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On the Rate of Convergence to Equilibrium of the Andersen Thermostat in Molecular Dynamics

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Abstract It has been shown in E and Li (Comm. Pure. Appl. Math., 2007, in press) that the Andersen dynamics is uniformly ergodic. Exponential convergence to the invariant measure is established with an error bound of the form

$$const \cdot \exp\left(-const \cdot \kappa(\nu)\nu^{2N} t\right),$$

where N is the number of particles, ν is the collision frequency and $\kappa(\nu) \to const$ as $\nu \to 0$. In this article we study the dependence on ν of the rate of convergence to equilibrium. In the one dimension and one particle case, we improve the error bound to be

$$const \cdot \exp\left(-const \cdot \kappa(\nu)\nu t\right).$$

In the d-dimension N-particle free-streaming case, it is proved that the optimal error bound is

$$const \cdot \exp\left(-const \cdot \frac{\nu}{N} t\right).$$

It is also shown that as $\nu \to \infty$, on the diffusive time scale, the Andersen dynamics converges to a Smoluchowski equation.

1 Introduction

We are interested in the rate of convergence to equilibrium of the Andersen thermostat, which is a commonly used algorithm in constant temperature molecular dynamics (CTMD) [7] simulations. For molecular systems, CTMD is used to calculate the canonical ensemble average of an observable A, i.e.,

$$\langle A \rangle_{ens} = \frac{1}{\mathcal{Z}} \int A(\mathbf{q}, \mathbf{p}) e^{-\beta H(\mathbf{q},\mathbf{p})} d\mathbf{p} d\mathbf{q}, \tag{1.1}$$

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where $\mathcal{Z}$ is the partition function, $H(q, p) = \sum_{i=1}^{N} \frac{|\mathbf{p}_i|^2}{2m} + \Phi(\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_N)$ and Φ is the potential energy. The integral (1.1) is a very high dimensional integral and direct numerical quadrature is not suitable for this problem [7]. CTMD computes (1.1) by looking for a process $X(t) = (\mathbf{p}(t), \mathbf{q}(t))$ such that $X(t)$ is ergodic with respect to the canonical measure. By ergodicity one can replace $\langle A \rangle_{ens}$ by a time average over the trajectory $X(t)$,

$$\langle A \rangle_{ens} = \langle A \rangle_{time} = \lim_{T\to\infty} \frac{1}{T} \int_0^T A(X(t))dt,$$

which is more computationally affordable. In CTMD there are many methods for designing the process $X(t)$. Some are deterministic in nature, such as the Berendsen thermostat [3] (also called velocity scaling), the Nosé-Hoover thermostat [9, 10, 18, 19], the Nosé-Hoover Chains thermostat [15], the Nosé-Poincaré thermostat [2] and Recursive Multiple Thermostat methods [12]. However the ergodicity of these deterministic methods is a major open problem [4, 7, 11, 25, 26]. The situation is better with the class of "stochastically perturbed" thermostats [4] including the Andersen thermostat [1], the Langevin thermostat [8], and the Dissipative Particle Dynamics thermostat [17, 23]. The ergodicity of these methods can be analyzed using standard stochastic analysis [6, 14, 16, 22, 24, 27]. We refer to [4] for a review and comparison of some of these methods and other sampling schemes.

In [1], Andersen introduced what is now called the Andersen thermostat to produce a canonical ensemble at any given fixed finite temperature. To recapture his idea, let us consider a d-dimensional system of N particles with inter-atomic potential $\Phi = \Phi(\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_N)$. Throughout this paper we shall assume for simplicity that Φ is infinitely differentiable although this assumption could be considerably relaxed in a number of places. At the end of exponentially distributed time intervals, we randomly select one particle from the system and let it collide with the heat bath. The effect of the collision is such that the chosen particle "forgets" its old velocity and picks its new velocity from a Maxwell-Boltzmann distribution defined by

$$g(\mathbf{v})d\mathbf{v} = \frac{1}{(2\pi)^{d/2}} \exp\left(-\frac{|\mathbf{v}|^2}{2}\right) d\mathbf{v}. \tag{1.2}$$

For simplicity let us choose a unit such that the temperature and mass is normalized to 1. Between the stochastic collisions the system still evolve according to the following Hamiltonian dynamics:

$$\begin{cases} \dot{\mathbf{q}}_i = \mathbf{v}_i \\ \dot{\mathbf{v}}_i = -\nabla_{\mathbf{q}_i} \Phi \quad i = 1, \dots, N. \end{cases} \tag{1.3}$$

It is clear that such a randomized Hamiltonian dynamics has the Gibbs distribution

$$\pi(d\mathbf{q}, d\mathbf{v}) := \frac{1}{Z} \exp\left\{-\left(\Phi(\mathbf{q}) + \frac{|\mathbf{v}|^2}{2}\right)\right\} d\mathbf{q} d\mathbf{v} \tag{1.4}$$

as an invariant measure since it is preserved by both the Hamiltonian dynamics and the stochastic collisions. A fundamental question is whether the Gibbs distribution is the only invariant distribution and if so what is the rate of convergence to equilibrium. In [6] we rigorously formulated the Andersen dynamics and showed that it is uniformly ergodic. More precisely, denote by $P_{\mathbf{x}}^t$ the Markov transition semigroup of the N-particle Andersen dynamics, we have

$$\|P_{\mathbf{x}}^t - \pi\|_{TV} \le const \cdot \exp(-const \cdot \kappa(\nu) \cdot \nu^{2N} t),$$

where ν is the collision frequency, $0 < \kappa(\nu) < \infty$ and $\kappa(\nu) \to const$ as $\nu \to 0$. Although such an error bound is quite satisfactory, we want to point out that it is not clear whether that the ν^{2N}-dependence in the exponent is sharp. Such a question is of importance since in molecular dynamics simulations one would like to know what criteria should be used to find an optimal collision frequency ν to achieve fast convergence to equilibrium. It is the purpose of this paper to give a partial answer to this question. In the one-dimensional one particle(with potential) case, we shall show that

$$\| P_x^t - \pi \|_{TV} \le const \cdot \exp\left(-const \cdot \kappa(\nu) \cdot \nu t\right).$$

In the *d-dimensional* N-particle free streaming case (the potential $\Phi = const$), we give a complete answer to this question. By Fourier methods we established a bound of the following form:

$$\| P_{\mathbf{x}}^t - \pi \|_{TV} \le const \cdot \exp\left(-const \cdot \frac{\nu}{N} t\right)$$

where N is the number of particles. We also study the limit of the Andersen dynamics as $\nu \to \infty$. We show that on the diffusive time scale, the Andersen dynamics converges to a Smoluchowski equation.

This paper is organized as follows. In Sects. 2 and 3 we recall the definition of continuous time and discrete time Andersen dynamics and give some elementary facts. In Sect. 4 we give the proof of exponential convergence to equilibrium in the one dimensional one particle continuous time case. A regularity result is also proved there. Similar results are proved for the discrete time case in Sect. 5. We establish more refined results for the free-streaming case in Sect. 6. In Sect. 7 we prove the diffusive limit of the Andersen dynamics. Some concluding remarks are given in Sect. 8.

2 Continuous Time Andersen Dynamics

Let us recall [6] the definition of d-dimensional N-particle Andersen dynamics. Let $\mathbb{D} = \mathbb{R}^{dN}/\mathbb{Z}^{dN}$ be the torus in $\mathbb{R}^{dN}$. We shall take $\mathbb{D}$ to be the configuration space and define $\Gamma = \mathbb{D} \otimes \mathbb{R}^{dN}$ as the phase space. For convenience let us first define the Andersen substitution operator.

Definition 2.1 (Andersen Substitution Operator) Let i be an integer between 1 and N. Let $\mathbf{u} \in \mathbb{R}^d$ and $\mathbf{x} = (\mathbf{q}_1, \ldots, \mathbf{q}_N, \mathbf{v}_1, \ldots, \mathbf{v}_N) \in \Gamma$. Then the Andersen substitution operator $\mathcal{S}(i, \mathbf{u}) : \mathbb{R}^{dN} \to \mathbb{R}^{dN}$ is defined as:

$$\mathcal{S}(i, \mathbf{u})\mathbf{x} := (\mathbf{q}_1, \ldots, \mathbf{q}_N, \mathbf{v}_1, \ldots, \mathbf{v}_{i-1}, \mathbf{u}, \mathbf{v}_{i+1}, \ldots, \mathbf{v}_N).$$

With these notations, the continuous time d-dimensional N-particle Andersen dynamics is defined as a Markov process on Γ.

