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HOMOGENIZATION APPROACH TO SMOOTHED MOLECULAR DYNAMICS

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1. INTRODUCTION

In classical molecular dynamics (MD) simulations the evolution of a molecular system in time is described via classical Hamiltonian equations of motion in which the unknowns are the positions $q_i \in \mathbf{R}^3$ and momenta $p_i \in \mathbf{R}^3$ of all atoms in the system. The interatomic forces are given by an empirically constructed interaction potential $\mathcal{V}$ so that the motion is governed by the Hamiltonian

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

where M is the diagonal mass matrix corresponding to the atomic masses. Typically, the potential can be split into two parts of essentially different stiffness. In order to indicate this separation we rewrite the potential as the sum

$$\mathcal{V}(q) \;=\; V(q) \;+\; \frac{1}{\epsilon^2}\,U(q),$$

where U represents the stiff parts and V the collection of all soft contributions. The number $\epsilon > 0$ is small ($\epsilon \ll 1$) and $1/\epsilon$ gives the ratio of the different time scales of the motion (i.e., the spectral norms of the Hessian matrices of U and V are comparably to each other). Thus, the stiff part U/ϵ^2 of the potential forces the solution of the equations of motion to oscillate on a very small time scale of order $\mathcal{O}(\epsilon)$. We are concerned with the following Hamiltonian equations of motion:

$$\left.\begin{aligned} \dot{q} &= M^{-1}p \\ \dot{p} &= -\operatorname{grad} V \;-\; \epsilon^{-2}\operatorname{grad} U \end{aligned}\right\} \;\Rightarrow\; M\,\ddot{q} \;+\; \operatorname{grad} V(q) \;+\; \frac{1}{\epsilon^2}\operatorname{grad} U(q) \;=\; 0, \tag{1.2}$$

in which gradient is taken with respect to $q \in \mathbf{R}^{3d}$. There is a strong need for eliminating the smallest time scales because they are a severe restriction for numerical long-term simulations of macromolecules. This leads to the idea of just freezing the high frequency degrees of freedom, i.e., constraining the system to the manifold of equilibrium positions of the stiff potential U while the motion is given by the tangential derivative of the soft potential V only. However, this naive approach via holonomic constraints is observed to produce incorrect results.

This article presents a mathematically rigorous discussion of the limit situation in which the stiffness of the stiff part of the potential is increased to infinity, i.e., of the limit $\epsilon \to 0$. It is demonstrated that the average of the *limit solution* indeed obeys a *constrained Hamiltonian system* where the constraints are given by the equilibrium positions of U but with a *corrected soft potential.*

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An explicit formula for the additive potential correction is given. This formula is based on two theorems which we will quote from the review [1]. While Theorem 3.2 can only be found in [1], the first proofs of Theorem 4.1 were given in an early paper by Rubin and Ungar [2], also by Takens [3]. In [1] these proofs are simplified via their unification in the context of weak convergences — an approach which we will exploit for the problems occuring in MD.

Unfortunately, the theory is valid only as long as the system does not run into certain resonances of the fast motions. Behind those resonances, there is no unique limit solution but a kind of choatic scenario for which the notion "Takens chaos" was coined. For demonstrating the relevance of this observation for MD, the theory is applied to a realistic, but still simple system: a single butan molecule. The appearance of "Takens chaos" in smoothed MD is illustrated and the consequences are discussed.

2. PRELIMINARIES

In a numerical solution of (1.2) we do not want to compute all the "unessential" oscillatory details on scale $\mathcal{O}(\epsilon)$. But if we want to get the physically relevant dynamical behavior of the considered system, we cannot simply ignore the fast degrees of freedom. The idea of *smoothed MD* is to compute the "running average" of the exact solution q of (1.2) only. In the simplest case we have $q(t) = q^0(t) + a\sin(2\pi t/\mathcal{T})$ with q^0 oscillating on scale $\mathcal{O}(1)$ and $\mathcal{T} = \mathcal{O}(\epsilon)$. Its running average is defined by

$$\bar{q}(t) \;=\; \frac{1}{\mathcal{T}} \int_{t-\mathcal{T}/2}^{t+\mathcal{T}/2} q(s)\,ds \;=\; q^0(t), \tag{2.1}$$

which is not any longer affected by the small time scale $\mathcal{T}$. Thus, a direct numerical computation of $\bar{q}$ would allow larger timesteps and, in turn, larger maximal time spans for MD-simulations.

