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Abstract

In this paper we generalize a result by Rubin and Ungar on Hamiltonian systems containing a strong constraining potential to Langevin dynamics. Such highly oscillatory systems arise, for example, in the context of molecular dynamics. We derive constrained equations of motion for the slowly varying solution components. This includes in particular the derivation of a correcting force-term that stands for the coupling of the slow and fast degrees of motion. We will identify two limiting cases: (i) the correcting force becomes, over a finite interval of time, almost identical to the force term suggested by Rubin and Ungar (weak thermal coupling) and (ii) the correcting force can be approximated by the gradient of the Fixman potential as used in statistical mechanics (strong thermal coupling). The discussion will shed some light on the question which of the two correcting potentials is more appropriate under which circumstances for molecular dynamics. In Sec. 7, we also discuss smoothing in the context of constant temperature molecular dynamics.

Keywords: Hamiltonian systems, Langevin dynamics, highly oscillatory solutions, smoothed dynamics, correcting potential, constrained systems.

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1 Introduction

Physical systems frequently exhibit fast oscillatory behavior coupled to a slowly varying motion. This is, for example, the case when the potential energy function $U(q)$ consists of a smooth contribution $V(q)$ and a strong constraining potential modeled through $[g(q)]^2/(2\epsilon^2)$ where $g(q)$ is a scalar-valued function and $\epsilon > 0$ is a small parameter, i.e.,

$$U(q) = V(q) + \frac{1}{2\epsilon^2}[g(q)]^2.$$

In the context of molecular dynamics [1], which provides the main motivation of this paper, the strong potential can, for example, stand for the bond stretching motion, i.e.,

$$g(q) = r(q) - r_0,$$

$r(q)$ the actual bond length and r_0 the equilibrium bond length, or for the bond angle bending motion, i.e.,

$$g(q) = \phi(q) - \phi_0,$$

$\phi(q)$ the actual bond angle and ϕ_0 the equilibrium bond angle. The parameter ϵ^2 is then the inverse of the corresponding force constant K , i.e., $\epsilon^2 = 1/K$. Assuming a positive definite mass matrix M , the Hamiltonian of the system is given by

$$H(q, p) = \frac{p^T M^{-1} p}{2} + U(q),$$

$q, p \in \mathbb{R}^{3N}$, and the corresponding equations of motion are

$$\frac{d}{dt}q = M^{-1}p, \tag{1}$$

$$\frac{d}{dt}p = -\nabla_q V(q) - \frac{1}{\epsilon^2}G(q)^T g(q), \tag{2}$$

$G(q)$ the Jacobian of $g(q)$, i.e., $G(q) = g_q(q)$. The system (1)-(2) exhibits rapid oscillations on a time-scale of order $O(\epsilon)$. The “interesting” dynamics happens however on time-scales of order $O(1)$. To capture this “essential” behavior of (1)-(2) one could, for example, send the solutions $(q(t), p(t))$ of (1)-(2) through a low-pass filter with cut-off frequency $\omega_c = O(1/\sqrt{\epsilon})$. Let us denote the corresponding time-functions by $(\langle q \rangle_{\sqrt{\epsilon}}(t), \langle p \rangle_{\sqrt{\epsilon}}(t))$, i.e., for example,

$$\langle q \rangle_{\sqrt{\epsilon}}(t) := \frac{1}{\sqrt{\epsilon}} \int_{-\infty}^{+\infty} \psi\left(\frac{t-t'}{\sqrt{\epsilon}}\right) q(t') dt' \tag{3}$$

with $\psi : \mathbb{R} \rightarrow \mathbb{R}$ an appropriate weight function [14]. The idea of *smoothed dynamics* [3], [14] is now to find equations of motion with smooth solutions $(Q(t), P(t))$ that satisfy

$$Q(t) = \langle q \rangle_{\sqrt{\epsilon}}(t) \quad \text{and} \quad P(t) = \langle p \rangle_{\sqrt{\epsilon}}(t).$$

Such equations can indeed be defined in the limit $\epsilon \rightarrow 0$ and were first derived in [16] by Rubin and Ungar and recently discussed by Schütte and Bornemann [3] in the context of molecular

dynamics (see also their review paper [2] on the mathematical material). One obtains the constrained Hamiltonian system

$$\frac{d}{dt}Q = M^{-1}P, \quad (4)$$

$$\frac{d}{dt}P = -\nabla_q V(Q) - \mu \nabla_q \sqrt{G(q)M^{-1}G(q)^T} - G(Q)^T \lambda, \quad (5)$$

$$0 = g(Q). \quad (6)$$

Note the additional potential energy term

$$V_c(Q) = \mu \sqrt{G(Q)^T M^{-1} G(Q)^T}, \quad (7)$$

where μ is an appropriately chosen constant. This potential energy term is due to a momentum related coupling of the fast and slow degrees of freedom (see the following sections and [16],[2] for details).