Definition 2.2 (Continuous Time Andersen Process) Suppose on a probability space $(\Omega, \mathcal{F}, \mathbf{P})$, $\{T_n\}_1^\infty$ are i.i.d. random variables which are exponentially distributed with mean $1/\nu$ ($\nu > 0$); $\{Y_n\}_1^\infty$ are i.i.d. random variables such that $P(Y_n = j) = 1/N$ for any integer j between 1 and N; $\{Z_n\}_1^\infty$ are i.i.d. random variables in $\mathbb{R}^d$ which obey a common Maxwell-Boltzmann distribution (1.2). Let N_t denote the Poisson counting process generated by $\{T_n\}$, then the continuous time Andersen dynamics starting at a point $\mathbf{x} \in \Gamma$ is defined as:

$$\begin{cases} X_t := \mathcal{H}(t - \sum_{n=1}^{N_t} T_n)[\prod_{n=1}^{N_t} \mathcal{S}(Y_n, Z_n)\mathcal{H}(T_n)]\mathbf{x}, \quad t > 0, \\ X_0 = \mathbf{x}, \end{cases} \tag{2.1}$$

where $\mathcal{H}(\cdot)$ is the Hamiltonian flow operator associated with (1.3) and X_t is related to the starting point $\mathbf{x}$ by applying successively a cascade of operators. Here for a sequence of operators $\mathcal{A}_n$, $\prod_1^N \mathcal{A}_n$ is defined as the backward product, i.e.

$$\prod_{n=1}^{N} \mathcal{A}_n = \mathcal{A}_N \mathcal{A}_{N-1} \cdots \mathcal{A}_1.$$

It is immediately obvious that the Andersen process has right-continuous sample trajectories and therefore its invariant distribution can be found by computing the infinitesimal generator associated with the process. To write down an explicit form of the infinitesimal generator, we first introduce the notion of Andersen collision operator:

Definition 2.3 Let $\mathbf{q} = (\mathbf{q}_1, \mathbf{q}_2, \ldots, \mathbf{q}_N)$, $\mathbf{v} = (\mathbf{v}_1, \mathbf{v}_2, \ldots, \mathbf{v}_N)$, $\mathbf{x} = (\mathbf{q}, \mathbf{v})$ and let $g(\cdot)$ be the probability density function of the aforementioned Maxwell-Boltzmann distribution (1.2), then the Andersen collision operator $\mathcal{A}$ is defined as:

$$(\mathcal{A}f)(\mathbf{x}) := \frac{1}{N}\sum_{i=1}^{N} \mathcal{A}_i f := \frac{1}{N}\sum_{i=1}^{N} g(\mathbf{v}_i) \int_{\mathbb{R}^d} f(\mathcal{S}(i, \mathbf{u})\mathbf{x}) d\mathbf{u}. \tag{2.2}$$

The adjoint $\mathcal{A}^*$ of the Andersen collision operator is given by

$$(\mathcal{A}^* f)(\mathbf{x}) := \frac{1}{N}\sum_{i=1}^{N} \int_{\mathbb{R}^d} f(\mathcal{S}(i, \mathbf{u})\mathbf{x}) g(\mathbf{u}) d\mathbf{u}.$$

The infinitesimal generator $\mathcal{G}$ of the Andersen process can be computed and is given by:

$$\mathcal{G} := \nu(\mathcal{A}^* - \mathcal{I}) + i\mathcal{L}$$

where $\mathcal{I}$ is the identity operator and the Liouville operator $i\mathcal{L}$ is defined as:

$$(i\mathcal{L}f)(\mathbf{q}, \mathbf{v}) := \mathbf{v} \cdot \nabla_{\mathbf{q}} f - \nabla_{\mathbf{q}} \Phi \cdot \nabla_{\mathbf{v}} f.$$

Let us recall the following definition of invariant measure.

Definition 2.4 (Definition of Invariant Measure) Suppose $(X, \mathcal{B})$ is a measurable space and $T : X \to X$ is a measurable transformation. A measure μ is said to be an invariant (probability) measure for T if $\mu(B) = \mu(T^{-1}B)$ for any $B \in \mathcal{B}$.

Suppose μ is an invariant measure of the Andersen process, then it has to satisfy:

$$\mathcal{G}^* \mu = 0$$

or in more explicit form:

$$[\nu(\mathcal{A} - \mathcal{I}) - i\mathcal{L}]\mu = 0.$$

It is not hard to verify that the Gibbs distribution (1.4) is a solution to the above equation. So immediately we have the following theorem:

Theorem 2.5 *The Gibbs distribution*

$$\pi(d\mathbf{q}, d\mathbf{v}) := \frac{1}{Z}\exp\left\{-\left(\Phi(\mathbf{q}) + \frac{|v|^2}{2}\right)\right\}d\mathbf{q}d\mathbf{v}$$

is an invariant measure of the continuous time Andersen dynamics (2.2).

3 Discrete Time Andersen Dynamics

The discrete time formulation of the Andersen process is given by the following random dynamical system:

Definition 3.1 Let $\{\alpha_n\}_{n=1}^{\infty}$ be i.i.d. random variables such that $\mathbb{P}(\alpha_n = 1) = \lambda = \nu\Delta t$ and $\mathbb{P}(\alpha_n = 0) = 1 - \lambda = 1 - \nu\Delta t$, retaining the same notion of Y_n and Z_n as before, the discrete Andersen dynamics is defined as:

$$\mathbf{x}_{n+1} = (1 - \alpha_n)\mathcal{H}(\Delta t)\mathbf{x}_n + \alpha_n\mathcal{S}(Y_n, Z_n)\mathcal{H}(\Delta t)\mathbf{x}_n. \tag{3.1}$$

It is straightforward to write down the evolution equation for the probability measures μ. Indeed, we have

$$\mu_{n+1} = (1 - \lambda)\mathcal{H}(-\Delta t)\mu_n + \lambda\mathcal{A}\mathcal{H}(-\Delta t)\mu_n. \tag{3.2}$$

To see how this is connected to the continuous case, let us note that any invariant measure μ has to satisfy:

$$\mu = (1 - \lambda)\mathcal{H}(-\Delta t)\mu + \lambda\mathcal{A}\mathcal{H}(-\Delta t)\mu$$

this is equivalent to:

$$\left(\frac{\mathcal{I} - e^{-i\mathcal{L}\Delta t}}{\Delta t}\right)\mu = \nu(\mathcal{A} - \mathcal{I})e^{-i\mathcal{L}\Delta t}\mu.$$

Now formally we can recover the continuous equation by letting Δt go to 0.

The following notation will be used in a number of places.

Definition 3.2 For $\mathbf{q} \in \mathbb{R}^{dN}$, denote by $\{\mathbf{q}\}$ the canonical projection of $\mathbf{q}$ into $\mathbb{D}$, i.e.

$$\mathbf{q} \equiv \{\mathbf{q}\}\text{mod }\mathbb{Z}^{dN}, \quad \text{where } \{\mathbf{q}\} \in \mathbb{D}.$$

Similarly we define $[\mathbf{q}] := \mathbf{q} - \{\mathbf{q}\} \in \mathbb{Z}^{dN}$.

Denote by M the set of Borel probability measures on Γ. To quantify the distance between probability measures, we introduce the following definition.

Definition 3.3 (Total Variational Norm) Let μ be a finite signed measure on $(\Gamma, \mathcal{B}(\Gamma))$, the total variational norm [13] of μ is defined by:

$$\|\mu\|_{TV} := \sup_{A\in\mathcal{B}(\Gamma)} |\mu(A)|.$$

If $\mu_1, \mu_2 \in M$ are absolutely continuous with respect to the Lebesgue measure on Γ, then we have,

$$\|\mu_1 - \mu_2\|_{TV} = \frac{1}{2}\int_\Gamma |\rho_1(\mathbf{x}) - \rho_2(\mathbf{x})| d\mathbf{x}$$

where $\rho_1 = \frac{d\mu_1}{d\mathbf{x}}$ and $\rho_2 = \frac{d\mu_2}{d\mathbf{x}}$ are the densities.

4 Proof of Exponential Convergence to Equilibrium: One-dimensional One-particle Case

Denote by $P^t_{x'}$ the transition semigroup of the continuous time Andersen dynamics, then $P^t_{x'}$ can be viewed as a mild solution to the following Duhamel equation:

$$P^t_{x'} = e^{-\nu t}\mathcal{H}^{-t}P^0_{x'} + \nu\int_0^t e^{\nu(s-t)}\mathcal{H}^{-(t-s)}\mathcal{A}P^s_{x'}ds.$$

We now state our main theorem.

Theorem 4.1 (Main Theorem) *There exists a constant $\nu_0 > 0$ such that for any $0 < \nu < \nu_0$ and for any $x' \in \Gamma$, $t > 0$, we have*

$$\|P^t_{x'} - \pi\|_{TV} \le c\exp(-\kappa\nu t)$$

where c is an absolute constant and κ is a constant depending possibly on Φ.

Before we give the proof of main theorem, we shall explain our strategy of proof. In [6] our method for proving convergence to equilibrium is to prove a Doeblin condition for $P^t_{x'}$ when t is sufficiently small. More precisely, there exists $t^* > 0$, a probability measure μ_{t^*} and a constant $0 < c < 1$, such that

$$P^{t^*}_{x'} \ge c\nu^2\mu_{t^*} \quad \text{for any } x' \in \Gamma.$$

This condition will imply the bound

$$\|P^t_{x'} - \pi\|_{TV} \le const \cdot \exp(-const \cdot \nu^2 t).$$

To improve the bound to $\exp(-const \cdot \nu t)$, let us observe that $P^t_{x'}$ has the following expansion:

$$\begin{aligned} P^t_{x'} &= e^{-\nu t}\mathcal{H}^{-t}P^0_{x'} + \nu\int_0^t e^{\nu(s-t)}\mathcal{H}^{-(t-s)}\mathcal{A}P^s_{x'}ds \\ &= e^{-\nu t}\mathcal{H}^{-t}\delta_{x'} + \nu e^{-\nu t}\int_0^t \mathcal{H}^{-(t-s)}\mathcal{A}\mathcal{H}^{-s}\delta_{x'}ds \\ &\quad + \nu^2 e^{-\nu t}\int_0^t\int_0^s \mathcal{H}^{-(t-s)}\mathcal{A}\mathcal{H}^{-(s-\tau)}\mathcal{A}\mathcal{H}^{-\tau}\delta_{x'}d\tau ds + \cdots. \end{aligned} \tag{4.1}$$

To get some insight it is helpful to analyze each term in the expansion more carefully. Consider for example the measure

$$\mathcal{H}^{-(t-s)}\mathcal{A}\mathcal{H}^{-(s-\tau)}\mathcal{A}\mathcal{H}^{-\tau}\delta_{x'}.$$