In order to deduce an equation directly for the average, we look at the *limit solution* q^0 of the solutions q^ϵ of (1.2) for $\epsilon \to 0$. Figure 1 shows some solutions of an example system of form (1.2) for different small ϵ. We observe that for decreasing ϵ the fast oscillation get faster and faster but the running average remains "invariant". Thus, the limit solution for $\epsilon \to 0$ may give us a good approximation of the running average. Hence, the question is posed whether one can derive a differential equation governing this limit solution q^0.

In order to give an answer to this question we have to introduce a suitable concept of convergence because another inspection of Figure 1 shows that the velocities $\dot{q}^\epsilon$ do not converge strongly although their "running average converges". The suitable type of convergence appears to be the weak*-convergence in $L^\infty[0,T]$: We have $x^\epsilon \overset{*}{\rightharpoonup} x^0$ for a sequence (x^ϵ) of functions, if and only if the averages

$$\int x^\epsilon(t)\,\phi(t)\,dt \;\to\; \int x^0(t)\,\phi(t)\,dt$$

converge for all $\phi \in L^1$. An even "weaker" notion of weak convergence is given, if we restrict these test functions ϕ to the space of infinitely continuous functions with compact support, which gives us the notion of weak convergence in the space of distributions $\mathcal{D}'$, $x^\epsilon \overset{\mathcal{D}'}{\rightharpoonup} x^0$.

The link to averaging, which makes weak*-convergence a suitable concept herein, may be illustrated for the easiest situation, i.e., for sequences of harmonic oscillations:

- In the case of constant amplitude with period ϵ, i.e., $x^\epsilon(t) = x^0(t) + a\,\sin(t/\epsilon)$ we have $x^\epsilon \overset{*}{\rightharpoonup} x^0$ (Riemann-Lebesgue-Lemma) but no strong convergence.
- If the amplitude a is of order $\mathcal{O}(\epsilon)$ also, e.g., $x^\epsilon(t) = x^0(t) + \epsilon\,\sin(t/\epsilon)$, we get strong convergence $x^\epsilon \to x^0$.

Furthermore, it is easy to understand the central problem of averaging: The strong (pointwise) convergence $x^\epsilon \to x^0$ of functions implies the strong convergence $f(x^\epsilon) \to f(x^0)$, where f is a function continuous in the point argument x. However, $x^\epsilon \overset{*}{\rightharpoonup} x^0$ does *not* imply $f(x^\epsilon) \overset{*}{\rightharpoonup} f(x^0)$. For example, we get $\sin^2(t/\epsilon) \overset{*}{\rightharpoonup} 1/2 \neq 0$. This fact — continuous functions do not in general constitute weak*-continuous operators — appears to be the reason for the necessity of the potential correction W mentioned above.

