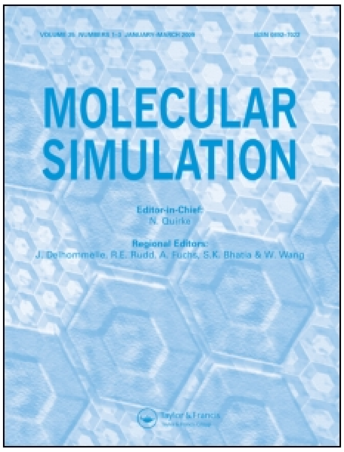

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

A Comparison Between Collisional Dynamics and Brownian Dynamics

A. S. Lemak[a]; N. K. Balabaev[a]
[a] Institute of Mathematical Problems of Biology, Russian Academy of Sciences Pushchino, Moscow Region, Russia

To cite this Article Lemak, A. S. and Balabaev, N. K.(1995) 'A Comparison Between Collisional Dynamics and Brownian Dynamics', Molecular Simulation, 15: 4, 223 — 231
To link to this Article: DOI: 10.1080/08927029508022336
URL: http://dx.doi.org/10.1080/08927029508022336

Molecular Simulation, 1995, Vol. 15, pp. 223–231
Reprints available directly from the publisher
Photocopying permitted by license only

Amsterdam B.V. Published under license by
Gordon and Breach Science Publishers SA
Printed in Malaysia

A COMPARISON BETWEEN COLLISIONAL DYNAMICS AND BROWNIAN DYNAMICS

A. S. LEMAK and N. K. BALABAEV

Institute of Mathematical Problems of Biology, Russian Academy of Sciences
Pushchino, Moscow Region, 142292, Russia

(Received September 20, 1994, accepted September 29, 1994)

This paper presents an analytical investigation for the velocity relaxation of a test particle coupled to a heat bath by two different mechanisms: the Brownian dynamics (BD) and the collisional dynamics (CD). Relation between the parameters of the methods is established. The velocity relaxation spectrum induced by the coupling in the CD method is shown to be different from the one in the BD method. The difference between the spectra disappears in the limit $\gamma \rightarrow O$, where γ is a mass ratio of the bath atoms and the test particle.

KEY WORDS: Molecular dynamics, Collisional dynamics, Brownian dynamics.

1 INTRODUCTION

Molecular dynamics (MD) simulations are considered today as an important source of information on processes in liquids, molecular solutions, and macromolecules. When simulating a system of particles, for a variety of reasons, some degrees of freedom are treated explicitly, whereas others are represented only by their stochastic influence on the former ones (i.e. by a heat bath). Various methods have been proposed for the stochastic coupling of a system under simulation to an external heat bath. They are: Brownian dynamics (BD) [1, 2], Andersen's method [3], collisional dynamics (CD) [4, 5], and generalized Langevin dynamics [6, 7]. We have restricted our consideration to the first three methods, which are relatively simple in implementation. These methods belong to canonical ensemble MD methods. That is, the average of any property over the trajectory is an approximation to the ensemble average of the property for the canonical ensemble. But from the dynamical point of view the methods differ from one another as the fluctuations of a dynamical variable about its average value are simulated differently. When we are interested in the dynamical property of the simulated system, it is important to know which method is preferable for a given problem. Any information concerning relations between various methods may be useful. Our article presents the simplest case of one test particle, which allows full analytical comparison of the dynamics simulated by two methods: the BD and the CD methods. (In this case the Andersen's method coincides with a particular case of the CD). The dynamics of the test particle is discussed in terms of time evolution of the velocity distribution function. A comparison is based on the relations between the parameters of both methods. These relations are found using an assumption that average force exerted on the particle by the bath in the CD method coincides with that in the BD method.

2 DYNAMICS OF TEST PARTICLE COUPLED TO A BATH BY CD AND BD METHODS

For simplicity, let us consider one test particle constrained to move in one dimension and coupled to an external bath by means of two different stochastic mechanisms which are the base of the Brownian dynamics method and collisional dynamics. While not being coupled to a bath, the particle moves with constant velocity v. A stochastic coupling turns the velocity v in the stochastic process. The dynamics of the equilibrium fluctuations of v is intimately related with the evolution of the velocity probability distribution function (p.d.f) $P(v, t)$ to its equilibrium one $P_{eq}(v)$. Further we will describe the dynamics of the particle in terms of time evolution of the p.d.f. $P(v, t)$.