The essence of our method in [6] is to show that for $s-\tau$ small,

$$\mathcal{H}^{-(t-s)}\mathcal{A}\mathcal{H}^{-(s-\tau)}\mathcal{A}\mathcal{H}^{-\tau}\delta_{x'} = \epsilon(s-\tau)\mu + (1-\epsilon(s-\tau))\mu_{x'}$$

where $0<\epsilon(s-\tau)<1$ is some constant and the measure μ is independent of x'. It is then natural to ask what happens if $s-\tau$ is large. It turns out that for all $s-\tau \geq t^*$, we have

$$\mathcal{H}^{-(t-s)}\mathcal{A}\mathcal{H}^{-(s-\tau)}\mathcal{A}\mathcal{H}^{-\tau}\delta_{x'} = \epsilon(t^*)\mu + (1-\epsilon(t^*))\mu_{x'}.$$

A more precise statement of this result is given in Lemma 4.4 below. The intuitive interpretation of this result is that the spreading effect of the operator $\mathcal{A}\mathcal{H}^{-t}\mathcal{A}$ in configuration space cannot become worse with time! Analogously it is natural to expect that the n-th ($n \geq 3$) term in the expansion (4.1) can be decomposed into a x'-dependent and x'-independent part. One can then estimate the total variational norm of all the x'-dependent parts and prove that it converges exponentially fast to zero with an error bound of the form $const \cdot \exp(-const \cdot \nu t)$. Let us point out that such an idea is very much like a coupling idea in that one tries to rewrite the semigroup $P^t_{x'}$ into parts which are x'-independent and x'-dependent. Such a rewriting can be done in an iterative fashion and one can then estimate how fast the x'-dependent part decreases with time.

Let us begin by introducing some notations. In the one-dimensional one-particle case, for any $u \in \mathbb{R}$ and $\tilde{q} \in \mathbb{D} = [0,1)$, let us denote by $\varphi^t_u \tilde{q}$ the position of the particle at time t by evolving according to equation (1.3) with initial position $\tilde{q}$ and initial velocity u. Our goal is to show that

$$\mathcal{A}\mathcal{H}^{-t}\mathcal{A}\delta_{x'} \geq \epsilon(t^*)\mu \quad \forall t \geq t^*.$$

In the one-dimensional one-particle case, it is enough for us to show

$$\int \delta(\{q-\varphi^t_u\tilde{q}\})G(u)du \geq \epsilon(t^*)\mu^{unif}$$

where μ^{unif} is the uniform probability measure on $\mathbb{D}$. To illustrate the difficulties, let us observe

$$\int \delta(\{q-\varphi^t_u\tilde{q}\})G(u)du = \sum_{k\in\mathbb{Z}} \int \delta(q+k-\varphi^t_u\tilde{q})G(u)du$$
$$= \sum_{k\in\mathbb{Z}} G(u)\left|\frac{\partial \varphi^t_u\tilde{q}}{\partial u}\right|^{-1}_{u:\ \varphi^t_u\tilde{q}=q+k}.$$

For u satisfying $\varphi^t_u\tilde{q} = q+k$, we have

$$q+k = \varphi^t_u\tilde{q} = \tilde{q} + ut - \int_0^t\int_0^s \Phi'(\varphi^\tau_u\tilde{q})d\tau ds.$$

So that $u \approx O(\frac{k}{t})$ for k and t large. On the other hand, a simple Gronwall estimate of $|\frac{\partial\varphi^t_u\tilde{q}}{\partial u}|$ suggests that

$$\left|\frac{\partial \varphi^t_u\tilde{q}}{\partial u}\right| \leq const \cdot \exp(const \cdot t).$$

These two estimates gives us

$$\int \delta(\{q-\varphi_u^t\tilde{q}\})G(u)du = \sum_{k\in\mathbb{Z}} G(u)\left|\frac{\partial\varphi_u^t\tilde{q}}{\partial u}\right|^{-1}_{u:\ \varphi_u^t\tilde{q}=q+k}$$

$$\geq \sum_{k\in\mathbb{Z}} G\left(const\cdot\frac{k}{t}\right)const\cdot\exp(-const\cdot t).$$

It is obvious such a lower bound will go to zero as t approaches infinity. To resolve the above difficulty, we shall do a cut-off in the velocity space and get a better estimate of $|\frac{\partial\varphi_u^t\tilde{q}}{\partial u}|$. As we will see later, it is helpful to introduce the following notion of "crossing time".

Lemma 4.2 (Crossing Time Estimate) *Let $\tilde{q}\in\mathbb{D}$ be arbitrary but fixed. Let $\epsilon<1$ be a fixed positive constant. Let $A>0$ be sufficiently large such that for any $u>A$, we have*

$$(1-\epsilon)u \leq v(\varphi_u^t\tilde{q}) \leq (1+\epsilon)u \quad \forall t\geq 0.$$

Then the $(\tilde{q},u)$-crossing time is defined as

$$t_u^{\tilde{q}} := \inf\{t>0:\ \varphi_u^t\tilde{q}=\tilde{q}+1\}$$

we have that $t_u^{\tilde{q}}$ satisfies the following list of properties:

(1) $\frac{1}{(1+\epsilon)u}\leq t_u^{\tilde{q}}\leq\frac{1}{(1-\epsilon)u}$
(2) *For any integer* $0\leq j\leq\frac{t}{t_u^{\tilde{q}}}$,

$$\varphi_u^t\tilde{q} = \varphi_u^{t-jt_u^{\tilde{q}}}\tilde{q}+j$$

(3) *There exist positive constants c_1, c_2, depending only on the potential Φ, such that*

$$\left|\frac{\partial t_u^{\tilde{q}}}{\partial u}\right| \leq \frac{c_1}{(1-\epsilon)u}\exp\left(\frac{c_2}{(1-\epsilon)u}\right).$$

Proof Let $A:=\frac{2\|\Phi\|_\infty+1}{\epsilon}$. By energy conservation, we have

$$\Phi(\tilde{q})+\frac{u^2}{2} = \Phi(\varphi_u^t\tilde{q})+\frac{v(\varphi_u^t\tilde{q})^2}{2}.$$

It is immediate that for $u>A$, we have

$$(1-\epsilon)u \leq v(\varphi_u^t\tilde{q}) \leq (1+\epsilon)u \quad \forall t\geq 0.$$

Clearly $\forall t\geq 0$, we have

$$\tilde{q}+(1-\epsilon)ut \leq \varphi_u^t\tilde{q} \leq \tilde{q}+(1+\epsilon)ut.$$

From this it is easy to see that $t_u^{\tilde{q}}$ exists and satisfies

$$\frac{1}{(1+\epsilon)u} \leq t_u^{\tilde{q}} \leq \frac{1}{(1-\epsilon)u}.$$

The second property of $t_u^{\tilde{q}}$ is obvious by its definition. Let us now prove the differentiability of $t_u^{\tilde{q}}$ as a function of u. By definition of $t_u^{\tilde{q}}$ we have

$$\varphi_u^{t_u^{\tilde{q}}} \tilde{q} = \tilde{q} + 1$$

differentiating with respect to u on both sides gives us,

$$\left.\frac{\partial \varphi_u^\tau \tilde{q}}{\partial u}\right|_{\tau = t_u^{\tilde{q}}} + v(\varphi_u^{t_u^{\tilde{q}}} \tilde{q}) \frac{\partial t_u^{\tilde{q}}}{\partial u} = 0.$$

One immediately sees that

$$\frac{\partial t_u^{\tilde{q}}}{\partial u} = -\frac{1}{v(\varphi_u^{t_u^{\tilde{q}}} \tilde{q})} \left.\frac{\partial \varphi_u^\tau \tilde{q}}{\partial u}\right|_{\tau = t_u^{\tilde{q}}}.$$

To estimate $|\frac{\partial t_u^{\tilde{q}}}{\partial u}|$, let us observe that a simple Gronwall estimate gives us

$$\left|\frac{\partial \varphi_u^t \tilde{q}}{\partial u}\right| \leq c_1 \exp(c_2 t), \quad \forall t \geq 0$$

where c_1,c_2 are some constants depending only on the potential Φ. We then have

$$\begin{aligned}
\left|\frac{\partial t_u^{\tilde{q}}}{\partial u}\right| &\leq \frac{1}{v(\varphi_u^{t_u^{\tilde{q}}} \tilde{q})} \left|\frac{\partial \varphi_u^\tau \tilde{q}}{\partial u}\right|_{\tau = t_u^{\tilde{q}}} \\
&\leq \frac{1}{(1-\epsilon)u} \cdot c_1 \exp(c_2 |t_u^{\tilde{q}}|) \\
&\leq \frac{c_1}{(1-\epsilon)u} \exp\left(\frac{c_2}{(1-\epsilon)u}\right)
\end{aligned}$$

proving the lemma. □

The next lemma establishes a form of solvability which be needed later.

