $\Phi^t(q_0,p_0)$ is the solution of (1.2) with initial conditions $(q,p)(0)=(q_0,p_0)$. Then, the *formal solution* of (3.1) can be given:

$$f\left(\Phi^t(q,p)\,,\,t\right) \;=\; f_0\,(q,p)\,. \tag{3.2}$$

From (3.2) we see that (3.1) describes the transport of the initial density along the integral curves of (1.2). Moreover, it is obvious that a solution of (3.1) is equivalent to the evaluation of the total flow Φ^t, i.e. equivalent to the solution of an infinite number of initial value problems with (1.2) as differential equation.

Fortunately, we are not interested in f itself but in the expectation values of physical observables with respect to f, i.e. with respect to our ensemble. An observable is a sufficiently smooth and f–integrable function

$$A:\;\mathbb{R}^{3N}\,\times\,\mathbb{R}^{3N}\;\to\;\mathbb{R}^m, \qquad m\in\mathbb{N}$$

and its expectation value is defined as

$$\langle A\rangle(t) \;=\; \int\limits_{\mathbb{R}^{6N}} A(q,p)\,f(q,p,t)\,dq\,dp.$$

So far, this can be found in textbooks on Statistical Mechanics, e.g. [7]. Now, Liouville's equation (3.1) gives us equations of motion for the expectation values (via partial integration):

$$\frac{d}{dt}\,\langle A\rangle \;=\; \langle D_qA\cdot M^{-1}p\rangle \;-\; \langle D_pA\cdot DV\rangle. \tag{3.3}$$

In particular, the equation of motion for the position and momenta observable $A(q,p)=(q,p)^T$ is

$$\frac{d}{dt}\begin{pmatrix}\langle q\rangle\\ \langle p\rangle\end{pmatrix} \;=\; \begin{pmatrix} M^{-1}\langle p\rangle \\ -\langle\, DV(q)\,\rangle\end{pmatrix} \tag{3.4}$$

and we observe the same fundamental problem of noncommutativity as we had in Section 2 (eq. (2.2)):

$$\langle DV(q)\rangle \;\neq\; DV(\langle q\rangle), \tag{3.5}$$

i.e. equation (3.4) is *not closed*, we need knowledge about f for the evaluation of its right hand side. More precisely, we do not need f but only the *reduced density*

$$F(q,t) \;:=\; \int\limits_{\mathbb{R}^{3N}} f(q,p,t)\,dp, \tag{3.6}$$

because of

$$\langle\, DV(q)\,\rangle \;=\; \int\limits_{\mathbb{R}^{3N}} DV(q)\,F(q,t)\,dq. \tag{3.7}$$

But again, we are not able to *deduce* this knowledge mathematically without solving (3.1) and we have to *construct* it using a physical model, i.e. we have to construct a *closing relation* $\langle DV(q)\rangle\rangle = D\tilde{V}(\langle q\rangle)$ *for the statistical equation of motion* (3.4). For the case of (nonequilibrium) thermal embedding $\tilde{V}$ can be constructed via a heuristical model for f (cf. Section 4). But before going into details we must give some comments on the definition of "temperature", "heat bath embedding", and the initial density f_0 ("solving" Problem 2 and 3 from the introduction).

3.2 Temperature and Heat Bath Embedding

All densities $f(q,p) = \psi(H(q,p))$ with a smooth and sufficiently decreasing function $\psi : \mathbb{R}^+ \to [0,1]$ are *stationary solutions* of Liouville's equation (3.1). One of these, the well–known *canonical ensemble*

$$f_c(q,p) \;=\; \frac{1}{Q}\exp(-\beta H(q,p)) \quad \text{with} \quad Q \;=\; \int\limits_{\mathbb{R}^{6N}} e^{-\beta H}\,dp\,dq, \tag{3.8}$$

is used to define "temperature": f_c is the probability density of our ensemble iff the ensemble is *in equilibrium with a heat bath of temperature*

$$T \;=\; \frac{1}{k_B\,\beta}, \qquad k_B:\ \text{Boltzmann constant.}$$

This statistical way of defining temperature has an interesting consequence for Hamiltonian of the form (1.1): If $\langle\cdot\rangle$ is the expectation value with respect to f_c it is $\langle p\rangle = 0$ and with the dyadic product $(p\otimes p)_{kl} = p_k p_l$ we find:

$$\langle p\otimes p\rangle \;=\; \frac{1}{\beta}\,M \;=\; M\,k_B T,$$

if $M = \mathrm{diag}(m_k)$ is diagonal (what we assume in the following). Together we have

$$\langle p\otimes p\rangle \;-\; \langle p\rangle\otimes\langle p\rangle \;=\; \frac{1}{\beta}\,M. \tag{3.9}$$