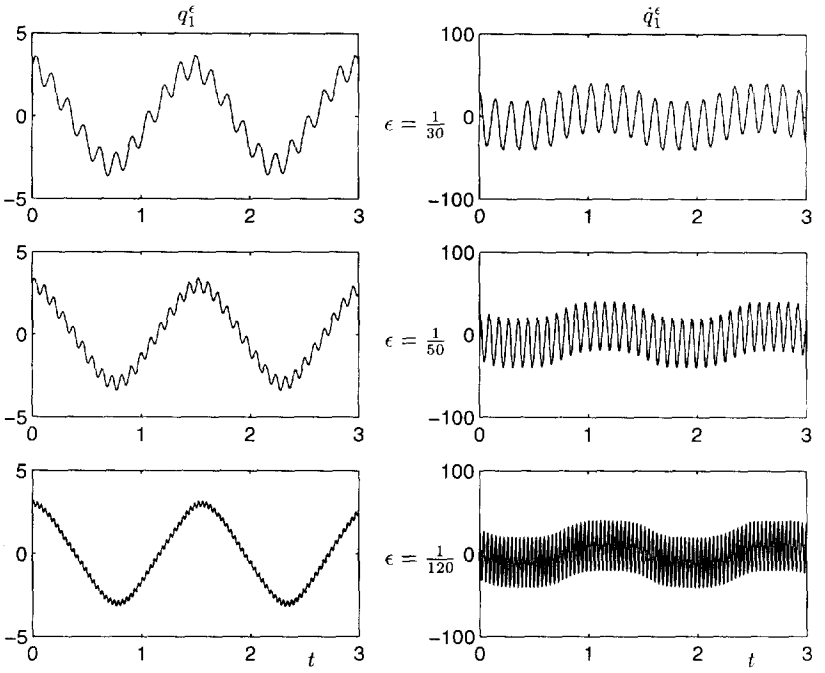

Figure 1: Illustration of the convergence with $\epsilon \to 0$ for the system (3.1) in the two-dimensional collinear case with $V(q) = q_1^4$ and $U(q) = (q_2 - q_1)^2/2$: on the left hand side the first component q_1^ϵ of the solution versus time for ϵ decreasing from top to bottom ($\epsilon = 1/30, 1/50, 1/120$), on the right hand side the corresponding derivatives $\dot{q}_1^\epsilon$ in the corresponding order. The total energy is identical in all three cases. Note that q_1^ϵ converges strongly to its running average while $\dot{q}_1^\epsilon$ converges only weakly.

3. LIMIT EQUATION FOR BOUNDED ENERGY

Let us now switch back to the derivation of the differential equation governing this limit solution q^0. To this end, we rewrite the equation of motion as the second order equation

$$\ddot{q}^\epsilon + F(q^\epsilon) + \frac{1}{\epsilon^2} G(q^\epsilon) = 0, \tag{3.1}$$

with forces $F(q) = M^{-1} \operatorname{grad} V(q)$ and $G(q) = M^{-1} \operatorname{grad} U(q)$. For the sake of notational simplicity we set $M = I$ throughout, which corresponds to a simple redefinition of the potentials V and U. Now, for an unique determination of the sequence of solutions q^ϵ we need the initial values

$$q^\epsilon(0) = q_0^\epsilon \quad \text{and} \quad \dot{q}^\epsilon(0) = \dot{q}_0^\epsilon,$$

which, moreover, determine the sequence of total energies corresponding to q^ϵ:

$$E^\epsilon = \frac{1}{2}|\dot{q}_0^\epsilon|^2 + V(q_0^\epsilon) + \frac{1}{\epsilon^2}U(q_0^\epsilon).$$

For the case that E^ϵ is a constant sequence, Figure 1 demonstrates that the momenta $\dot{q}^\epsilon$ *converge only weakly*, because they oscillate with constant amplitude but period $\mathcal{O}(\epsilon)$ around their running average. This observation can be generalized as the following lemma states:

LEMMA 3.1 *Let the sequence (E^ϵ) of total energies be bounded, i.e., there is a bound $C > 0$ such that $|E^\epsilon| < C$ for all $\epsilon > 0$, then the following three assertions hold (up to a possible extraction of subsequences):*

1. *q^ϵ converges strongly in C^0: $q^\epsilon \to q^0$.*
2. *$\dot{q}^\epsilon$ converges weakly in L^∞: $\dot{q}^\epsilon \overset{*}{\rightharpoonup} \dot{q}^0$.*
3. *$\ddot{q}^\epsilon = \mathcal{O}(\epsilon^{-1})$ converges in the sense of distributions: $\ddot{q}^\epsilon \overset{\mathcal{D}'}{\rightharpoonup} \ddot{q}^0$.*

A proof for this statement may be found in [1]. Therein, one can also find an example which shows that for unbounded (E^ϵ) even q^ϵ does in general not converge strongly but only weakly.

For the following we remain with the case of bounded energy. We also restrict ourselves to potentials U which are strictly convex in directions orthogonal to the manifold $\mathcal{M}$ of its equilibrium positions with $U|_{\mathcal{M}} = 0$ and $\operatorname{grad} U|_{\mathcal{M}} = 0$. This is the typical case for the stiff bond potentials in MD.

By multiplying (3.1) with ϵ^2 and using the convergences from Lemma 3.1 we directly get that $G(q^0) = 0$, i.e., that q^0 indeed lives on the constraints manifold

$$\mathcal{M} = \{q : \quad G(q) = \operatorname{grad} U(q) = 0\},$$

i.e., it is fixed to the equilibrium positions of the stiff potential U.

Now, the following notation will be useful: The orthogonal projection of a position q on $\mathcal{M}$ will be denoted with q_M. Each position q in a sufficiently small neighborhood of $\mathcal{M}$ can uniquely be written as the sum of its projection and the distance vector q_N normal to the manifold: $q = q_M + q_N$. We may assume that q^ϵ is in such a neighborhood, because its distance to $\mathcal{M}$ is of order $\mathcal{O}(\epsilon)$.