Lemma 4.3 (Existence of Solutions) *Let $t^* > 0$ be arbitrary but fixed. Let $A := \frac{2\|\Phi\|_\infty + 1}{\epsilon}$, where $\epsilon < 1$ is a positive number. Let $\beta_1 = (1+\epsilon)A + \frac{1}{t^*}$ and $\beta_2 > \beta_1$. Then for any integer k satisfying $\beta_1 t \leq k \leq \beta_2 t$, the equation in u*

$$\varphi_u^t \tilde{q} = q + k$$

has a solution $u = u_k$ which satisfies

$$A \leq u_k \leq \frac{1}{(1-\epsilon)t^*} + \frac{\beta_2}{1-\epsilon}. \tag{4.2}$$

Furthermore there exists a constant $c(\epsilon, \Phi, t^*, \beta_2)$ such that for $u = u_k$, we have

$$\left|\frac{\partial \varphi_u^t \tilde{q}}{\partial u}\right| \leq c(\epsilon, \Phi, t^*, \beta_2) t. \tag{4.3}$$

Proof From energy conservation, we have if $u \geq A$, then the following simple inequality holds

$$(1-\epsilon)u \leq v(\varphi_u^t \tilde{q}) \leq (1+\epsilon)u, \quad \forall t > 0. \tag{4.4}$$

Immediately we have for $u \geq A$,

$$\tilde{q} + (1-\epsilon)ut \leq \varphi_u^t \tilde{q} \leq \tilde{q} + (1+\epsilon)ut.$$

With this inequality the existence of solution is proved by an easy application of the intermediate value theorem. The estimate of $u = u_k$ (4.2) is obvious. The estimation (4.3) is not trivial. Let us begin by introducing "crossing time" defined for any $u \geq A$:

$$t_u^{\tilde{q}} := \inf\{t > 0 : \ \varphi_u^t \tilde{q} = \tilde{q} + 1\}.$$

Let j be an nonnegative integer whose value to be chosen later, then by Lemma 4.2 we have,

$$\varphi_u^t \tilde{q} = \varphi_u^{t - j t_u^{\tilde{q}}} \tilde{q} + j.$$

Taking derivative with respect to u on both sides and we get

$$\frac{\partial \varphi_u^t \tilde{q}}{\partial u} = \frac{\partial \varphi_u^\tau \tilde{q}}{\partial u}\bigg|_{\tau = t - j t_u^{\tilde{q}}} + j \cdot \frac{\partial t_u^{\tilde{q}}}{\partial u} \cdot v(\varphi_u^{t - j t_u^{\tilde{q}}} \tilde{q}).$$

A simple Gronwall estimate on the first term of the right hand side of the above equality gives us:

$$\left|\frac{\partial \varphi_u^t \tilde{q}}{\partial u}\right| \leq c_1 \cdot \exp(c_2 |t - j t_u^{\tilde{q}}|) + j \cdot (1+\epsilon) u \left|\frac{\partial t_u^{\tilde{q}}}{\partial u}\right|$$

where $c_1 = c_1(\Phi)$ and $c_2 = c_2(\Phi)$ are positive constants. Choosing $j = [t / t_u^{\tilde{q}}]$ gives us

$$\left|\frac{\partial \varphi_u^t \tilde{q}}{\partial u}\right| \leq c_1 \exp(c_2 t_u^{\tilde{q}}) + (1+\epsilon) \frac{t|u|}{t_u^{\tilde{q}}} \cdot \left|\frac{\partial t_u^{\tilde{q}}}{\partial u}\right|.$$

Now it is clear that we only need to estimate $t_u^{\tilde{q}}$ and $|\frac{\partial t_u^{\tilde{q}}}{\partial u}|$. By Lemma 4.2 we have

$$\frac{1}{\frac{1+\epsilon}{(1-\epsilon)t^*} + \frac{\beta_2(1+\epsilon)}{1-\epsilon}} \leq \frac{1}{(1+\epsilon)u} \leq |t_u^{\tilde{q}}| \leq \frac{1}{(1-\epsilon)u} \leq \frac{1}{(1-\epsilon)A}$$

and

$$\left|\frac{\partial t_u^{\tilde{q}}}{\partial u}\right| \leq \frac{c_3}{(1-\epsilon)u} \exp\left(\frac{c_4}{(1-\epsilon)u}\right) \leq \frac{c_3}{(1-\epsilon)A} \exp\left(\frac{c_4}{(1-\epsilon)A}\right).$$

The lemma then follows easily. □

Now we are ready to prove our main lemma.

Lemma 4.4 (Long Time Spreading in Configuration Space) *Let μ^{uni} be the uniform probability measure on $\mathbb{D}$. Then for any $t^* > 0$, there exists a constant $\epsilon(t^*, \Phi)$ such that $\forall t \geq t^*$*

and $\forall\tilde{q}\in\mathbb{D}$, *we have*

$$\int \delta(\{q-\phi_u^t\tilde{q}\})G(u)du \geq \epsilon(t^*,\Phi)\mu^{uni}.$$

Proof Using the same notations as in the previous lemma, we have

$$\begin{aligned}
&\int \delta(\{q-\varphi_u^t\tilde{q}\})G(u)du \\
&\quad\geq \int_{u\geq A}\delta(\{q-\varphi_u^t\tilde{q}\})G(u)du \\
&\quad\geq \sum_{\beta_1 t\leq k\leq\beta_2 t} G(u)\left|\frac{\partial\varphi_u^t\tilde{q}}{\partial u}\right|^{-1}_{u:\varphi_u^t\tilde{q}=q+k \text{ and } u\geq A} \\
&\quad\geq (\beta_2-\beta_1)t\cdot G\left(\frac{1}{(1-\epsilon)t^*}+\frac{\beta_2}{1-\epsilon}\right)\cdot\frac{1}{c(\epsilon,\Phi,t^*,\beta_2)t} \\
&\quad\geq \epsilon(t^*,\Phi)\mu^{uni}.
\end{aligned}$$

□

Lemma 4.5 (Short Time Spreading in Configuration Space) *For any* $0<t<\frac{1}{1+3\|\Phi''\|_\infty+\|\Phi'\|_\infty}$ *and* $\forall\tilde{q}\in\mathbb{D}$, *we have*

$$\int \delta(\{q-\varphi_u^t\tilde{q}\})G(u)du \geq \frac{2}{3t}G\left(\frac{3}{t}\right)\mu^{uni}.$$

Proof Let us start from

$$\begin{aligned}
\int \delta(\{q-\varphi_u^t\tilde{q}\})G(u)du &= \sum_k G(u)\left|\frac{\partial\varphi_u^t\tilde{q}}{\partial u}\right|^{-1}_{u:\ \varphi_u^t\tilde{q}=q+k} \\
&\geq G(u)\left|\frac{\partial\varphi_u^t\tilde{q}}{\partial u}\right|^{-1}_{u:\varphi_u^t\tilde{q}=q+1}.
\end{aligned}$$

It remains to show the existence of solution to the equation in u:

$$\varphi_u^t\tilde{q}=q+1$$

and estimate the corresponding u and $|\frac{\partial\varphi_u^t\tilde{q}}{\partial u}|$. This is easy if one makes use of the following equality:

$$\varphi_u^t\tilde{q}=\tilde{q}+ut-\int_0^t\int_0^s\Phi'(\varphi_u^\tau\tilde{q})d\tau ds.$$

We omit the details. □

Combining previous two lemmas, we obtain the following

Corollary 4.6 (All Time Spreading in Configuration Space) *Let* μ^{uni} *be the uniform probability measure on* $\mathbb{D}$. *Then* $\forall t>0$ *and* $\forall\tilde{q}\in\mathbb{D}$, *we have*

$$\int \delta(\{q-\varphi_u^t\tilde{q}\})G(u)du \geq \epsilon(t)\mu^{uni}$$

where

$$\epsilon(t) = \begin{cases} \epsilon_0, & \text{if } t > t^*, \\ \frac{2}{3t} G(\frac{3}{t}), & 0 < t \le t^*, \end{cases}$$

and t^*, ϵ_0 *are constants depending only on the potential* Φ.

The next corollary is a generalized version of the previous one and will be needed in the proof of our main theorem.

Corollary 4.7 *Let* $t_1, \ldots, t_n$ *be an arbitrary sequence of positive numbers with* $n \ge 1$. *Let* $s \ge 0$ *be arbitrary but fixed. Then there exists a probability measure* $\mu_{t_1,\ldots,t_n}$ *on* $\mathbb{D}$ *such that for any* $x' \in \Gamma$, *we have*

$$\begin{aligned} &\mathcal{A}\mathcal{H}^{-t_n}\mathcal{A}\mathcal{H}^{-t_{n-1}} \cdots \mathcal{A}\mathcal{H}^{-t_1}\mathcal{A}\mathcal{H}^{-s}\delta_{x'} \\ &\quad = \left[1 - \prod_{j=1}^{n}(1-\epsilon(t_j))\right]\mu_{t_1,\ldots,t_n} \otimes G(v)dv + \left[\prod_{j=1}^{n}(1-\epsilon(t_j))\right]\mu^{x'}_{t_1,\ldots,t_n} \otimes G(v)dv \end{aligned}$$

where $\mu^{x'}_{t_1,\ldots,t_n}$ *is a probability measure on* $\mathbb{D}$ *which may depend on* x'.