In particular, the deviation of the measurement of $\langle p_l\rangle$ in the canonical ensemble is controlled by the temperature:

$$\Delta(p_l) \;:=\; \langle p_l^2\rangle \;-\; \langle p_l\rangle^2 \;=\; \frac{m_l}{\beta} \;=\; m_l k_B T.$$

A concrete computation of an expectation value $\langle A\rangle$ with respect to f_c remains a very hard problem, because a careful approximation of the corresponding high–dimensional integrals (e.g. in the evaluation of Q) produces dramatically large computational effort. Moreover, in the typical MD context, we often are not interested in describing the *equilibrium state* of the molecular system. Certainly, we want to simulate the system in interaction with a heat bath of fixed temperature but *not necessarily* in equilibrium with it. Thus, our question is how to construct a density which describes this situation? This is a crucial point. Let us be careful and therefore precise. The solution f of Liouville's equation with initial condition $f(\cdot,0) = f_0$ describes an ensemble of single system of type S, which *all* are *totally characterized* by the Hamiltonian H, i.e. the evolution of each single systems is totally determined by H and the corresponding initial condition for this system. But H doesn't include the heat bath: systems of type S are free, i.e. they are not interacting with a heat bath. Then, what is the meaning of the statement "f_c describes equilibrium heat bath embedding of the S–ensemble"? It states, that there is *a particular initial density* $f_0 = f_c$ which *models* the situation of heat bath embedding of S in the sense that the expectation values with respect to the corresponding solution $f(\cdot,t) = f_c$ of Liouville's equation are correct descriptions for S in thermal equilibrium! This shows the importance of the initial density in this statistical approach, i.e. the importance of the *initial preparation* of the ensemble. If $f_0 \neq f_c$ we do not know how to model "thermal embedding". We may go the way of changing the Hamiltonian $H \to \hat{H}$, e.g. by adding additional stochastic forces. Or we may construct a *model* for the density f which, then, must no more fulfil Liouville's equation for H but a "corrected" one. This last approach is realized herein (cf. Section 4). As a first step it should be noted that (3.9) is not equivalent to the canonical ensemble, i.e. if (3.9) is fulfilled for the expectation values with respect to a density f this does not imply $f = f_c$. We may use this freedom and *define* that a density f which fulfils (3.9) describes an ensemble in interaction with a heat bath with temperature $T = 1/k_B\beta$ (in *local* equilibrium).

3.3 Initial Density

What is the "right" initial density $f_0 = f(\cdot,\cdot,0)$ for (3.1) if we are in the situation explained in Problem 3 in the introduction? Equation (1.5) leads us to the following model for the "spatial part" of f_0:

$$f_0(q,p) \;=\; \phi(p) \prod_{k=1}^{3N} w_k \left(\frac{q_k - q_k^0}{\delta_k} \right)$$

where ϕ must still be defined and the $w_k : \mathbb{R} \to [0,1]$ are suitable *weight functions* with $\int w(x)dx = 1$. If we assume normal distribution for the error of the spatial measurements we will e.g. use

$$w_k(x) \;=\; \frac{1}{\sqrt{\pi}} \exp(-x^2).$$

If f_0 is the initial density of an ensemble in interaction with a heat bath of temperature $T = 1/k_B\beta$, the usual model for ϕ is normal distribution with a variance controlled by temperature

$$\phi(p) \;=\; \frac{1}{\alpha} \exp\left(-\frac{\beta}{2}\, p^T M^{-1} p \right)$$

with α so that f_0 is normalized, i.e.

$$f_0(q,p) \;=\; \frac{1}{\alpha} \exp\left(-\frac{\beta}{2}\, p^T M^{-1} p \right) \prod_{l=1}^{3N} w_k \left(\frac{q_k - q_k^0}{\delta_k} \right) \qquad (3.10)$$

with

$$\alpha \;=\; \left(\frac{\sqrt{2\pi}}{\sqrt{\beta}}\right)^{3N} \prod_{k=1}^{3N} \delta_k \sqrt{m_k}.$$

This construction guarantees that f_0 fulfils (3.9) and that

$$\langle p \rangle \;=\; 0 \qquad \text{and} \qquad \langle q_k \rangle \;=\; q_k^0. \tag{3.11}$$

In particular, the form of the spatial part shows that $f_0 \neq f_c$, i.e. the initial preparation of our ensemble given by the spatial measurement (1.5) does not fit in the context of *thermal equilibrium* (see above).