We are interested in an equation for the motion of q^0 on $\mathcal{M}$. Therefore, let us now investigate the consequences of the different types of convergence in (3.1) directly:

$$\underbrace{\ddot{q}^\epsilon}_{\overset{\mathcal{D}'}{\to}\ddot{q}^0} + \underbrace{F(q^\epsilon)}_{\to F(q^0)} + \underbrace{\frac{1}{\epsilon^2}G(q^\epsilon)}_{\overset{\mathcal{D}'}{\to}\mathcal{D}'\text{-}\lim_{\epsilon\to 0} G(q^\epsilon)/\epsilon^2} = 0. \tag{3.2}$$

In order to compute the desired $\mathcal{D}'$-limit of $G(q^\epsilon)/\epsilon^2$ one can use Taylor expansion of $G(q^\epsilon)$ around the projection q_M^ϵ of q^ϵ on $\mathcal{M}$. A careful treatment of the different convergences (strong, weak*, weak in $\mathcal{D}'$) in this expansion leads to the following theorem, which is proved in our paper [1].

THEOREM 3.2 *For the case of bounded energy the limit average q^0 fulfills*

$$\begin{aligned} \ddot{q}^0 + F(q^0) + \operatorname{grad} G(q^0)^T \cdot \lambda + \tfrac{1}{2} D^2 G(q^0) : \Sigma &= 0 \\ G(q^0) &= 0, \end{aligned} \tag{3.3}$$

where $\eta^\epsilon/\epsilon \overset{\mathcal{D}'}{\rightharpoonup} \lambda$ and $\eta^\epsilon \otimes \eta^\epsilon \overset{*}{\rightharpoonup} \Sigma$ with the quantity $\eta^\epsilon = (q^\epsilon - q_M^\epsilon)/\epsilon \overset{*}{\rightharpoonup} 0$. D^2 denotes the second derivative with respect to q.

In this result, only the correction term $D^2G : \Sigma/2$ is surprising. If it is not there, equation (3.3) describes a system in which the fast degrees of freedom normal to $\mathcal{M}$ are *frozen* and the fast oscillations on scale $\mathcal{O}(\epsilon)$ are loosing any impact on the motion in the limit $\epsilon \to 0$. But *in general*, this is not the case. Although we have $\eta^\epsilon \overset{*}{\rightharpoonup} 0$ it is $\Sigma \neq 0$ in general because squaring a function is *not* a weak*-continuous operation as we have already observed above. Unfortunately, λ and Σ are not directly known and it may be that $D^2G : \Sigma$ vanishes in certain cases, e.g., if G is linear or gives only a correction of the Lagrange parameter λ (cf. below).

In order to compute the correction $D^2G : \Sigma$ we have to construct an explicit formula for Σ. This is done in the next section.

4. AN EXPLICIT FORMULA FOR THE CORRECTING POTENTIAL

We will now see that we can compute Σ from the total energy of the fast *oscillations normal* to $\mathcal{M}$. At first, let us restrict the discussion to the case in which $\mathcal{M}$ is of codimension one. In a neighborhood of q^ϵ_M the stiff potential U is harmonic with "spring constant"

$$\omega^2(q) \;=\; D^2_N U(q), \qquad q \in \mathcal{M}, \tag{4.1}$$

where D_N denotes the derivation normal to $\mathcal{M}$. $D^2_N U$ is a positive scalar value because $\mathcal{M}$ is of codimension 1 and U is assumed to be strictly convex in normal direction to $\mathcal{M}$. Thus, ω is a positive scalar function on $\mathcal{M}$. Since $q^\epsilon - q^\epsilon_M = \mathcal{O}(\epsilon)$, one intuitively assumes that the normal oscillation of q^ϵ is nearly harmonic with this frequency $\omega(q^\epsilon_M)$.

Thus, the *normal energy* corresponding to a state $(q, \dot q)$ may be defined as

$$E_N(q,\dot q) \;=\; \underbrace{\frac{1}{2}\,|\dot q_N|^2}_{=T_N} + \underbrace{\frac{1}{2}\,\omega^2\left(q_M(t)\right)\; q_N^2}_{=U_N}. \tag{4.2}$$

Since $q^\epsilon_N = \mathcal{O}(\epsilon)$, the total energy splits as

$$E^\epsilon \;=\; \frac{1}{2}|\dot q^\epsilon|^2 \;+\; V(q^\epsilon_M) + E^\epsilon_N + \mathcal{O}(\epsilon).$$