Proof We use induction. Consider first $n = 1$. Let μ^{uni} be the uniform probability measure on $\mathbb{D}$, then by previous lemma, we have

$$\int dv \mathcal{H}^{-t_1}\mathcal{A}\mathcal{H}^{-s}\delta_{x'} \ge \epsilon(t_1)\mu_{t_1}$$

with $\mu_{t_1} = \mu^{uni}$. If we define

$$\mu^{x'}_{t_1} := \frac{\int dv \mathcal{H}^{-t_1}\mathcal{A}\mathcal{H}^{-s}\delta_{x'} - \epsilon(t_1)\mu_{t_1}}{1-\epsilon(t_1)}.$$

Then clearly we have

$$\mathcal{A}\mathcal{H}^{-t_1}\mathcal{A}\mathcal{H}^{-s}\delta_{x'} = \epsilon(t_1)\mu_{t_1} \otimes G(v)dv + (1-\epsilon(t_1))\mu^{x'}_{t_1} \otimes G(v)dv.$$

Assume now for $k \ge 2$ and $n < k$ the claim is true. Then for $n = k$, by using the induction hypothesis, we have

$$\begin{aligned} &\mathcal{A}\mathcal{H}^{t_k}\mathcal{A}\mathcal{H}^{t_{k-1}} \cdots \mathcal{A}\mathcal{H}^{t_1}\mathcal{A}\mathcal{H}^{s}\delta_{x'} \\ &\quad = \left[1 - \prod_{j=1}^{k-1}(1-\epsilon(t_j))\right]\mathcal{A}\mathcal{H}^{t_k}(\mu_{t_1,\ldots,t_{k-1}} \otimes G(v)dv) \\ &\qquad + \left[\prod_{j=1}^{k-1}(1-\epsilon(t_j))\right]\mathcal{A}\mathcal{H}^{t_k}(\mu^{x'}_{t_1,\ldots,t_{k-1}} \otimes G(v)dv). \end{aligned}$$

By using Corollary 4.6, we have

$$\mathcal{A}\mathcal{H}^{t_k}(\mu^{x'}_{t_1,\ldots,t_{k-1}} \otimes G(v)dv) = \int_{\mathbb{D}} \mu^{x'}_{t_1,\ldots,t_{k-1}}(d\tilde{q})\mathcal{A}\mathcal{H}^{t_k}(\delta_{\tilde{q}} \otimes G(v)dv)$$

$$\geq \int_{\mathbb{D}} \mu^{x'}_{t_1,\ldots,t_{k-1}}(d\tilde{q})\epsilon(t_k)\mu^{uni} \otimes G(v)$$
$$= \epsilon(t_k)\mu^{uni} \otimes G(v).$$

Clearly then

$$\mu_{t_1,\ldots,t_k} \otimes G(v)dv \cdot \left(1 - \prod_{j=1}^{k}(1-\epsilon(t_j))\right)$$
$$= \left[1 - \prod_{j=1}^{k-1}(1-\epsilon(t_j))\right]\mathcal{A}\mathcal{H}^{t_k}(\mu_{t_1,\ldots,t_{k-1}} \otimes G(v)dv)$$
$$+ \epsilon(t_k)\left[1 - \prod_{j=1}^{k-1}(1-\epsilon(t_j))\right]\mu^{uni} \otimes G(v)dv.$$

The corollary is proved. □

We are now ready to prove our main theorem.

Proof of Theorem 4.1 We begin by observing the following expansion of $P^t_{x'}$:

$$P^t_{x'} = e^{-\nu t}\mathcal{H}^{-t}P^0_{x'} + \nu\int_0^t e^{\nu(s-t)}\mathcal{H}^{-(t-s)}\mathcal{A}P^s_{x'}ds$$
$$= e^{-\nu t}\mathcal{H}^{-t}\delta_{x'} + \nu e^{-\nu t}\int_0^t \mathcal{H}^{-(t-s)}\mathcal{A}\mathcal{H}^{-s}\delta_{x'}ds + \sum_{n\geq 2}\nu^n e^{-\nu t}\rho^{(n)}_{x'},$$

where for $n \geq 2$,

$$\rho^{(n)}_{x'} := \int_0^t\int_0^{t_0}\cdots\int_0^{t_{n-2}}\mathcal{H}^{-(t-t_0)}\mathcal{A}\mathcal{H}^{-(t_0-t_1)}\mathcal{A}\cdots$$
$$\times\mathcal{H}^{-(t_{n-2}-t_{n-1})}\mathcal{A}\mathcal{H}^{-t_{n-1}}\delta_{x'}dt_{n-1}dt_{n-2}\cdots dt_0.$$

Clearly $\forall x', y' \in \mathbb{D}$, we have

$$\|P^t_{x'} - P^t_{y'}\|_{TV} \leq 2(1+\nu t)e^{-\nu t} + \sum_{n\geq 2}\nu^n e^{-\nu t}\|\rho^{(n)}_{x'} - \rho^{(n)}_{y'}\|_{TV}.$$

By Corollary 4.7, we have

$$\|\rho^{(n)}_{x'} - \rho^{(n)}_{y'}\|_{TV} \leq 2\int_0^t\int_0^{t_0}\cdots\int_0^{t_{n-2}}\prod_{j=0}^{n-2}(1-\epsilon(t_j - t_{j+1}))dt_{n-1}dt_{n-2}\cdots dt_0.$$

So that

$$\|P^t_{x'} - P^t_{y'}\|_{TV}$$
$$\leq 2(1+\nu t)e^{-\nu t}$$

$$+ 2e^{-\nu t} \sum_{n\geq 2} \nu^n \int_0^t \int_0^{t_0} \cdots \int_0^{t_{n-2}} \prod_{j=0}^{n-2} (1-\epsilon(t_j - t_{j+1})) dt_{n-1} dt_{n-2} \cdots dt_0$$

$$\leq \frac{2}{1-\epsilon_0} \alpha(\nu, t) e^{-\nu t}$$

where $\alpha(\nu, t)$ satisfies:

$$\alpha(\nu, t) = 1 + \nu \int_0^t (1-\epsilon(t-s)) \alpha(\nu, s) ds.$$

By Corollary 4.6 and a simple Gronwall argument, we obtain for $0 < \nu < \frac{1}{t^*}$:

$$\alpha(\nu, t) \leq \frac{1}{1-\nu t^*} \exp\left(\frac{1-\epsilon_0}{1-\nu t^*} \nu t\right).$$

Now let us take $\nu_0 = \min\{\frac{\epsilon_0}{2t^*}, \frac{1}{2t^*}\}$. Then for any $0 < \nu < \nu_0$, we have

$$\begin{aligned} \|P_{x'}^t - P_{y'}^t\|_{TV} &\leq \frac{2}{(1-\epsilon_0)(1-\nu t^*)} \exp\left(-\frac{\epsilon_0 - \nu t^*}{1-\nu t^*} \nu t\right) \\ &\leq \frac{4}{1-\epsilon_0} \exp\left(-\frac{\epsilon_0}{2} \nu t\right). \end{aligned}$$

Now recall that ϵ_0 can be chosen $< \frac{1}{2}$ and the theorem follows easily. □

A reexamination of Corollary 4.7 suggests that we can obtain the following regularity result for the transition semigroup $P_{x'}^t$.

Theorem 4.8 (Exponential Decomposition of the Transition Semigroup) *For any $x' \in \Gamma$ and any $t > 0$, there exists a constant $\kappa > 0$ which depends possibly on the potential Φ such that the Markov semigroup $P_{x'}^t$ admits the following decomposition*:

$$P_{x'}^t = (1 - 4e^{-\kappa \nu t}) \mu_t^{abs} + 4e^{-\kappa \nu t} \cdot \mu_{x'}$$

where μ_t^{abs} is a probability measure on Γ which is absolutely continuous with respect to the Lebesgue measure on Γ, and $\mu_{x'}$ is some probability measure which may possibly depend on x'.

Proof We start by observing that in Corollary 4.7 the measure which are x'-dependent is actually absolutely continuous with respect to the Lebesgue measure. It follows easily that in the expansion of $P_{x'}^t$, the total variational norm of the x'-dependent part is at most

$$(1+\nu t) \exp(-\nu t)$$

$$+ e^{-\nu t} \sum_{n\geq 2} \nu^n \int_0^t \int_0^{t_0} \cdots \int_0^{t_{n-2}} \prod_{j=0}^{n-2} (1-\epsilon(t_j - t_{j+1})) dt_{n-1} dt_{n-2} \cdots dt_0$$

$$\leq \frac{1}{1-\epsilon_0} \alpha(\nu, t) e^{-\nu t}$$

where $\alpha(\nu,t)$ satisfies:

$$\alpha(\nu,t)=1+\nu\int_0^t(1-\epsilon(t-s))\alpha(\nu,s)ds.$$

The proof is finished by the same estimate of $\alpha(\nu,t)$ at the end of the proof of Theorem 4.1. □

Remark 4.9 Let us point out that such an exponential decomposition is the best one can hope for in the sense that $P^t_{x'}$ will always contain a singular part which is exponentially decaying in time. To see this, consider the one-dimensional one-particle free-streaming case. Suppose the initial distribution is of the form:

$$\rho|_{t=0}=\mu^{uni}\otimes\delta_{v'}$$

where μ^{uni} is the uniform probability measure in the configuration space and $\delta_{v'}$ is the Dirac distribution at $v'\in\mathbb{R}$. Then it is obvious that the time evolution equation for ρ is given by

$$\partial_t\rho=\nu(\mathcal{A}-I)\rho.$$

The solution to this equation is given by

$$\begin{aligned}\rho_t&=\mu^{uni}\otimes(e^{-\nu t}\delta_{v'}+(1-e^{-\nu t})G(v)dv)\\&=e^{-\nu t}\mu^{uni}\otimes\delta_{v'}+(1-e^{-\nu t})\mu^{uni}\otimes G(v)dv\end{aligned}$$

one sees immediately that ρ_t and therefor $P^t_{x'}$ will always contain a singular part which is exponentially decaying in time.

5 Exponential Convergence to Equilibrium: Discrete Time Case

In this section we will establish analogous results for the discrete time one-dimensional one-particle Andersen dynamics. For any integer $n\geq 1$, let us denote by $(P^{\Delta t}_{x'})^n$ the n-step transition probability of the discrete Andersen dynamics. We have the following theorem:

Theorem 5.1 *There exist constants $\nu_0=\nu_0(\Phi)>0$ and $\Delta t_0=\Delta t_0(\Phi)$ such that for any $0<\nu<\nu_0$, $0<\Delta t<\Delta t_0$ and any $x'\in\Gamma$, we have*

$$\|(P^{\Delta t}_{x'})^n-\pi\|_{TV}\leq c\exp(-\kappa n\nu\Delta t)\quad\forall n\geq 1$$

where c is an absolute constant and κ depends only on Φ.