4 Smoothed MD and Spatial Averaging

In "standard" MD–approaches the statistical nature of our problem may be taken into account by computing a *representatively large number* of trajectories with different, f_0–distributed initial values and (1.2) as equation of motion. Then, interesting expectation values are computed as mean values over all these trajectories. If this is done carefully it produces an enormous computational effort. Is it possible to evaluate these expectation values from *one* trajectory only, for instance the solution of our statistical equations of motion (3.4)? This would only be possible if we found a closing relation $\langle DV(q) \rangle \;=\; D\tilde{V}(\langle q \rangle)$ for (3.4) and adequate initial values. In the following such a closing relation and initial values are *constructed* from a model for the nonstationary probability density for thermally embedded systems which fits to the initial conditions (3.10). The reformulated equation of motion will again be Hamiltonian with a smoothed effective potential $\tilde{V}$ leading to smoother trajectories. But let us start proving some useful properties of "separable" densities.

4.1 Separable Densities

In this subsection we assume that the considered density f is *separable*, i.e. for all $t \geq 0$ it holds

$$f(q,p,t) \;=\; Q(q,t) \cdot P(p,t) \tag{4.1}$$

with both, Q and P, being normalized and with

$$\lim_{|p_k|\to\infty} P(p,t) \;=\; \lim_{|q_k|\to\infty} Q(q,t) \;=\; 0 \qquad \forall k = 1,\ldots,3N. \tag{4.2}$$

In this situation the following theorem holds:

THEOREM 1. *Let $\langle\cdot\rangle$ be the expectation value with respect to a separable density. Then the equations of motion (3.4) for the position and momenta expectation can be written in closed form and as a new Hamiltonian system*

$$\begin{aligned} \frac{d}{dt}\langle q\rangle &= D_p\tilde{H}(\langle q\rangle,\langle p\rangle) &= M^{-1}\langle p\rangle \\ \frac{d}{dt}\langle p\rangle &= -D_q\tilde{H}(\langle q\rangle,\langle p\rangle) &= -D\tilde{V}(\langle q\rangle), \end{aligned} \tag{4.3}$$

with a corrected Hamiltonian

$$\tilde{H}(q,p) \;=\; \frac{1}{2}p^T M^{-1} p \,+\, \tilde{V}(q). \tag{4.4}$$

Thus, the closing relation for system (3.4) is deduced*: $\langle DV(q)\rangle = D\tilde{V}(\langle q\rangle)$. The new potential $\tilde{V}$ only depends on the old one V and on the initial density $f(\cdot,\cdot,0)$.*

Proof. (4.1) implies for the reduced density (3.6)

$$F(q,t) \;=\; Q(q,t)$$

and, in particular:

$$\int\limits_{\mathbb{R}^{3N}} p\,P(p,t)\,dp \;=\; \langle p\rangle(t). \tag{4.5}$$

In this situation we can deduce an equation for $F = Q$ alone. Therefore, integrate (3.1) over p and use (4.2) to get

$$\begin{aligned} \partial_t F &= -\,D_qF\,\cdot\,M^{-1}\int\limits_{\mathbb{R}^{3N}} p\;P(p,t)\,dp \\ &= -\,D_qF\,\cdot\,M^{-1}\,\langle p\rangle. \end{aligned} \tag{4.6}$$

If $\langle p\rangle(t)$ and the initial reduced density

$$F_0 \; = \; F(\cdot, 0)$$

are known, the solution of (4.6) can be written as

$$F(q,t) \; = \; F_0\left(q \,-\, M^{-1}\int\limits_0^t \langle p\rangle(s)\,ds\right),$$

and we can use our general formula (3.4) to get

$$M^{-1}\int\limits_0^t \langle p\rangle(s)\,ds \; = \; \langle q\rangle(t) \,-\, \langle q\rangle(0)$$

and from this

$$F(q,t) \; = \; F_0\,(q \,-\, \langle q\rangle(t) \,+\, \langle q\rangle(0))\,.$$