Hence, in the limit we have

$$E^0 \;=\; \frac{1}{2}|\dot q^0|^2 \;+\; V(q^0_M) \;+\; E^0_N$$

i.e., the limit E^0_N of the normal energy occurs as a correction of the soft potential V in the limit of the total energy. In order to construct an explicit limit equation we still have to find two missing links:

1. We need the relation of E^0_N to the correction term $D^2G : \Sigma$, i.e., to the normal part Σ_{NN} of Σ. Because of the strong convergence $q^\epsilon_M \to q^0$ we easily compute

$$U^\epsilon_N \;=\; \frac{1}{2}\,\omega^2\left(q^\epsilon_M(t)\right)\;(q^\epsilon_N)^2 \;\overset{*}{\rightharpoonup}\; \frac{1}{2}\,\omega^2(q^0)\,\Sigma_{NN}. \tag{4.3}$$

   Moreover, It turns out that, in the limit $\epsilon \to 0$, E^0_N is *equipartioned* into its kinetic and its potential part, i.e., $T^0_N = U^0_N = E^0_N/2$ (cf. [1] for details). This equipartition is a well known fact for the *time averages* of these energy parts for harmonic oscillations and is connected to the so called *Virial Theorem* of Statistical Mechanics, a *mathematical* result which has the appearance of an ergodic theorem, but no ergodicity is assumed, cf. [4]. Together with (4.3), the equipartition gives the desired equation:

$$E^0_N \;=\; \omega^2(q^0)\,\Sigma_{NN}. \tag{4.4}$$

2. We also need a formula for E_N^0 allowing an explicit computation of its value as a function of $q^0 \in \mathcal{M}$. This formula is given by the observation that $E_N^0/\omega(q^0)$ is *an adiabatic invariant* in the limit $\epsilon \to 0$. A proof for this statement can again be found in [1]. It results from inserting the abstract limit equation (3.3) from Theroem 3.2 in the expression for the first time derivative of E_N^0 and using (4.4).

Conclusively, we find (cf. [1], Theorem 4.4):

THEOREM 4.1 *The sequence* $E_N^\epsilon = E_N(q^\epsilon, \dot{q}^\epsilon)$ *converges strongly,* $E_N^\epsilon \to E_N^0$. *The magnitude* $E_N^0/\omega(q^0)$ *is an* adiabatic invariant *of the motion in the limit* $\epsilon \to 0$, *i.e., it exists a constant* $\Theta \in \mathbf{R}$ *such that*

$$E_N^0 = \Theta\,\omega(q^0), \qquad \Sigma_{NN} = \frac{\Theta}{\omega(q^0)}. \tag{4.5}$$

This constant Θ *can uniquely be determined via the initial positions* $q_0^0 = \lim_{\epsilon\to 0} q_0^\epsilon$ *of the limit average* q^0 *in* $t = 0$,

$$\Theta = E_N^0(0)/\omega(q_0^0). \tag{4.6}$$

The limit average q^0 *obeys the following* constrained Hamiltonian system

$$\begin{aligned} \ddot{q}^0 + \operatorname{grad}(V+W)(q^0) + D^2U(q^0)\cdot\lambda &= 0 \\ \operatorname{grad} U(q^0) &= 0, \end{aligned} \tag{4.7}$$

in which the correcting potential W *is given by the limit of the normal energy*

$$W(q) = \Theta\,\omega(q)$$

for $q \in \mathcal{M}$.

Now we can directly see in which cases the correction will vanish: The initial conditions may lead to a constant $\Theta = 0$ (vanishing normal energy), or ω may be constant on $\mathcal{M}$ (constant gully width). The first case is given if $E_N^\epsilon \to 0$. It can be shown that then we have $q_N^\epsilon = \mathcal{O}(\epsilon^2)$ and $\Sigma = 0$, cf. [5]. The second case is the case of the so–called Arnold-theorem [6][7] with

$$D_N^2 U\Big|_{\mathcal{M}} = \text{const.}$$

Using the general result of Theorem 3.2, we have shown in [1] that the correction does not contribute in *precisely* these two cases — *independently* of the codimension of $\mathcal{M}$.

Typical MD–applications do not belong to one of these cases, i.e., we have to expect a nonvanishing correcting potential. It was mistakenly argued in the literature [8] that the potential correction is given by the well–known FIXMAN–potential. An illustrative test example for the correcting potential W effected by stiff bond angle potentials and the comparison with the FIXMAN–potential can be found in [9].