Proof By (3.2) we have

$$\begin{aligned}(P^{\Delta t}_{x'})^n&=[(1-\nu\Delta t)\mathcal{H}^{-\Delta t}+\nu\Delta t\mathcal{A}\mathcal{H}^{-\Delta t}]^n\delta_{x'}\\&=\sum_{k=0}^n(1-\nu\Delta t)^{n-k}(\nu\Delta t)^k\sum_{\substack{\sum_{j=0}^k r_j=n-k\\ r_j\geq 0,0\leq j\leq k}}\mathcal{H}^{-r_0\Delta t}\mathcal{A}\mathcal{H}^{-(r_1+1)\Delta t}\cdots\mathcal{A}\mathcal{H}^{-(r_k+1)\Delta t}\delta_{x'}.\end{aligned}$$

By Corollary 4.7, the total variational norm of x'-dependent parts in the above sum is at most

$$\begin{aligned}&\sum_{k=0}^{n}(1-\nu\Delta t)^{n-k}(\nu\Delta t)^{k}\sum_{\substack{\sum_{j=0}^{k} r_j=n-k\\ r_j\ge 0,0\le j\le k}}\prod_{i=1}^{k-1}(1-\epsilon((r_i+1)\Delta t))\\ &\quad\le\frac{(1-\nu\Delta t)^{n}}{1-\epsilon_0}a(n,\nu,\Delta t)\end{aligned}$$

where $a(n,\nu,\Delta t)$ satisfies

$$a(n,\nu,\Delta t)=1+\frac{\nu\Delta t}{1-\nu\Delta t}\sum_{j=1}^{n}(1-\epsilon(j\Delta t))a(n-j,\nu,\Delta t).$$

By Lemma 4.4, we have

$$\begin{aligned}&a(n,\nu,\Delta t)\\ &\quad\le 1+\frac{\nu\Delta t}{1-\nu\Delta t}\Bigg(\sum_{i:\, i\Delta t\le t^*}(1-\epsilon(i\Delta t))a(n-i,\nu,\Delta t)\\ &\qquad+\sum_{i:\, i\Delta t>t^*}(1-\epsilon(i\Delta t))a(n-i,\nu,\Delta t)\Bigg)\\ &\quad\le 1+\frac{\nu\Delta t}{1-\nu\Delta t}\sum_{i:\, i\Delta t\le t^*}a(n-i,\nu,\Delta t)+\frac{(1-\epsilon_0)\nu\Delta t}{1-\nu\Delta t}\sum_{i=1}^{n}a(n-i,\nu,\Delta t).\end{aligned}$$

Now observe that $a(n,\nu,\Delta t)$ as a function of n is non-decreasing so that,

$$(1-\nu\Delta t-\nu t^*)a(n,\nu,\Delta t)\le 1+(1-\epsilon_0)\nu\Delta t\sum_{i=1}^{n}a(n-i,\nu,\Delta t).$$

Now a simple Gronwall estimate gives

$$a(n,\nu,\Delta t)\le\left(1+\frac{(1-\epsilon_0)\nu\Delta t}{1-\nu(\Delta t+t^*)}\right)^{n}.$$

Clearly it follows that the x'-dependent part in $(P_{x'}^{\Delta t})^n$ is at most

$$\frac{(1-\nu\Delta t)^{n}}{1-\epsilon_0}\left(1+\frac{(1-\epsilon_0)\nu\Delta t}{1-\nu(\Delta t+t^*)}\right)^{n}\le\frac{1}{1-\epsilon_0}\exp\left(-\frac{\epsilon_0-\nu(\Delta t+t^*)}{1-\nu(\Delta t+t^*)}n\nu\Delta t\right).$$

It follows easily that $\forall x',y'\in\Gamma$, we have

$$\|(P_{x'}^{\Delta t})^n-(P_{x'}^{\Delta t})^n\|_{TV}\le c\exp(-\kappa n\nu\Delta t)\quad\forall n\ge 1$$

where c is an absolute constant and κ depends only on Φ. □

The following corollary is obvious

Corollary 5.2 (Exponential Decomposition of the Transition Semigroup) *For any $x' \in \Gamma$ and any $t > 0$, there exists a constant $\kappa > 0$ which depends possibly on the potential Φ such that $(P_{x'}^{\Delta t})^n$ admits the following decomposition*:

$$(P_{x'}^{\Delta t})^n = (1 - 2e^{-\kappa \nu t})\mu_n^{abs} + 2e^{-\kappa \nu t} \cdot \mu_{x'}$$

where μ_n^{abs} is a probability measure on Γ which is absolutely continuous with respect to the Lebesgue measure on Γ, and $\mu_{x'}$ is some probability measure which may possibly depend on x'.

6 Free Streaming Case: A Better Bound

If the inter-atomic potential is switched off, then we can obtain a better bound by using Fourier methods. Again let us start with the Duhamel expansion of $P_{x'}^t$ as follows:

$$\begin{aligned} P_{x'}^t &= e^{-\nu t}\mathcal{H}^{-t}P_{x'}^0 + \nu \int_0^t e^{\nu(s-t)}\mathcal{H}^{-(t-s)}\mathcal{A}P_{x'}^s ds \\ &= e^{-\nu t}\mathcal{H}^{-t}\delta_{x'} + \nu e^{-\nu t}\int_0^t \mathcal{H}^{-(t-s)}\mathcal{A}\mathcal{H}^{-s}\delta_{x'} ds \\ &\quad + \nu^2 e^{-\nu t}\int_0^t \int_0^s \mathcal{H}^{-(t-s)}\mathcal{A}\mathcal{H}^{-(s-\tau)}\mathcal{A}\mathcal{H}^{-\tau}\delta_{x'} d\tau ds + \sum_{n\geq 3}\nu^n e^{-\nu t}\rho^{(n)} \end{aligned}$$

where for $n \geq 3$,

$$\begin{aligned} \rho^{(n)} := \int_0^t \int_0^{t_0} \cdots \int_0^{t_{n-2}} \mathcal{H}^{-(t-t_0)}\mathcal{A}\mathcal{H}^{-(t_0-t_1)}\mathcal{A}\cdots \\ \times \mathcal{H}^{-(t_{n-2}-t_{n-1})}\mathcal{A}\mathcal{H}^{-t_{n-1}}\delta_{x'} dt_{n-1}dt_{n-2}\cdots dt_0. \end{aligned}$$

Lemma 6.1 *We have for $n \geq 3$*

$$\left\| \rho^{(n)} - \frac{t^n}{n!}G(v) \right\|_{TV} \leq \sum_{k\neq 0} t \cdot \left(\frac{1}{2\sqrt{2\pi}|k|} \right)^{n-1}.$$

Proof Let's write

$$\begin{aligned} \rho^{(n)} &= \int_0^t \int_0^{t_0} \cdots \int_0^{t_{n-2}} \mathcal{H}^{-(t-t_0)}\mathcal{A}\mathcal{H}^{-(t_0-t_1)}\mathcal{A}\cdots\mathcal{H}^{-(t_{n-2}-t_{n-1})}\mathcal{A}\mathcal{H}^{-t_{n-1}}\delta_{x'}dt_{n-1}dt_{n-2}\cdots dt_0 \\ &= G(v)\int_{\mathbb{R}^{n-1}} du_1 du_2\cdots du_{n-1}G(u_1)G(u_2)\cdots G(u_{n-1}) \\ &\quad \times \int_0^t \int_0^{t_0} \cdots \int_0^{t_{n-2}} dt_{n-1}dt_{n-2}\cdots dt_0 \\ &\quad \times \delta(\{q - q' - v(t-t_0) - u_1(t_0 - t_1) - u_2(t_1 - t_2) - \cdots \\ &\quad - u_{n-1}(t_{n-2} - t_{n-1}) - v't_{n-1}\}) \\ &= \frac{t^n}{n!}G(v) + G(v)\int_0^t \int_0^{t_0} \cdots \int_0^{t_{n-2}} dt_{n-1}dt_{n-2}\cdots dt_0 \end{aligned}$$

$$\times \sum_{k\neq 0} \exp\{2\pi \iota k(q-q'-v(t-t_0)-v't_{n-1})\} \exp\left\{-2(\pi k)^2 \sum_{j=0}^{n-2}(t_j-t_{j+1})^2\right\}$$

where the last equality follows from Fourier transformation. Then we have

$$\begin{aligned}&\left\|\rho^{(n)}-\frac{t^n}{n!}G(v)\right\|_{TV}\\ &\quad\le \sum_{k\neq 0}\int_0^t\int_0^{t_0}\cdots\int_0^{t_{n-2}} dt_{n-1}dt_{n-2}\cdots dt_0 \exp\left\{-2(\pi k)^2\sum_{j=0}^{n-2}(t_j-t_{j+1})^2\right\}\\ &\quad\le \sum_{k\neq 0} t\cdot\left(\frac{1}{2\sqrt{2\pi}|k|}\right)^{n-1}\end{aligned}$$

the above series in k obviously converges since $n\ge 3$. □

Theorem 6.2 *In the 1D free streaming case, we have* $\forall 0<\nu<2\sqrt{2\pi}$ *and* $\forall x'\in\Gamma$,

$$\|P^t_{x'}-\pi\|_{TV}\le\left\{2\left(1+\nu t+\frac{\nu^2t^2}{2}\right)+\frac{\pi\nu^3 t}{24(1-\frac{\nu}{2\sqrt{2\pi}})}\right\}e^{-\nu t}.$$