If we switch to the *centered* initial density

$$\tilde{F}_0(q) \; := \; F_0(q + \langle q\rangle(0)) \tag{4.7}$$

we finally have

$$F(q,t) \; = \; \tilde{F}_0(q \,-\, \langle q\rangle(t)), \tag{4.8}$$

i.e. the initial probabilities $\tilde{F}_0(q)$ are transported along the curves $\langle q\rangle(t)$ of the spatial expectation value (cf.(3.2)). With (4.8) the desired consequences for the equation (3.4) follow directly: From (3.7) we get

$$\begin{aligned}
\langle DV(q)\rangle(t) \; &= \; \int\limits_{\mathbb{R}^{3N}} DV(q)\,F(q,t)\,dq \\
&= \; \int\limits_{\mathbb{R}^{3N}} DV(q)\,\tilde{F}_0\,(q - \langle q\rangle(t))\;dq \\
&= \; \int\limits_{\mathbb{R}^{3N}} DV\,(q' + \langle q\rangle(t))\;\tilde{F}_0(q')\,dq' \\
&= \; D_q\tilde{V}(\langle q\rangle(t))
\end{aligned}$$

with a new potential

$$\tilde{V}(q) \; := \; \int\limits_{\mathbb{R}^{3N}} V(q' + q)\,\tilde{F}_0(q')\,dq'. \tag{4.9}$$

This implies the statement of the theorem. □

Our theorem has additional nice consequences. If we consider an arbitrary spatial observable $A = A(q)$ one can show by the same calculations starting with (3.3) that

$$\frac{d}{dt}\langle A\rangle \;=\; D\tilde{A}(\langle q\rangle)\; M^{-1}\langle p\rangle \tag{4.10}$$

with a new function

$$\tilde{A}(q) \;:=\; \int\limits_{\mathbb{R}^{3N}} A(q'+q)\,\tilde{F}_0(q')\,dq',$$

i.e. solving (4.3) makes the computation of all spatial expectation values possible.

4.2 Probability Density for Thermally Embedded Systems

We want to construct a density f_β for an ensemble which describes (non-stationary) thermal embedding. This density shall allow us to find a closing relation for (3.4). Theorem 1 states that we can *deduce* the desired closing relation if f_β is separable. Therefore, consider the following density:

$$f_\beta(q,p,t) \;=\; F(q,t)\cdot\frac{1}{\alpha}\exp\left(-\frac{\beta}{2}(p-\langle p\rangle(t))^T M^{-1}(p-\langle p\rangle(t))\right) \tag{4.11}$$

with

$$\alpha \;=\; \prod_{l=1}^{3N}\sqrt{\frac{2\pi\, m_l}{\beta}}.$$

It is *separable* in the sense of (4.1), *nonstationary*, fulfils the initial condition (3.10) with

$$\begin{aligned} F(q,0) \;&=\; F_0(q) \;=\; \prod_{l=1}^{3N}\frac{1}{\delta_k}\,w_k\left(\frac{q_k-q_k^0}{\delta_k}\right) \\ \text{and}\quad \langle p\rangle(0) \;&=\; 0, \end{aligned} \tag{4.12}$$

and has the property

$$\langle p\otimes p\rangle \;-\; \langle p\rangle\otimes\langle p\rangle \;=\; \frac{1}{\beta}\,M,$$

which is (3.9), our defining equation for nonstationary embedding in a heat bath of temperature β.

Thus, f_β models the situation which we wanted to describe with the "corrected spatial Liouville equation"

$$\partial_t F \;=\; -\,D_q F \,\cdot\, M^{-1}\,\langle p\rangle \tag{4.13}$$

and

$$\frac{d}{dt}\langle p\rangle \;=\; -\int\limits_{\mathbb{R}^{3N}} DV(q)\,F(q,t)\,dp$$

as equations of motion (cf. the proof of Theorem 1) and (4.12) as initial condition.