5. APPLICATION TO MOLECULAR DYNAMICS

Let us now switch to the general case in which $\mathcal{M}$ is of codimension $r > 1$. We restrict ourselves to a short review of the results of TAKENS. He calls the Hessian matrix D_N^2U of the stiff potential in the normal directions of $\mathcal{M}$ *diagonizable*, if there is a field $(e_N^1, \ldots, e_N^r)$ of orthonormal bases of $N\mathcal{M}$, which are eigenvectors of D_N^2U, i.e.,

$$D_N^2U(q) : (e_N^i(q) \otimes e_N^j(q)) = \omega_i^2(q)\cdot\delta_{ij} \qquad \forall q \in \mathcal{M}. \tag{5.1}$$

Here, the eigenfrequencies ω_i shall depend *smoothly* on $q \in \mathcal{M}$. TAKENS proves ([3, Theorem 1]) that the adiabatic invariance of the ratio of normal energy and frequency holds for each normal component, if one can exclude certain *resonances*, i.e., if for $x \in \mathcal{M}$ we always have

$$\omega_i(x) \neq \omega_j(x) \qquad 1 \leq i, j \leq r,\ i \neq j, \tag{5.2}$$

and

$$\omega_i(x) \neq \omega_j(x) + \omega_k(x), \qquad 1 \leq i, j, k \leq r.$$

Using this result, we can extend Theorem 4.1 to these "no–resonance" cases.

But TAKENS [3, Theorem 3] also constructed an example with $r = 2$, where a one-parameter family of initial data $q^\epsilon(0;\mu)$, $\dot{q}^\epsilon(0;\mu)$, depending on $\mu \in [0,1]$ but with μ–independent Θ_i, yields an one-parameter family of limit solutions $q^0(t;\mu)$ having the following property: There is a time $t_* > 0$ at which the no–resonance conditions are hurt for the first time. For $0 \leq t \leq t_*$ the solutions

$$q^0(t;\mu) = q^0(t)$$

do not depend on the parameter μ, as Theorem 4.1 states. But for fixed $t > t_*$ the values of $q^0(t;\mu)$, $\mu \in [0,1]$, constitute a *continuum*. Thus, for time spans larger than t_* and for a fixed parameter μ we cannot describe the limit q^0 by a uniquely solvable initial value problem. KOILLER [10] coined the notion "Takens-chaos" for this effect.

In general, this effect will occur in smoothed MD as can be illustrated in one of the most simple realistic examples, the lumped butan molecule. The model for the butan molecule ($CH_3CH_2CH_2CH_3$) consists of four mass points (the four "units" CH_k, $k = 2, 3$) with the corresponding positions $q_i \in \mathbf{R}^3$ and momenta $p_i \in \mathbf{R}^3$, $i = 1, \ldots, 4$. Thus, the state space has dimension 24 and the position and momenta states are

$$q = (q_1, \ldots, q_4) \in \mathbf{R}^{12} \quad \text{and} \quad p = (p_1, \ldots, p_4) \in \mathbf{R}^{12}.$$

The stiff part of the interaction potential $\mathcal{V}$ is given by bond stretching and bond angle contributions

$$U(q)/\epsilon^2 = \sum_{k=1}^{3} U_{st}(q_k, q_{k+1}) + U_{an}(q_1, q_2, q_3) + U_{an}(q_2, q_3, q_4)$$

Therein, the three bonds are modelled as 3d–springs with forces only depending on the deviation from the equilibrium length

$$U_{st}(x, y) = \frac{\alpha}{2}\left(|x - y| - r_0\right)^2,$$

while the bond–angle interactions are "quasi–harmonically" given by the angle $\phi(x, y, z)$ between the two bonds connecting x with y, and y with z:

$$U_{an}(x, y, z) = \frac{\beta}{2}(\cos\phi(x, y, z) - \cos\phi_0)^2 \quad \text{with} \quad \cos\phi(x, y, z) = \frac{(x - y)^T(z - y)}{|x - y|\,|z - y|}.$$

The soft part V of $\mathcal{V}$ is the so–called *torsion angle potential*

$$V(q) = V_{tor}(q) = V_{tor}(\theta(q)).$$

The torsion angle $\theta = \theta(q)$ is the angle between the two 2d–planes which are spanned by q_1, q_2, q_3 and q_2, q_3, q_4, respectively. The torsion angle potential V_{tor} has more than one equilibrium angle but three local minima (cf. Figure 2). Herein, the coefficients $\alpha = 83.7$ kcal/(mol Å^2) and $\beta = 43.1$ kcal/mol and the potential V_{tor} are taken from [11]. The mass matrix M is given by the masses of