In this paper, we generalize the results by Rubin and Ungar to thermally embedded systems

$$\frac{d}{dt}q = M^{-1}p, \quad (8)$$

$$\frac{d}{dt}p = -\nabla_q U(q) - \gamma p + \xi(t) \quad (9)$$

with $U(q)$ as before, $1/\gamma \gg \sqrt{\epsilon}$ a positive friction constant, and $\xi(t) \in \mathbb{R}^{3N}$ a Gaussian white noise process with zero mean value and variance

$$\langle \xi(t) \xi(t + \tau)^T \rangle = 2\gamma k_B T M \delta(\tau),$$

k_B the Boltzmann constant, T the temperature of the heat bath, and $\langle \cdot \rangle$ denotes the average over all realizations of the stochastic process $\xi(t)$ [1],[11]. We seek smooth Langevin equations of motion that possess solutions $(Q(t), P(t))$ such that the average $(\langle Q \rangle(t), \langle P \rangle(t))$ over all realizations of the stochastic process $\xi(t)$ satisfies

$$\langle Q \rangle(t) = \langle \langle q \rangle_{\sqrt{\epsilon}} \rangle(t)$$

and

$$\langle P \rangle(t) = \langle \langle p \rangle_{\sqrt{\epsilon}} \rangle(t)$$

in the limit $\epsilon \rightarrow 0$. As we will show in Sec. 4, the equations of motion are

$$\frac{d}{dt}Q = M^{-1}P, \quad (10)$$

$$\frac{d}{dt}P = -\nabla_Q V(Q) - \mu(t) \nabla_Q \sqrt{G(Q)M^{-1}G(Q)^T} - \gamma P + \xi(t) - G(Q)^T \lambda, \quad (11)$$

$$0 = g(Q). \quad (12)$$

Note that the correcting potential

$$V_c(Q, t) = \mu(t) \sqrt{G(Q)M^{-1}G(Q)^T} \quad (13)$$

is now time dependent. The differential equations for $\mu(t)$ will be derived in Sec. 5. We will see that $\mu(t)$ can be considered as constant over time intervals of order $1/\gamma$. If this time interval is short compared to the dynamics due to the force term $-\nabla_Q V(Q)$, then the correcting potential V_c can be approximated by the Fixman potential [6],[13] as used in statistical mechanics [1], i.e.,

$$V_c(Q) \approx \frac{k_B T}{2} \ln[G(Q)M^{-1}G(Q)^T]. \quad (14)$$

These results seem particularly interesting in the context of molecular dynamics for the following reasons:

- Often it is more realistic to solve the Langevin equations (8)-(9) instead of the Hamiltonian equations of motion (1)-(2). This is true in particular whenever various degrees of freedom have been neglected throughout the modeling process [1].
- Even if we assume that (1)-(2) contains all relevant degrees of freedom and correctly reflects the physical behavior of interest, the equations (10)-(12) seem to provide a more realistic model for the smoothed dynamics of (1)-(2) than (4)-(6). This is due to the fact that, in molecular dynamics, the force $-\nabla_q V(q)$ contains terms that are relatively strong compared to $-G(q)^T g(q)/\epsilon^2$. These terms are basically given by the close Lennard-Jones interactions of molecules and they lead to an energy transfer between the slow and fast degrees of motion. In the smoothed equations (4)-(6) this energy transfer is completely neglected ($\mu = \text{const.}$ in (7)) while the smoothed Langevin equations (10)-(12) allow one to include this effect in a stochastic manner through a properly chosen friction constant γ or, in other words, through a time-dependent $\mu(t)$ in the correcting potential (13).
- To be able to deal with the finite spectral gap between the fast and slow motion, we introduced in [14] the assumption of *quasi-stationarity* to derive smoothed equations of motion. The analysis of this paper will allow us to discuss this assumption in more detail and to characterize the cases in which this assumption seems appropriate. This also extends the analysis of Helfand [9] on the Fixman potential and its application in molecular dynamics.

2 Equations of motion in local coordinates

We follow in this section the notations introduced in [14], i.e., we define local coordinates (q_1, q_2) by

$$\begin{aligned} q_1 &= g(q), \\ q_2 &= b(q), \end{aligned}$$

where $b(q)$ is a vector-valued function such that $B(q)M^{-1}G(q)^T = 0$, $B(q) = b_q(q)$, and the composed matrix $[G(q)^T B(q)^T]$ is invertible and well conditioned. The corresponding conjugate momenta are given by

$$[G(q)^T B(q)^T] \begin{bmatrix} p_1 \\ p_2 \end{bmatrix} = p$$

which results in the Hamiltonian

$$H(q_1, p_1, q_2, p_2) = \frac{p_1 G M^{-1} G^T p_1}{2} + \frac{p_2^T B M^{-1} B^T p_2}{2} + V(q_1, q_2) + \frac{1}{2\epsilon^2} [q_1]^2,$$

where, for notational convenience, we suppressed the arguments in the mappings $G(q_1, q_2)$ and $B(q_1, q_2)$. The Langevin equations (8)-(9) are now equivalent to

$$\frac{d}{dt} q_1 = G M^{-1} G^T p_1, \quad (15)$$

$$\frac{d}{dt} p_1 = -\frac{1}{\epsilon^2} q_1 - \nabla_{q_1} \frac{p_1 G M^{-1} G^T p_1}{2} - \nabla_{q_1} E_T(q_1, q_2, p_2) - \gamma p_1 + \xi_1(t), \quad (16)$$

and

$$\frac{d}{dt} q_2 = B M^{-1} B^T p_2,$$

$$\frac{d}{dt} p_2 = -\nabla_{q_2} E_T(q_1, q_2, p_2) - \nabla_{q_2} \frac{p_1 G M^{-1} G^T p_1}{2} - \gamma p_2 + \xi_2(t)$$

with

$$E_T(q_1, q_2, p_2) = \frac{p_2^T B M^{-1} B^T p_2}{2} + V(q_1, q_2). \quad (17)$$