Collisional Dynamics Coupling

While coupling to a bath according to the CD, the particle with mass m suffers impulsive collisions with a bath atom, which has the velocity v_0 chosen at random from a Maxwellian distribution

$$P_M(v_0)=\left(\frac{m_0}{2\pi k_B T_0}\right)^{1/2}\exp\left(-\frac{m_0 v_0^2}{2k_B T_0}\right).$$

Here m_0 is the mass of the bath atom, while T_0 is the bath temperature. The collisions occur in accordance with a Poisson process specified by the only parameter λ_0 – the mean number of collisions which the particle suffers per unit time (collision frequency). The probability for precisely n collisions to occur during the time interval $[0, t]$ is

$$g_n(t)=\frac{1}{n!}(\lambda_0 t)^n \exp(-\lambda_0 t). \tag{1}$$

Between the stochastic collisions the velocity of the particle is constant. The velocity u after a collision is expressed via the velocity v before the collision by the following formula

$$\begin{aligned} u &= (1-\alpha)v+\alpha v_0, \\ \alpha &= 2m_0/(m+m_0). \end{aligned} \tag{2}$$

The velocity of the particle is a Markov stochastic process. A kinetic or master equation for the time evolution of the p.d.f. $P(v, t)$ has the following form [8,9]

$$\begin{aligned} \frac{\partial}{\partial t}P(v,t) &= \int_{-\infty}^{+\infty}[W(z,v)P(z,t)-W(v,z)P(v,t)]\,dz \\ &= -\lambda_0 P(v,t)+\int_{-\infty}^{+\infty}W(z,v)P(z,t)\,dz. \end{aligned} \tag{3}$$

Here $W(v,u)$ is the transition probability (per unit time) for a $v \to u$ transition. $W(v,u)$ can be found using (2) provided that the velocity of the bath particle is taken from a Maxwellian distribution. It has the following form

$$W(v,u)=\frac{\lambda_0}{\alpha}\left(\frac{m_0}{2\pi k_B T_0}\right)^{1/2}\exp\left(-\frac{m_0}{\alpha^2 2k_B T_0}((\alpha-1)v+u)^2\right).$$

The equilibrium solution of the Equation (3) is a Maxwellian distribution. Any initial distribution $P_0(v)$ approaches this unique equilibrium distribution $P_{\mathrm{eq}}(v)$ as $t \to \infty$. A solution of the Equation (3) is found in the form

$$f(x,t)=\frac{1}{\sqrt{\pi\gamma}}\exp\left(-\frac{x^2}{2\gamma}\right)\psi(x)\exp(-\nu\lambda t), \tag{4}$$

where $x=v(m_0/2k_B T_0)^{1/2}$ is a reduced variable, and $\gamma=m_0/m$ is the mass ratio. A substitution of this function in (3) yields

$$(1-\nu)\psi(x)=A[\psi(x)].$$

Here the operator A is defined as follows

$$A[\psi(x)]=\frac{1}{\alpha\sqrt{\pi}}\int_{-\infty}^{+\infty}\exp(-\tfrac{1}{2}(x^2+y^2)-\rho(y-x)^2)\psi(y)dy,$$

$$\rho=(1-\gamma^2)/(4\gamma^2).$$

The values of ν under which the solution of (3) exists in the form (4) are connected with the eigenvalues μ of the operator A through $\nu=1-\mu$. In order to find the eigenvalue μ_n, it must be noted that

$$A\left[x^n\exp\left(-\frac{x^2}{2\gamma}\right)\right]=\left(\frac{1}{2\rho}\right)^n\exp(-(0.5+\rho)x^2)\frac{\partial^n}{\partial x^n}(\exp((\alpha\rho x)^2)).$$

This formula can also be expressed as

$$A\left[x^n\exp\left(-\frac{x^2}{2\gamma}\right)\right]=(\mu_1)^n\left[x^n+\sum_{m=1}^{k}C_m^n x^{n-2m}\right]\exp\left(-\frac{x^2}{2\gamma}\right), \tag{5}$$

where $\mu_1=\alpha^2\rho=(1-\gamma)/(1+\gamma)$, while $k=\mathrm{int}(n/2)$ is an integer part of $n/2$. Under any n the coefficients C_m^n could be obtained at once by the differentiation in the left side of the Equation (5). Further it is supposed that all C_m^n are known.