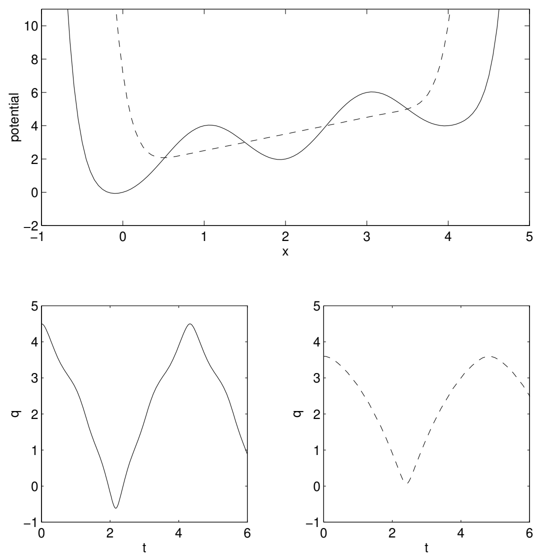

FIG. 4. Original (solid line) and smoothed potential (dotted line) and the corresponding Hamiltonian dynamics. Already in this simple example numerical integration of the smoothed dynamics needs 3 times less steps than in the original case.

Finally, we know from Theorem 1, that the separability of f_β, the initial conditions (4.12), and the new potential $\tilde{V}$ from (4.9) give us new and closed Hamiltonian equations of motion for the expectation values of ensembles modelling nonstationary thermal embedding:

$$\begin{aligned} \frac{d}{dt}\langle q\rangle &= M^{-1}\langle p\rangle & \langle q\rangle(0) &= (q_k^0)_{k=1,\ldots,3N} \\ \frac{d}{dt}\langle p\rangle &= -D\tilde{V}(\langle q\rangle) & \langle p\rangle(0) &= 0. \end{aligned} \tag{4.14}$$

4.3 Averaged Potentials for MD Calculations

According to (4.14) we have to use (4.9) to compute the new potential $\tilde{V}$ with a centered density $\tilde{F}_0$ given by (4.7) and (4.12):

$$\tilde{V}(q) = \int_{\mathbb{R}^{3N}} V(q+q') \prod_{l=1}^{3N} \frac{1}{\delta_k} w_k\left(\frac{q'_k}{\delta_k}\right) \; dq'_1 \cdots dq'_{3N}. \tag{4.15}$$

This means that $\tilde{V}$ is constructed from V by *weighted (spatial) averaging* on scales δ_l, e.g. with Gaussians

$$\tilde{V}(q) = \int_{\mathbb{R}^{3N}} V(q+q') \prod_{l=1}^{3N} \frac{1}{\sqrt{\pi}\delta_k} \exp\left(\left(\frac{q'_k}{\delta_k}\right)^2\right) \; dq'_1 \cdots dq'_{3N}. \tag{4.16}$$

Therefore, the new system (4.14) has smoothed trajectories in comparison to the original system (1.2) and its integration produces less computational effort (cf. Figure 4). Because of this, things explained in Sections 2.2 and 2.3 are valid for (4.14), too.
For typical MD potentials V the explicit evaluation of the integrals in (4.15) is possible, because they are sums of "simple" potentials $V^{(k)}$:

$$V(q) = \sum_{k=1}^{m} \sum_{(j_1 \ldots j_{N_k}) \in B_k} V^{(k)}\left(q_{j_1}, \ldots, q_{j_{N_k}}\right),$$

wherein N_k is small for all types $k = 1, \ldots, m$. Realization of this evaluation and efficient numerical integration of (4.14) for realistic molecular systems will be subject of further work.

5 Conclusion

Typical MD simulations for (macro)molecular systems with nonstationary thermal embedding necessarily require the computation of a representatively large (statistical) ensemble of trajectories and expectation values as corresponding ensemble averages. In addition, the evaluation of each of these trajectories produces large computational effort because hard stepsize limitations are demanded in order to ensure stability of the time integration. We have presented an approach which leads to a reduction of computational effort in both cases:

The construction of a model for the nonstationary probability density for the considered situation allows us to deduce a closing relation for the equation of motion (3.4) which is the equation for the (q,p)–observable. Thus, we are able to evaluate the expectation values of all spatial observables via (4.10) by computing *only one* trajectory $(\langle q\rangle, \langle p\rangle)$ as the solution of a new Hamiltonian system (4.14) with uniquely determined initial values. The potential $\tilde{V}$ of this Hamiltonian system is determined as a weighted spatial average of the original potential V. Thus, in comparison to the original trajectories, our single trajectory $(\langle q\rangle, \langle p\rangle)$ is smoother, i.e. it allows larger stepsizes and has also the other advantages of a smoothed MD (gain in efficiency, reduction of error amplification, increased stability).

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