Here $\xi_1(t)$ and $\xi_2(t)$ are Gaussian white noise processes with zero mean value and variance

$$\langle \xi_1(t) \xi_1(t + \tau) \rangle = 2\gamma k_B T [G M^{-1} G^T]^{-1} \delta(\tau)$$

and

$$\langle \xi_2(t) \xi_2(t + \tau)^T \rangle = 2\gamma k_B T [B M^{-1} B^T]^{-1} \delta(\tau).$$

Following [16],[2], we also define the energy $E_N(q_1, q_2, p_1)$ in the fast degree of motion by

$$E_N(q_1, q_2, p_1) = \frac{p_1 G M^{-1} G^T p_1}{2} + \frac{1}{2\epsilon^2} [q_1]^2.$$

(Note that $H = E_T + E_N$.) The time derivative of E_N is given by

$$\frac{d}{dt} E_N = \left(\frac{d}{dt} q_2 \right)^T \nabla_{q_2} \frac{p_1 G M^{-1} G^T p_1}{2} + p_1 G M^{-1} G^T (-\nabla_{q_1} E_T - \gamma p_1 + \xi_1(t)) \quad (18)$$

which is of order $O(1)$ with respect to the small parameter ϵ . Thus, as already pointed out in [16], the energy E_N in the fast degree of motion varies slowly although the motion itself is rapidly oscillating. This implies that, over time-scales of order $\sqrt{\epsilon}$, the motion in the fast degree of motion is approximately given by

$$\frac{d}{dt}q_1 = GM^{-1}G^T p_1, \quad (19)$$

$$\frac{d}{dt}p_1 = -\frac{1}{\epsilon^2}q_1 \quad (20)$$

with constant energy E_N . Note that the slow variable (q_2, p_2) does not change over this time-scale. (A careful review of this analysis can be found in [2].)

3 Averaging in time

In this section we apply the time-averaging operator (3) to the equations (8)-(9). From the analysis of the previous section it follows that, in the limit $\epsilon \rightarrow 0$, $\langle q_2 \rangle_{\sqrt{\epsilon}}(t) = q_2(t)$, $\langle p_2 \rangle_{\sqrt{\epsilon}}(t) = p_2(t)$, and $\langle E_N \rangle_{\sqrt{\epsilon}}(t) = E_N(t)$. For the (on time-scales of order $\sqrt{\epsilon}$ harmonic) fast degree of motion we obtain relations such as $\langle q_1 \rangle_{\sqrt{\epsilon}}(t) = 0$, $\langle p_1 \rangle_{\sqrt{\epsilon}}(t) = 0$, and, by equipartitioning of energy [16],

$$\langle q_1^2 \rangle_{\sqrt{\epsilon}}(t) = \epsilon^2 E_N(t)$$

as well as

$$\langle p_1^2 \rangle_{\sqrt{\epsilon}}(t) = \frac{E_N(t)}{GM^{-1}G^T}$$

(compare [16] or [2] for details). Using also the fact that the time-averaging operator (3) commutes with taking the time derivative [14], this yields, in the limit $\epsilon \rightarrow 0$, the following smoothed equations of motion in the variables (Q_2, P_2) :

$$\frac{d}{dt}Q_2 = \nabla_{P_2} \hat{H}(Q_2, P_2) = BM^{-1}B^T P_2, \quad (21)$$

$$\frac{d}{dt}P_2 = -\nabla_{Q_2} \hat{H}(Q_2, P_2) - \frac{E_N(t)}{2GM^{-1}G^T} \nabla_{Q_2} GM^{-1}G^T - \gamma P_2 + \Xi_2(t). \quad (22)$$