Let us define the function $\psi_n(x)$ as follows

$$\psi_n(x)=\left[x^n+\sum_{m=1}^{k}B_m^n x^{n-2m}\right]\exp\left(-\frac{x^2}{2\gamma}\right),\quad k=\operatorname{int}\left(\frac{n}{2}\right). \tag{6}$$

The constants B_m^n can be chosen in such a way that the function $\psi_n(x)$ will be an eigenfunction of the operator A corresponding to the eigenvalue μ_n. That is

$$A[\psi_n]=\mu_n\psi_n,\quad \mu_n=\left(\frac{1-\gamma}{1+\gamma}\right)^n,\quad n=0,1,\ldots,\infty. \tag{7}$$

Indeed, substituting (6) in (7) and using (5), the following recurrent relations are obtained, from which the coefficients B_m^n can be calculated by means of C_p^k

$$((\mu_1)^n-(\mu_1)^{n-2})B_1^n=(\mu_1)^n C_1^n$$

. . . .

$$((\mu_1)^n-(\mu_1)^{n-2m})B_m^n=(\mu_1)^n C_m^n+\sum_{i=1}^{m-1}(\mu_1)^{n-2i}C_{m-i}^{n-2i}B_{m-1}^n$$

. . . .

$$((\mu_1)^n-(\mu_1)^{n-2k})B_k^n=(\mu_1)^n C_k^n+\sum_{i=1}^{k-1}(\mu_1)^{n-2i}C_{k-i}^{n-2i}B_{k-1}^n$$

This system of equations has a unique solution for each $0<\gamma<1$. Finally, any solution of the kinetic Equation (3) can be represented in the form

$$P(v,t)=P_{\mathrm{eq}}(v)+\sum_{n=1}^{\infty}D_n\Phi_n(v)\exp(-v_n t). \tag{8}$$

Here the eigenvalues v_n and the eigenfunctions Φ_n are given by the following relations

$$\begin{gathered} v_n=\lambda\left(1-\left(\frac{1-\gamma}{1+\gamma}\right)^n\right),\\ \Phi_n(v)=\left(\frac{m}{2\pi k_B T_0}\right)^{1/2}\exp\left(-\frac{mv^2}{2k_B T_0}\right)\mathrm{p}_n\left(\left(\frac{m_0}{2k_B T_0}\right)^{1/2}v\right),\\ \mathrm{p}_n(x)=x^n+\sum_{m=1}^{k}B_m^n x^{n-2m},\quad k=\operatorname{int}\left(\frac{n}{2}\right). \end{gathered} \tag{9}$$

The constants D_n are determined by the initial conditions.

Brownian Dynamics Coupling

In the Brownian dynamics a force, which affects the particle from the bath, consists of two parts – a systematic friction $F_T = -m\eta v$ with damping constant η, and a stochastic noise F_S. The random force $F_S(t)$ is a Gaussian process with the following properties

$$\langle F_S(t)\rangle = 0, \quad \langle F_S(t)F_S(t+\tau)\rangle = 2k_B T_0 m\eta\delta(\tau).$$

In this case the particle velocity $v(t)$ is a Markov diffusional process. Evolution of the velocity p.d.f. $P(v,t)$ is governed by the Fokker-Plank equation

$$\frac{\partial}{\partial t}P(v,t) = \eta\left\{\frac{\partial}{\partial v}(vP) + \frac{k_B T_0}{m}\frac{\partial^2}{\partial v^2}P(v,t)\right\}. \tag{10}$$

The solution of (10) with an initial condition $P_0(v)$ can be represented in the form of Equation (8) with the following eigenvalues v_n^B and eigenfunctions Φ_n^B [10]

$$\begin{gathered} v_n^B = n\eta, \quad n = 1,\dots,\infty, \\ \Phi_n^B(v) = \exp\left(-\frac{mv^2}{2k_B T_0}\right)H_n\left(\left(\frac{m}{2k_B T_0}\right)^{1/2} v\right). \end{gathered} \tag{11}$$

Here $H_n(x)$ are the Hermite polynomial of the order of n.

3 RELATIONS BETWEEN PARAMETERS

To compare collisional dynamics and Brownian dynamics a connection between the parameters of these methods should be established. These parameters in the CD method are m, T_0, m_0, λ_0 and in the BD method m, T_0, η. Therefore an expression for damping coefficient η in terms of λ_0 and m_0 is the only needed one. There are several ways to find this expression. Here we present two ways with the same result, but each of them is worth by itself.