Proof Let us note that in the free streaming case, we have $\pi(dqdv)=dq\otimes G(v)dv$. Now $\forall 0<\nu<2\sqrt{(2\pi)}$, by the previous lemma and the expansion of $P^t_{x'}$ preceding the lemma, we have

$$\begin{aligned}\|P^t_{x'}-\pi\|_{TV}&\le 2\left(1+\nu t+\frac{(\nu t)^2}{2}\right)e^{-\nu t}+e^{-\nu t}\sum_{n\ge 3}\nu^n\left\|\rho^{(n)}-\frac{t^n}{n!}G(v)\right\|_{TV}\\ &\le 2\left(1+\nu t+\frac{(\nu t)^2}{2}\right)e^{-\nu t}+te^{-\nu t}\sum_{k\neq 0}\sum_{n\ge 3}\frac{\nu^n}{(2\sqrt{2\pi}|k|)^{n-1}}\\ &\le\left\{2\left(1+\nu t+\frac{(\nu t)^2}{2}\right)+\frac{\pi\nu^3t}{24(1-\frac{\nu}{2\sqrt{2\pi}})}\right\}e^{-\nu t}.\end{aligned}$$

□

It is possible to generalize to dimension $d\ge 1$, indeed, we have the following theorem:

Theorem 6.3 *In the d-dimensional free streaming case, we have* $\forall 0<\nu<2\sqrt{2\pi}$ *and* $\forall \mathbf{x}'\in\Gamma$,

$$\|P^t_{\mathbf{x}'}-\pi\|_{TV}\le\left\{2\left(1+\nu t+\frac{\nu^2t^2}{2}+\cdots+\frac{(\nu t)^{d+1}}{(d+1)!}\right)+\frac{t\nu^{d+2}}{1-\frac{\nu}{2\sqrt{2\pi}}}\cdot\frac{1}{2^{\frac{d+1}{2}}\sqrt{\pi}\Gamma(\frac{d}{2})}\right\}e^{-\nu t}$$

where $\Gamma(\cdot)$ is the usual Gamma function.

Proof By using a d-dimensional version of Lemma 6.1, we have

$$\|P^t_{\mathbf{x}'}-\pi\|_{TV}$$

$$\leq 2e^{-\nu t}\left(1+\nu t+\frac{\nu^2t^2}{2}+\cdots+\frac{(\nu t)^{d+1}}{(d+1)!}\right)+te^{-\nu t}\cdot\sum_{\mathbf{0}\neq\mathbf{k}\in\mathbb{Z}^d}\sum_{n\geq d+2}\frac{\nu^n}{(2\sqrt{2\pi}|\mathbf{k}|)^{n-1}}$$

$$\leq\left\{2\left(1+\nu t+\frac{\nu^2t^2}{2}+\cdots+\frac{(\nu t)^{d+1}}{(d+1)!}\right)\right.$$

$$\left.+\frac{t\nu^{d+2}}{1-\frac{\nu}{2\sqrt{2\pi}}}\cdot\frac{1}{(2\sqrt{2\pi})^{d+1}}\cdot\sum_{\mathbf{0}\neq\mathbf{k}\in\mathbb{Z}^d}\frac{1}{|\mathbf{k}|^{d+1}}\right\}e^{-\nu t}.$$

The proof is finished by an application of the elementary inequality:

$$\sum_{\mathbf{0}\neq\mathbf{k}\in\mathbb{Z}^d}\frac{1}{|\mathbf{k}|^{d+1}}\leq\frac{2^{d+1}\pi^{\frac{d}{2}}}{\Gamma(\frac{d}{2})}.$$

□

Let us further generalize the above theorem to the N-particle, d-dimensional free streaming case. Since there is no interaction amongst particles, the following lemma is obvious.

Lemma 6.4 (Propagation of Molecular Chaos) *For the N-particle, d-dimensional free streaming case, suppose*

$$P^0_{\mathbf{x}'}=\prod_{j=1}^{N}\delta(\{\mathbf{q}_j-\mathbf{q}'_j\})\delta(\mathbf{v}_j-\mathbf{v}'_j)$$

then we have $\forall t>0$

$$P^t_{\mathbf{x}'}=\prod_{j=1}^{N}P^{(j)}\left(\frac{t}{N},\mathbf{q}_j,\mathbf{v}_j;\mathbf{q}'_j,\mathbf{v}'_j\right)$$

where $P^{(j)}$ is the Markov transition semigroup for j-th particle.

Proof It suffices to note that

$$\mathcal{G}=\frac{1}{N}\sum_{j=1}^{N}\mathcal{G}_j$$

where $\mathcal{G}_j=\nu(\mathcal{A}_j-Id)-\mathbf{v}_j\cdot\nabla_j$ and $\mathcal{G}_j$ are commutable. □

The following theorem is immediate:

Theorem 6.5 *In the N-particle, d-dimensional free streaming case, we have* $\forall 0<\nu<2\sqrt{2\pi}$ *and* $\forall\mathbf{x}'\in\Gamma$,

$$\|P^t_{\mathbf{x}'}-\pi\|_{TV}\leq\left\{2Nh(t)+\frac{t\nu^{d+2}}{1-\frac{\nu}{2\sqrt{2\pi}}}\cdot\frac{1}{2^{\frac{d+1}{2}}\sqrt{\pi}\Gamma(\frac{d}{2})}\right\}e^{-\frac{\nu t}{N}}$$

where

$$h(t):=1+\frac{\nu t}{N}+\frac{1}{2}\left(\frac{\nu t}{N}\right)+\cdots+\frac{1}{(d+1)!}\left(\frac{\nu t}{N}\right)^{d+1}$$

and $\Gamma(\cdot)$ is the usual Gamma function.

Proof Use Lemma 6.4 and Theorem 6.3. □

7 Proof of Convergence to the Smoluchowski Equation

Throughout this section we shall assume the number of particles $N=1$. The analysis done for $N=1$ is enough to explain the problem of choosing large ν. Let us begin by noting that the perturbation analysis developed in [20] is directly applicable to our problem. Although it is very common to apply the analysis there to the backward Kolmogorov equation, here we find it more convenient to work directly with the forward Kolmogorov equation. To fix the notations, let us introduce the Banach space M of finite signed Borel measures on Γ endowed with the total variational norm. The Andersen collision operator $\mathcal{A}$ (2.2) has a natural extension on M, i.e. for any $\mu\in M$, and any Borel sets $A\subset\mathbb{D}$, $B\subset\mathbb{R}^d$, we have

$$(\mathcal{A}\mu)(A\otimes B)=\mu(A\otimes\mathbb{R}^d)\int_B G(\mathbf{v})d\mathbf{v}.$$

It is clear that $\mathcal{A}$ is a projection operator on M. For any smooth real-valued function f on the configuration space $\mathbb{D}$, the Smoluchowski operator is defined by:

$$\mathcal{B}f=\nabla\cdot(f\nabla\Phi)+\triangle f.$$

Let M_1 be the Banach space of finite signed Borel measures on the configuration space $\mathbb{D}$. The Smoluchowski operator $\mathcal{B}$ generates a strongly continuous contraction semigroup on M_1 which is denoted by $S_1(t)$. Let $N=\mathcal{A}M$ be the range of the Andersen collision operator $\mathcal{A}$ in M. Obviously if $\mu\in N$ then $\mu(d\mathbf{q}\otimes d\mathbf{v})=\mu_1(d\mathbf{q})\otimes G(\mathbf{v})d\mathbf{v}$, where $\mu_1\in M_1$ is the marginal measure of μ on $\mathbb{D}$. We can then extend $S_1(t)$ to a strongly continuous contraction semigroup $S(t)$ on N. $S(t)$ is defined by

$$(S(t)\mu)(d\mathbf{q}\otimes d\mathbf{v}):=(S_1(t)\mu_1)(d\mathbf{q})\otimes G(\mathbf{v})d\mathbf{v},$$

where $\mu\in N$ and μ_1 is the marginal of μ on $\mathbb{D}$. For convenience we shall also define $S(t)\mu_1$ for any $\mu_1\in M_1$ by the same relation above. We have the following simple proposition.

Proposition 7.1 *Let $\mu\in N$ be such that the marginal measure μ_1 on the configuration space $\mathbb{D}$ has an infinitely differentiable density with respect to the Lebesgue measure on $\mathbb{D}$. Then for any $T>0$, there exists a positive constant $C_{\mu,\Phi,T}$ depending only on (μ,Φ,T), such that*

$$\sup_{0\le t\le T}\|(i\mathcal{L})^k\rho_j(t)\|_{TV}\le C_{\mu,\Phi,T}\quad\forall k=1,2,3\quad\textit{and}\quad j=1,2$$

where $\rho_1(t)=S(t)(\mathcal{B}\mu_1)$ and $\rho_2(t)=S(t)\mu$.

Proof Observe that the Smoluchowski operator is an elliptic operator so that $S_1(t)\mu_1$ is infinitely differentiable in both $(t,\mathbf{q})$. The proof is obvious. □

Consider the rescaled Andersen infinitesimal generator (for measures):

$$\mathcal{G}_\nu^*:=\nu^2(\mathcal{A}-\mathcal{I})-\nu i\mathcal{L}.\tag{7.1}$$

Denote by $T_\nu(t)$ the continuous contraction semigroup on M generated by $\mathcal{G}_\nu^*$. We shall prove the following theorem.