Here \hat{H} is defined through

$$\hat{H}(Q_2, P_2) = E_T(Q_1 = 0, Q_2, P_2)$$

with E_T given by (17). The stochastic process $\Xi_2(t)$ is formally defined by $\Xi_2(t) = \langle \xi_2 \rangle_{\sqrt{\epsilon}}(t)$ which, in the limit $\epsilon \rightarrow 0$, can again be modeled as a Gaussian white noise process with the same properties as $\xi_2(t)$. The equations (21)-(22) can be written as a constrained Hamiltonian system in the smoothed variables (Q, P) . This yields

$$\frac{d}{dt}Q = M^{-1}P, \quad (23)$$

$$\begin{aligned} \frac{d}{dt}P = & -\nabla_Q V(Q) - \frac{E_N(t)}{\sqrt{G(Q)M^{-1}G(Q)^T}} \nabla_Q \sqrt{G(Q)M^{-1}G(Q)^T} - \\ & -\gamma P + \xi(t) - G(Q)^T \lambda, \end{aligned} \quad (24)$$

$$0 = g(Q). \quad (25)$$

Here the time-dependent force term

$$F_c(Q, t) = -\frac{E_N(t)}{\sqrt{G(Q)M^{-1}G(Q)^T}} \nabla_Q \sqrt{G(Q)M^{-1}G(Q)^T} \quad (26)$$

stands now for the correction due to the nonlinear coupling of the fast and slow degrees of motion. To close the equations of motion we still need the time-evolution of the energy $E_N(t)$. This will be the subject of the following section.

4 Time-evolution of E_N

The differential equation (18) for the time-evolution of $E_N(t)$ contains highly oscillatory terms that do not contribute to the time-evolution of E_N over time-scales of order $O(1)$. These are the terms

$$p_1 G M^{-1} G^T \nabla_{q_1} E_T,$$

$$\left(\frac{d}{dt}q_2\right)^T \nabla_{q_2} \frac{p_1 G M^{-1} G^T p_1}{2} - \frac{E_N}{\sqrt{G M^{-1} G^T}} \left(\frac{d}{dt}Q_2\right)^T \nabla_{Q_2} \sqrt{G M^{-1} G^T},$$

and

$$\gamma p_1 G M^{-1} G^T p_1 - \gamma E_N.$$

Thus we are left with the differential equation

$$\frac{d}{dt}E_N = \frac{E_N}{\sqrt{G M^{-1} G^T}} \left(\frac{d}{dt}Q_2\right)^T \nabla_{Q_2} \sqrt{G M^{-1} G^T} - \gamma E_N + p_1 G M^{-1} G^T \xi_1(t).$$

As shown in Appendix A

$$\langle p_1(t) G M^{-1} G^T \xi_1(t) \rangle = \gamma k_B T$$

and we replace $p_1(t) G M^{-1} G^T \xi_1(t)$ by $[\Xi_1(t)]^2$ with $\Xi_1(t)$ a Gaussian white noise process with zero mean and variance

$$\langle \Xi_1(t) \Xi_1(t + \tau) \rangle = \gamma k_B T \delta(\tau).$$

Thus we finally derive the equation

$$\frac{d}{dt}E_N = \frac{E_N}{\sqrt{GM^{-1}G^T}} \left(\frac{d}{dt}Q_2 \right)^T \nabla_{Q_2} \sqrt{GM^{-1}G^T} - \gamma E_N + [\Xi_1(t)]^2. \quad (27)$$

Upon neglecting fluctuations in $E_N(t)$ due to $\Xi_1(t)$, equation (27) can be simplified to

$$\frac{d}{dt}E_N = \frac{E_N}{\sqrt{GM^{-1}G^T}} \left(\frac{d}{dt}Q_2 \right)^T \nabla_{Q_2} \sqrt{GM^{-1}G^T} - \gamma E_N + \gamma k_B T. \quad (28)$$

5 Generalization to more than one constraint

If $g(q)$ becomes vector-valued, i.e., we consider more than one constraint, then $G(q)M^{-1}G^T(q)$ is a positive definite matrix. Thus there are orthogonal matrices $V(q)$ depending smoothly on q such that $A(q) := V(q)^T[GM^{-1}G^T]V(q)$ is diagonal. Upon introducing the canonical transformation $\tilde{q}_1 = V(q)^T q_1$ and $\tilde{p}_1 = V(q)^T p_1$, the equations (15)-(16) become

$$\begin{aligned} \frac{d}{dt}\tilde{q}_1 &= A\tilde{p}_1, \\ \frac{d}{dt}\tilde{p}_1 &= -\frac{1}{\epsilon^2}\tilde{q}_1 - \nabla_{\tilde{q}_1} \frac{\tilde{p}_1^T A \tilde{p}_1}{2} - \nabla_{\tilde{q}_1} E_T - \gamma \tilde{p}_1 + \tilde{\xi}_1(t) \end{aligned}$$

which decouple in m , $m = \dim(g(q))$, equations of motion for the pairs $(\tilde{q}_1^i, \tilde{p}_1^i)$, $i = 1, \dots, m$, except for the term $\nabla_{\tilde{q}_1} E_T$. Assuming that there are no resonances [18],[2], this term can be neglected and we obtain a set of m completely decoupled equations of motion. The smoothing over each of these degrees of freedom can now be done as described in Sec.'s 2-5 for the scalar case where we have to replace now $GM^{-1}G^T$ by A_{ii} .