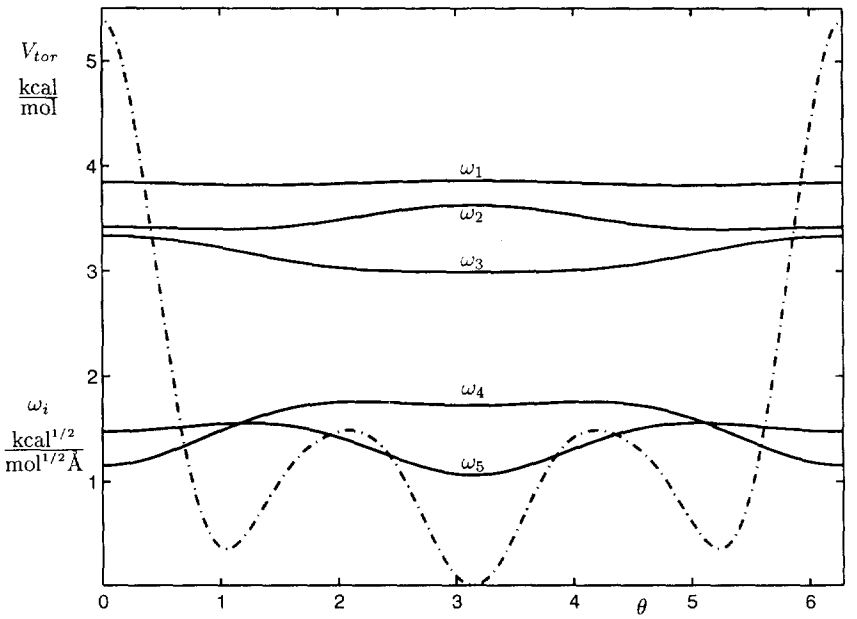

Figure 2: Dashed line: Torsion angle potential V_{tor} versus torsion angle θ. Note that the potential is symmetric with respect to the main minimum located at $\theta = \pi$ with two equal local minima near $\theta = \pi/3, 5\pi/3$. Solid lines: Frequencies ω_i of the fast oscillations normal to $\mathcal{M}$ versus the torsion angle θ. Note the crossings of the two lowest frequencies near the local minima of V_{tor}. They are connected to resonances of the fast oscillations.

CH_3 ($m_1 = m_4 = 15\mu$) and CH_2 ($m_2 = m_3 = 14\mu$), where μ is the atomic mass unit $\mu = 1.67 \cdot 10^{-27}$ kg.

Note, that the stiff potential U can be rewritten as

$$U(q) = \frac{1}{2}|\psi(q)|^2 = \sum_{k=1}^{5} \psi_k(q)^2$$

with $\psi = (\psi_1, \ldots, \psi_5)$ where the ψ_k denote the different contributions from U_{st} and U_{an} scaled with ϵ^2. Thus, the manifold $\mathcal{M}$ of equilibrium positions of U has codimension $r = 5$. Some simple calculus shows, that the condition (5.1) for computing the frequencies ω_i of the fast normal oscillations results in the eigenvalue problem for the 5×5 *Gram matrix* G:

$$\underbrace{\operatorname{grad}\psi^T \, M^{-1} \operatorname{grad}\psi}_{=G} \, \lambda = \omega^2 \lambda,$$

where $\operatorname{grad}\psi^T$ denotes the 5×12 Jacobian matrix of ψ. The corresponding eigenvectors λ of G allow the evaluations of the constants Θ_i for the correcting potential

$$W(q) = \sum_{i=1}^{5} \Theta_i \, \omega_i(q).$$

A direct evaluation of G shows that it depends on q only via the torsion angle θ: $G(q) = G(\theta(q))$. Thus, the frequencies ω_i may be given as functions of θ which is done in Figure 2. We observe that

TAKENS' "no–resonance" condition (5.2) is hurt for two values of the torsion angle. Thus, for certain initial conditions, i.e., in general, this butan model will develop TAKENS–chaos. In particular cases, i.e., for initial data for which the constants Θ_i for the two lower frequencies ω_1 and ω_2 are zero, there is no TAKENS–chaos and our Theorem 4.1 governs the limit solution.