Theorem 7.2 (Convergence to the Smoluchowski Equation on the Diffusive Time Scale) *Let $\mu \in N$ be such that the marginal measure μ_1 on the configuration space $\mathbb{D}$ has an infinitely differentiable density with respect to the Lebesgue measure on $\mathbb{D}$. Then for any $0 < T < \infty$, there exists a positive constant $C_{\mu,\Phi,T}$ depending only on (μ, Φ, T), such that*

$$\sup_{0\le t\le T} \|T_\nu(t)\mu - S(t)\mu\|_{TV} \le \frac{C_{\mu,\Phi,T}}{\nu} \quad \forall \nu \ge 1.$$

Proof Let $u_\nu(t) = T_\nu(t)\mu$, $v(t) = S(t)\mu$, following [20] we have

$$\begin{aligned}
&\left(\frac{d}{dt} - G_\nu\right)\left(u_\nu(t) - v(t) + \frac{1}{\nu} i\mathcal{L}v(t) - \frac{1}{\nu^2}(i\mathcal{L})^2 v(t)\right)\\
&= \left(\frac{d}{dt} - \nu^2(\mathcal{A} - \mathcal{I}) + \nu i\mathcal{L}\right)\left(-v(t) + \frac{1}{\nu} i\mathcal{L}v(t) - \frac{1}{\nu^2}(i\mathcal{L})^2 v(t)\right)\\
&= \frac{1}{\nu}(-(i\mathcal{L})^3 v(t) + i\mathcal{L}\rho_1(t)) - \frac{1}{\nu^2}((i\mathcal{L})^2\rho_1(t))
\end{aligned}$$

where $\rho_1(t) = S(t)(\mathcal{B}\mu_1)$. By Proposition 7.1, it is immediate that the right hand side of the above equation is bounded by a constant independent of ν. Using the smoothness of solutions, we have for any $T < \infty$, and $\nu \ge 1$,

$$\sup_{0\le t\le T} \left\| u_\nu(t) - v(t) + \frac{1}{\nu} i\mathcal{L}v(t) - \frac{1}{\nu^2}(i\mathcal{L})^2 v(t)\right\| \le \frac{C_1}{\nu}$$

where C_1 is some positive constant depending only on (μ, Φ, T). Now use Proposition 7.1 again and the proof is finished. □

Remark 7.3 The picture of the Andersen dynamics on the diffusive time scale is now intuitively obvious. In the $\nu \gg 1$ limit, the velocity distribution is stationary and Gaussian, and the particle's motion is governed by an elliptic diffusion in the configuration space. It is well known that for the Smoluchowski equation the convergence to equilibrium is exponentially fast. Due to the scaling in (7.1), it is not hard to see that the convergence to equilibrium is "slowed down" as we increase ν in the $\nu \gg 1$ limit, since the "true" time for the Smoluchowski equation is given by $\frac{t}{\nu}$.

The following easy corollary shows that on the advective time scale, the Andersen dynamics may not converge at all.

Corollary 7.4 (Non-convergence to the True Equilibrium on the Advective Time Scale) *Let $\mu \in N$ be such that the marginal measure μ_1 on the configuration space $\mathbb{D}$ has an infinitely differentiable density with respect to the Lebesgue measure on $\mathbb{D}$. Let $T_\nu^0(t) := T_\nu(\frac{t}{\nu})$ be the strongly continuous contraction semigroup generated by the unscaled Andersen infinitesimal generator. Then for any $0 < T < \infty$, we have*

$$\lim_{\nu\to\infty} \sup_{0\le t\le T} \|T_\nu^0(t)\mu - \mu\|_{TV} = 0.$$

Proof This is obvious using the fact that $S(t)$ is strongly continuous. □

8 Concluding Remarks

To understand better the role of the collision frequency, it is instructive to compare the Andersen thermostat to the well known hybrid Monte Carlo methods (HMC) introduced by Duane et al. [5]. The HMC method samples the so called configurational canonical measure which is obtained from the canonical measure by integrating out the momentum variables. In HMC at integer time steps one also generates fictitious momentum kicks, but only to make moves in the configuration space. There are several differences between HMC and Andersen. In terms of calculating the ensemble average, it is clear that the HMC method is more efficient since in the Andersen thermostat the momentum variables are always kept. However the Andersen thermostat can be used to calculate the transport properties of the system in the low collision frequency limit [6], whereas HMC cannot be used for this purpose. We also want to add that in HMC the role of ν is played by $1/\Delta t$ where Δt is the integration time step since the rejection rate depends on the choice of Δt. In a sense the problem we are addressing here also appears in HMC for which the choice of Δt is a delicate problem [4, 21]. However for the Andersen thermostat, due to the perhaps spurious desire to preserve the real dynamics, the rate of convergence to equilibrium is more subtle. As we have shown here, for the 1-d one particle and n-d ideal gas case, the true time scale coincides with the intuitive time scale which is N/ν.

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References

1. Andersen, H.C.: Molecular dynamics at constant pressure and/or temperature. J. Chem. Phys. **72**, 2384–2393 (1980)
2. Bond, S.D., Leimkuhler, B.J., Laird, B.B.: The Nosé-Poincaré method for constant temperature molecular dynamics. J. Comput. Phys. **151**, 114–134 (1999)
3. Berendsen, H.J.C., Postma, J.P.M., van Gunsteren, W.F., DiNola, A., Haak, J.R.: Molecular dynamics with coupling to an external bath. J. Chem. Phys. **81**(8), 3684–3690 (1984)
4. Cancès, E., Legoll, F., Stoltz, G.: Theoretical and numerical comparison of some sampling methods for molecular dynamics, IMA preprint. Math. Model. Numer. Anal. **41**(2), 351–389 (2007)
5. Duane, S., Kennedy, A.D., Pendleton, B.J., Roweth, D.: Hybrid Monte Carlo. Phys. Lett. B **195**(2), 216–222 (1987)
6. E, W., Li, D.: The Andersen thermostat in molecular dynamics. Comm. Pure. Appl. Math. (2007, in press). doi: 10.1002/cpa.20198
7. Frenkel, D., Smit, B.: Understanding Molecular Simulation, from Algorithms to Applications, 2nd ed. Academic Press, San Diego (2002)
8. Grest, G.S., Kremer, K.: Molecular-dynamics simulation for polymers in the presence of a heat bath. Phys. Rev. A **33**(5), 3628–3631 (1986)
9. Hoover, W.G.: Equilibrium phase-space distributions. Phys. Rev. A **31**, 1695–1697 (1985)
10. Hoover, W.G.: Constant pressure equations of motion. Phys. Rev. A **34**, 2499–2500 (1986)
11. Legoll, F., Luskin, M., Moeckel, R.: Non-ergodicity of the Nose-Hoover thermostatted harmonic oscillator. Arch. Ration. Mech. Anal. **184**(3), 449–463 (2007)
12. Leimkuhler, B.J., Sweet, C.R.: A Hamiltonian formulation for recursive multiple thermostats in a common timescale. SIAM J. Appl. Dyn. Syst. **4**(1), 187–216 (2005)
13. Lindvall, T.: Lectures on the Coupling Method. Wiley Series in Probability and Mathematical Statistics. Wiley, New York (1992)
14. Meyn, S.P., Tweedie, R.L.: Markov Chains and Stochastic Stability. Springer, Berlin (1993)
15. Martyna, G.J., Klein, M.L., Tuckerman, M.E.: Nosé-Hoover chains: The canonical ensemble via continuous dynamics. J. Chem. Phys. **97**, 2635–2645 (1992)
16. Mattingly, J.C., Stuart, A.M., Higham, D.J.: Ergodicity for SDEs and approximations: Locally Lipschitz vector fields and degerate noise. Stoch. Process. Appl. **101**, 185–232 (2002)

17. Nikunen, P., Karttunen, M., Vattulainen, I.: How would you integrate the equations of motion in dissipative particle dynamics simulations? Comput. Phys. Commum. **153**(3), 407–423 (2003)
18. Nosé, S.: A molecular dynamics method for simulations in the canonical ensemble. Mol. Phys. **52**, 255–268 (1984)
19. Nosé, S.: A unified formulation of the constant temperature molecular dynamics method. J. Chem. Phys. **81**, 511–519 (1985)
20. Papanicolaou, G.C.: Some probabilistic problems and methods in singular perturbations. Rocky Mt. Math. J. **6**, 653–674 (1976)
21. Schütte, C.: Conformational dynamics: Modelling, theory, algorithm, and application to biomolecules. Habilitation Thesis, Free University Berlin (1999)
22. Shardlow, T., Yan, Y.: Geometric ergodicity for dissipative particle dynamics. Stoch. Dyn. **6**(1), 123–154 (2006)
23. Soddemann, T., Dünweg, B., Kremer, K.: Dissipative particle dynamics: A useful thermostat for equilibrium and nonequilibrium molecular dynamics simulations. Phys. Rev. E **68**(4), 046702 (2003)
24. Talay, D.: Stochastic Hamiltonian dissipative systems: exponential convergence to the invariant measure, and discretization by the implicit Euler scheme. Markov Process. Relat. Fields **8**, 163–198 (2002)
25. Tuckerman, M.E., Liu, Y., Ciccotti, G., Martyna, G.J.: Non-Hamiltonian molecular dynamics: Generalizing Hamilton phase space principles to non-Hamiltonaian systems. J. Chem. Phys. **116**, 1678 (2001)
26. Tuckerman, M.E., Martyna, G.J.: Understanding modern molecular dynamics: Techniques and applications. J. Phys. Chem. B **104**, 159–178 (2000)
27. Tropper, M.M.: Ergodic properties and quasideterministic properties of finite-dimensional stochastic systems. J. Stat. Phys. **17**, 491–509 (1977)