6 Discussion and examples

Let us now discuss a few consequences of formula (28). First we rewrite the correcting force (26) as

$$F_c(Q, t) = -\mu(t) \nabla_Q \sqrt{G(Q)M^{-1}G(Q)^T}$$

with

$$\mu(t) = \frac{E_N(t)}{\sqrt{G(Q(t))M^{-1}G(Q(t))^T}}.$$

The corresponding differential equation for $\mu(t)$ follows from (28) to

$$\frac{d}{dt}\mu = -\gamma\mu + \frac{\gamma k_B T}{\sqrt{G(Q(t))M^{-1}G(Q(t))^T}}. \quad (29)$$

Two cases seem of special interest: (i) γ small which leads to the correcting potential (7) over time intervals of order $1/\gamma$ and (ii) γ large or $G(Q(t))M^{-1}G(Q(t))^T \approx \text{const.}$ which lead to

$$\mu(t) \approx \frac{k_B T}{\sqrt{G(Q(t))M^{-1}G(Q(t))^T}}$$

and thus to the Fixman potential (14). In terms of reaction rate theory [8], case (i) corresponds to the energy-diffusion-limit and case (ii) to the spatial-diffusion-limit.

What are the consequences of this for smoothed molecular dynamics? The limiting process $\epsilon \rightarrow 0$ is artificial. It assumes that there is a clear-cut separation between fast and slow degrees of motion. As already pointed out in the Introduction, this strong separation of time-scales does not exist in molecular dynamics. In particular, the Lennard-Jones interactions seem to lead to a slow but constant energy flow between fast and slow degrees of motion (see Example 1 below). The approach to smoothed molecular dynamics as suggested by Bornemann and Schütte [3] (and also briefly considered by Helfand in [9]) completely ignores this energy transfer (this corresponds to our case (i) with $\gamma = 0$). We feel that one might include energy transfer between fast and slow degrees of freedom through the Langevin dynamics approach described in this paper and an appropriate choice of the friction constant γ .

The simplifying assumption of *quasi-stationarity*, as made in [14] (which corresponds to our case (ii)), is approximately satisfied for the bond stretching motion but might not hold for the bond angle bending motion over time-intervals that are short compared to $1/\gamma$. However, the assumption of quasi-stationarity leads to the correct reduced macrocanonical distribution function [6],[15]. This can be seen as follows: The Fokker-Planck equation [11] corresponding to the equations (8)-(9) possesses the macrocanonical distribution function

$$\rho(q, p) = \exp(-\beta H(q, p)),$$

$\beta = (k_B T)^{-1}$, as an asymptotically stable stationary solution [11]. In the limit $\epsilon \rightarrow 0$, one can, in the local coordinates (q_1, p_1, q_2, p_2) , explicitly integrate over the variables (q_1, p_1) which yields the reduced distribution function

$$\rho_{\text{red}}(q_2, p_2) = \int \int dq_1 dp_1 \rho(q_1, p_1, q_2, p_2).$$

The Hamiltonian that is associated with $\rho_{\text{red}}(q_2, p_2)$ is called the free energy of the system (8)-(9) with respect to the variables (q_2, p_2) . As shown, for example, in [6],[15], the free energy \mathcal{H} is given by

$$\mathcal{H}(q_2, p_2) = \hat{H}(q_2, p_2) + \frac{k_B T}{2} \ln G(q_2)M^{-1}G(q_2)^T$$

and the additional potential energy term is equivalent to the Fixman potential. Note that Langevin dynamics applied to (4)-(6) yields a different additional potential energy term and thus a different macrocanonical distribution function.

We like to point out that the correcting force derived in this paper for small/moderate values of γ differs from the modifications to the Fixman potential discussed by Helfand in [9]. His approach is based on the Mori projection calculus [7]. We also like to mention that one

could discuss the introduction of modified constraint functions as suggested in [4],[14],[15] for the equations (1)-(2) (which is another manifestation of the finite “spectral” gap between the fast and slow motions).

Example 1. To demonstrate the energy transfer between the “fast” bond stretching and bond angle bending motions and the “slow” translational, rotational and torsion angle motions, we simulated the collision of two butane molecules. The force field for butane and the Lennard-Jones interaction between molecules was taken from [19]. We started the two molecules from zero internal energy and $k_B T \approx 0.6$ kcal/mol translational energy per molecule. The total energy in the fast degrees of motion (bond lengths and bond angles) as a function of time can be found in Fig. 1. Note that the variation in energy after the collision is due to the changes of the matrix $GM^{-1}G$ along the internal motion. It is obvious that the Lennard-Jones interaction of the two outer CH_3 groups caused an energy transfer to the fast degrees of motion. For comparison we also plot the energy in the Lennard-Jones potential as a function of time (Fig. 1). Note that the maximum energy in the Lennard-Jones potential is less than $k_B T$ which is a realistic value for Lennard-Jones interactions.