For one of these cases ($\Theta_i = 0$ for all $i \neq 4$) the corresponding correcting potential W is shown in Figure 3. Herein, the initial data has been chosen so that only $\Theta_4 \neq 0$ corresponding to the normal energy $E_N = 3.5$ kcal/mol which is half of the average kinetic energy of a butan molecule in a gas at temperature $T = 300$K collected in this single degree of freedom. Note, that in this case the correcting potential leads to an inversion of the importance of the local minima.

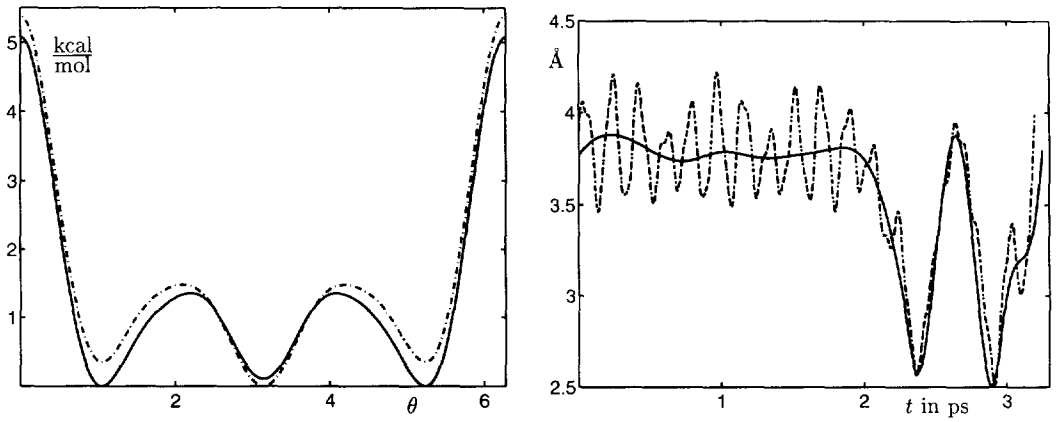

Figure 3: Left hand side: Torsion angle potential V_{tor} (dashed line) and the corrected potential $V_{tor} + W$ for the scenario explained in the text (solid line) in kcal/mol versus the torsion angle θ. In the corrected potential the minimum at $\theta = \pi$ is no longer the global minimum. Right hand side: Evolution of the distance $|q_1 - q_4|$ with t for the original MD–solution (dashed line) and for the limit solution (solid line) for the scenario explained in the text.

For corresponding initial data the right hand subfigure in Figure 3 illustrates the original and limit solutions. Obviously, in this case, the limit solution is a good approximation of the running average of the original solution up to the time shown in the figure. For larger times the two solutions increasingly deviate from each other. This must be expected because, for values $\epsilon > 0$, the spectral gap between fast and slow motions is finite and introduces a direct coupling of both kinds of motion which effects the adiabaticity of E_N/ω to be valid only *approximately*. The *time steps* in a numerical integration of the limit solution can be a *factor 8 larger* than those used for integrating the original solution (comparable accuracy). Thus, the corresponding computational effort is smaller, but unfortunately, only by a factor of 2, because of the repeated diagonalizations of the Gram matrix G.

For initial data with $\Theta_1 \neq 0$ or $\Theta_2 \neq 0$ (resonant cases) the limit solution again is a good approximation of the running average but only as long as the system remains inside the potential well of the main minimum of V_{tor} at $\theta = \pi$. The deviation increases if the system switches to one of the local minima of V_{tor} and significantly before the crossing of ω_1 and ω_2 is reached.

6. CONCLUSIVE REMARKS

We discussed the limit $\epsilon \to 0$ for the Hamiltonian system (1.2) and its usefulness for applications to MD. In addition to the construction of the explicit limit equation away from resonance points

and the observation that these points can effect a non–uniqueness called TAKENS–chaos, two main results were collected:

1. Even if the limit solution is determined uniquely, it is a good approximation for the running average of MD–solutions for a relatively short time span only. This is due to the fact that for realistic MD–applications the resulting ϵ is not small enough. For the same reason the oscillations on scale $\mathcal{O}(\epsilon)$ are not fast enough in order to effect a significant gain in efficiency if their evaluation is avoided by solving the limit equation.

2. The observation of TAKENS–chaos means that *in general the homogenization problem is not solvable.* The present authors assume that the corresponding problem of the resonances of the fast degrees of freedom will be the bottleneck for *any* mathematical approach to the running average, even for $\epsilon > 0$, because any "averaging" or "smoothing" technique must skip some of the information about the phases of fast motions. But exactly this "phase information" is *necessary* for an accurate description of the resonant scenario.

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