Example 2. Let us now consider an artificial four-bead-three-bond structure. To make the effect of the correcting potentials more pronounced [13], we set the ratio of the masses of the outer and inner beads equal to ten. (For equal masses, like in butane, this effect would be about four times smaller.) The bond stretching and bond angle bending motions are modeled by strong harmonic potentials with a force constant corresponding to $1/\epsilon^2 = 100$ kcal/mol. The equilibrium length of the bonds is $r_0 = 1.53$ and the equilibrium angle $\phi_0 = 109.5^\circ$. We assume that initially, at the *trans* conformation (torsion angle $\psi = 0$), we have an energy of $E_N = k_B T$ in each fast degree of motion. The resulting Fixman and Rubin/Ungar correcting potentials as a function of the torsion angle can be found in Fig. 2. Note that the correcting potentials are not small compared to, for example, the torsion potential

$$V_{\text{tors}}(\psi) = \frac{K}{2}(1 - \cos(3\psi))$$

with $K = 1.5$ kcal/mol and $k_B T = 0.6$ kcal/mol. To see the effect of coupling the structure to a heat-bath, we simulated the system with a moderate coupling parameter $\gamma = 0.1$. The average normal energy E_N in each fast degree of motion along a trajectory plotted as a function of the torsion angle ψ can be found in Fig. 3. (Here the average is to be understood as the average over the five fast degrees of motion.) Note that *quasi-stationarity* assumes that $E_N \approx k_B T$ which we find satisfied near the local minima of the potential $V_{\text{tors}}(\psi)$, i.e., near the *trans* and *gauche* conformations. Here, through the heat-bath coupling, the system relaxes to thermal equilibrium and the Fixman correcting potential seems appropriate. The situation is different for transitions between the local minima. Now the assumption $\mu = \text{const.}$ seems more suitable and the corresponding correcting potential would be the Rubin/Ungar potential. However, this effect is of the size of a few tenths of $k_B T$ and is, therefore, small compared to the torsion potential $V_{\text{tors}}(\psi)$ at room temperature. Thus the Fixman correcting potential seem a good bet for Langevin dynamics simulations even for small/moderate values of the coupling parameter γ . For example, consider the transition from the *trans* to *gauche* conformation: As before, we fit the Rubin/Ungar potential such that it is equivalent to the

Fixman potential at the *trans* conformation (Fig. 2). The resulting effective torsion potentials in kcal/mol can be found in Fig. 4. What is of interest here is the different barrier height for the two correcting potentials. Since this difference amounts to about 0.1 kcal/mol it is small and might be neglected. (Note that we would take a different Rubin/Ungar potential for the *gauche* to *trans* transitions. In this case we would fit the Rubin/Ungar potential to the Fixman potential at the *gauche* conformations ($\psi = \pm 2\pi/3$.)

7 Application to constant temperature molecular dynamics

An interesting application of the ideas developed in this paper is related to constant temperature molecular dynamics [12],[10]. In the Hoover formulation, the equations of motion are

$$\frac{d}{dt}q = M^{-1}p, \quad (30)$$

$$\frac{d}{dt}p = -\nabla_q U(q) - \gamma p, \quad (31)$$

$$\frac{d}{dt}\gamma = [p^T M^{-1}p - Xk_B T] / D, \quad (32)$$

where γ is now a time-dependent friction constant, D a parameter, and X the number of degrees of freedom. As shown in [10], the macrocanonical distribution function is a steady equilibrium solution of these equations for the variables (q, p) . Furthermore, the time-evolution of γ is unique in the sense that no other differential equation for γ would lead to the macrocanonical distribution function [10]. If

$$U(q) = V(q) + \frac{1}{2\epsilon^2}[g(q)]^2,$$

then one can, in the limit $\epsilon \rightarrow 0$, again average over the fast degree of motion to obtain smoothed equations of motion. These equations are

$$\frac{d}{dt}Q = M^{-1}P, \quad (33)$$

$$\frac{d}{dt}P = -\nabla_Q V(Q) - \mu \nabla_Q \sqrt{G(Q)M^{-1}G(Q)^T} - \gamma P - G(Q)^T \lambda, \quad (34)$$

$$0 = g(Q), \quad (35)$$

$$\frac{d}{dt}\mu = -\gamma \mu, \quad (36)$$

$$\frac{d}{dt}\gamma = [E_N + P^T M^{-1}P - Xk_B T] / D \quad (37)$$

with

$$E_N = \mu \sqrt{G(Q)M^{-1}G(Q)^T}$$

as before (see Appendix B for details). If one is only interested in the configurational part of the macrocanonical distribution function and neglects fluctuations in the kinetic energy, then one can use the constraint formulation

$$\begin{aligned} \frac{d}{dt}Q &= M^{-1}P, \\ \frac{d}{dt}P &= -\nabla_Q V(Q) - \mu \nabla_Q \sqrt{G(Q)M^{-1}G(Q)^T} - \gamma P - G(Q)^T \lambda, \\ 0 &= g(Q), \\ \frac{d}{dt}\mu &= -\gamma \mu, \\ 0 &= E_N + P^T M^{-1}P - X k_B T \end{aligned}$$

which is obtained by formally setting $D \rightarrow 0$ [12]. Furthermore, taking into account that, for the macrocanonical distribution function, we have $\langle E_N \rangle = k_B T$, this simplifies to

$$\begin{aligned} \frac{d}{dt}Q &= M^{-1}P, \\ \frac{d}{dt}P &= -\nabla_Q V(Q) - \frac{k_B T}{2} \nabla_Q \ln[G(Q)M^{-1}G(Q)^T] - \gamma P - G(Q)^T \lambda, \\ 0 &= g(Q), \\ 0 &= P^T M^{-1}P - (X - 1)k_B T. \end{aligned}$$

To extend these ideas to the isobaric/isothermal-isobaric case [12],[10],[5] is straightforward.

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Appendix A

In this appendix, we consider Langevin dynamics of (19)-(20), i.e.,

$$\frac{d}{dt}q_1 = GM^{-1}G^T p_1, \tag{38}$$

$$\frac{d}{dt}p_1 = -\frac{1}{\epsilon^2}q_1 - \gamma p_1 + \xi_1(t), \tag{39}$$

where we assume, for simplicity, that the matrix $GM^{-1}G^T$ is constant. As before, $\xi_1(t)$ is a Gaussian white noise process with variance

$$\langle \xi_1(t) \xi_1(t + \tau) \rangle = 2\gamma k_B T [GM^{-1}G^T]^{-1} \delta(\tau).$$

We are interested in the time-evolution of the energy

$$E_N = \frac{p_1 GM^{-1}G^T p_1}{2} + \frac{1}{2\epsilon^2} [q_1]^2$$

which is governed by the differential equation

$$\frac{d}{dt} E_N = -\gamma p_1 GM^{-1}G^T p_1 + p_1 GM^{-1}G^T \xi_1(t). \quad (40)$$

Since it is not obvious how to solve this differential equation, we will find the time-evolution of the expectation value $\langle E_N \rangle(t)$ by explicitly solving the Langevin equations (38)-(39). For that reason we rewrite (38)-(39) as

$$\frac{d}{dt} x = Ax + \Xi(t)$$

with $x = (q_1, p_1)^T$, $\Xi(t) = (0, \xi_1(t))^T$, and $A = JH + S$ where

$$H = \begin{bmatrix} \frac{1}{\epsilon^2} & 0 \\ 0 & GM^{-1}G^T \end{bmatrix},$$

$$S = \begin{bmatrix} 0 & 0 \\ 0 & -\gamma \end{bmatrix},$$

and

$$J = \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix}.$$

The solutions of (38)-(39) are now given by

$$x(t) = e^{tA} x_0 + e^{tA} \int_0^t dt' e^{-t'A} \Xi(t').$$

Note that, in the limit $\epsilon \rightarrow 0$, the exponential function $\exp(tA)$ can be approximated by

$$e^{tA} \approx e^{-t\frac{\gamma}{2}} e^{tJH}.$$

Using this in the evaluation of $\langle E_N \rangle(t)$ and taking note of the independence of x_0 and $\Xi(t)$, we obtain

$$\begin{aligned} \langle E_N \rangle(t) &= \left\langle \frac{x^T H x}{2} \right\rangle(t) \\ &= e^{-t\gamma} E_N(0) + e^{-t\gamma} \int_0^t dt' \int_0^t ds' e^{(t'+s')\frac{\gamma}{2}} \langle \Xi(t')^T \frac{H}{2} e^{(t'-s')JH} \Xi(s') \rangle \\ &= e^{-t\gamma} E_N(0) + k_B T (1 - e^{-t\gamma}). \end{aligned}$$

The corresponding differential equation is

$$\frac{d}{dt} \langle E_N \rangle = -\gamma \langle E_N \rangle + \gamma k_B T$$

and comparison with (40) yields $\langle p_1 GM^{-1}G^T \xi_1 \rangle(t) = \gamma k_B T$.

Appendix B

In this appendix, we indicate how to derive smoothed equations of motion for constant temperature molecular dynamics.

In the local coordinates (q_1, p_1, q_2, p_2) , the equations (30)-(32) are equivalent to

$$\begin{aligned}\frac{d}{dt}q_1 &= GM^{-1}G^T p_1, \\ \frac{d}{dt}p_1 &= -\frac{1}{\epsilon^2}q_1 - \nabla_{q_1} \frac{p_1 GM^{-1}G^T p_1}{2} - \nabla_{q_1} E_T(q_1, q_2, p_2) - \gamma p_1,\end{aligned}$$

and

$$\begin{aligned}\frac{d}{dt}q_2 &= BM^{-1}B^T p_2, \\ \frac{d}{dt}p_2 &= -\nabla_{q_2} E_T(q_1, q_2, p_2) - \nabla_{q_2} \frac{p_1 GM^{-1}G^T p_1}{2} - \gamma p_2\end{aligned}$$

as well as

$$\frac{d}{dt}\gamma = \left[p_1 GM^{-1}G^T p_1 + p_2^T BM^{-1}B^T p_2 - Xk_B T \right] / D.$$

Taking note that γ is a slowly varying variable, averaging in time results in

$$\begin{aligned}\frac{d}{dt}Q_2 &= BM^{-1}B^T P_2, \\ \frac{d}{dt}P_2 &= -\nabla_{Q_2} \hat{H}(Q_2, P_2) - \mu(t) \nabla_{Q_2} \sqrt{GM^{-1}G^T} - \gamma P_2\end{aligned}$$

and

$$\frac{d}{dt}\gamma = \left[E_N(t) + P_2^T BM^{-1}B^T P_2 - Xk_B T \right] / D.$$

The time-evolution of $\mu(t)$, $E_N(t)$ respectively, is determined by

$$\frac{d}{dt}\mu = -\gamma\mu.$$

Reformulating everything in terms of the Cartesian coordinates (Q, P) , we obtain (33)-(37).

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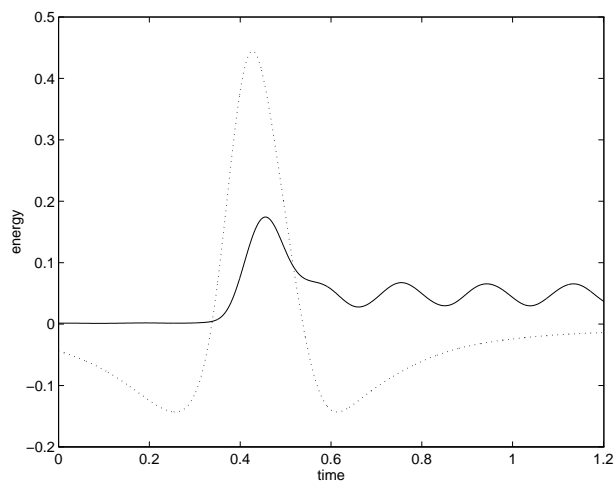


Figure 1: Solid line: total energy in the fast degrees of motion in kcal/mol; dotted line: energy in the Lennard-Jones potential in kcal/mol as a function of time in ps.

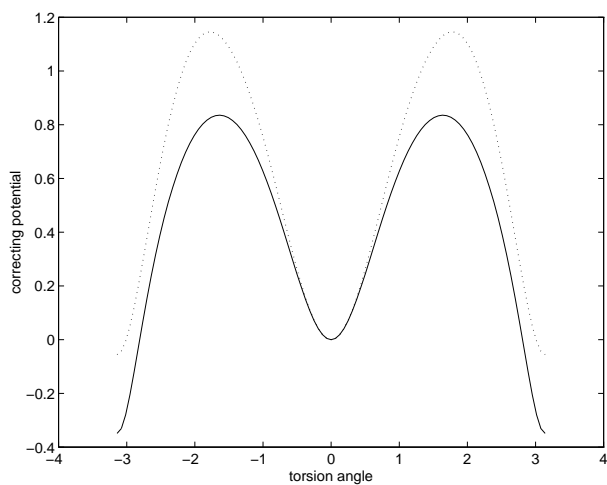


Figure 2: Solid line: Fixman correcting potential in $k_B T$; dotted line: Rubin/Ungar correcting potential in $k_B T$.

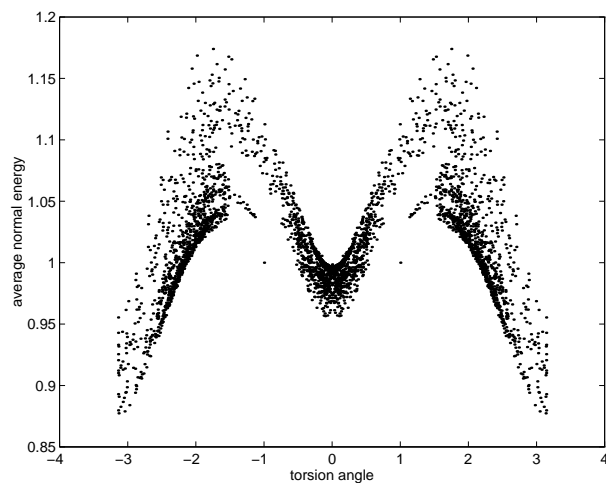


Figure 3: Average normal energy E_N per fast degree of motion in $k_B T$ along a trajectory plotted as a function of the torsion angle ψ .

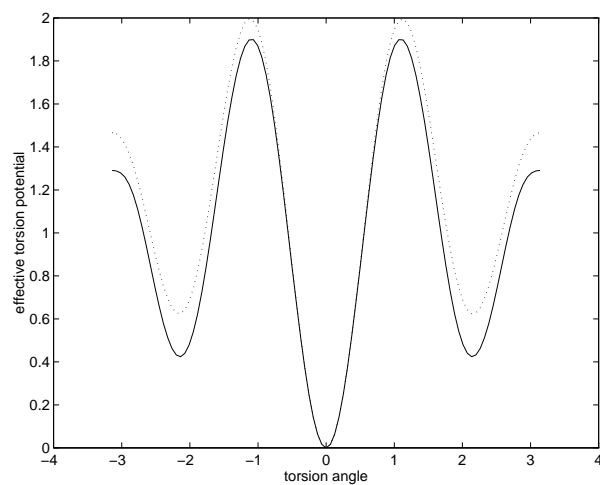


Figure 4: Solid line: effective torsion potential in kcal/mol using the Fixman correcting potential; dotted line: using the Rubin/Ungar potential fitted at the *trans* conformation.