1. There is an asymptotical relation: the Brownian dynamics approximates the collisional dynamics in the limit $\alpha \to 0$. This diffusional approximation of the collisional dynamics can be obtained with the Van Kampen's method [9] from an expansion of the master Equation (3) in powers of small parameter α. The first order approximation yields the second order differential equation for the p.d.f. $P(v,t)$ instead of the integral one. This equation coincides with the Fokker-Plank Equation (10) if we set [4]

$$\eta = \lambda_0 \alpha. \tag{12}$$

If the damping constant η is fixed, according to (12), the collisional frequency λ_0 must approach an infinite limit ($\lambda_0 \to \infty$) as $\alpha \to 0$. This is in agreement with the well known condition of physical correspondence for the Brownian dynamics to frequent collisions with light particles.

2. Now, let us suppose that in the CD simulation the velocity of the particle at an initial time is given as $v^{(0)}$. Using the Equation(2), one can find that after k collisions the velocity of the particle becomes equal to

$$v^{(k)} = (1-\alpha)^k v^{(0)} + \alpha \sum_{i=1}^{k} (1-\alpha)^{k-i} v_0^{(i)}.$$

Here index i specifies the collisions, while $v_0^{(i)}$ is the velocity of the virtual bath atom at a collision number i. $v_0^{(i)}$ are the uncorrelated Gaussian random variables with properties

$$\langle v_0^{(i)} \rangle = 0, \quad \langle v_0^{(i)} v_0^{(j)} \rangle = \frac{k_B T_0}{m_0} \delta^{ij}.$$

Here δ^{ij} stands for Kronecker's delta. Now we can express random value of the particle velocity at any time t in the following form using Equation (1).

$$\begin{aligned} v(t) &= \sum_{k=0}^{\infty} v(k) g_k(t) \\ &= \left\{ v^{(0)} + \sum_{k=1}^{\infty} \left[(1-\alpha)^k v^{(0)} + \alpha \sum_{i=1}^{k} (1-\alpha)^{k-i} v_0^{(i)} \right] \frac{(\lambda_0 t)^k}{k!} \right\} \exp(-\lambda_0 t). \end{aligned} \tag{13}$$

By averaging Equation (13), one can find the mean value of the particle velocity at any time t in the CD simulations with the initial velocity $v^{(0)}$

$$\langle v(t) \rangle = v^{(0)} \exp(-\lambda_0 \alpha t). \tag{14}$$

The mean force acting on the particle can be defined via the velocity acceleration obtained from (13) by differentiation. It yields

$$\begin{aligned} F(t) &= m \left\langle \frac{dv(t)}{dt} \right\rangle = -m\lambda_0 \alpha v^{(0)} \exp(-\lambda_0 \alpha t) \\ &= -m\lambda_0 \alpha \langle v(t) \rangle. \end{aligned} \tag{15}$$

Thus, at any time t the mean force acting on the particle in the collisional dynamics is proportional to the mean velocity of the particle. Actually, it is a frictional force with damping coefficient equal to $\lambda_0 \alpha$. The requirement that this damping coefficient should coincide with the one in the Brownian dynamics leads to the relation (12). Let us note, that under condition (12) the mean particle velocity in the BD simulation at any time is also given by the expression (14).

4 COMPARISON BETWEEN COLLISIONAL DYNAMICS AND BROWNIAN DYNAMICS

Now we can compare the CD and the BD methods in two aspects assuming that the relation (12) is valid.

Energy Exchange Between Particle And Bath

Coupling to an external heat bath by means of the collisional dynamics provides a global exchange of energy between the particle and the bath according to the following mean rate [5]

$$\frac{dE}{dt}=\frac{1}{\tau_E}[\tfrac{1}{2}k_B T_0 - E_k(t)], \tag{16}$$

$$\tau_E=\frac{(1+\gamma)^2}{4\lambda_0\gamma}. \tag{17}$$

Here $E_k(t)$ is the current kinetic energy of the particle. If coupling to the bath is accomplished by the BD method, the Equation (16) is also valid. In this case, coupling time constant in the Equation (16) is found to be $\tau_E^B = 1/2\eta$. Thus, the global energy exchange between the particle and the bath in the CD simulation has greater relaxation time then it does in the BD simulation: $\tau_E/\tau_E^B = 1+\gamma$.

Velocity Relaxation Spectrum

Now we compare the considered methods in the aspect of the coupling induced velocity relaxation of the particle. The velocity relaxation is discussed in terms of the eigenvalue spectrum associated with the kinetic equation that describes the evolution of p.d.f. $P(v,t)$. In the case of the collisional dynamics the eigenvalues ν_n are given by the Equation (9). When $0<\gamma<1$, the relaxation spectrum $\{\nu_n\}$ is discrete and consists of the infinite number of points confined in the finite interval $[\lambda_0\alpha, \lambda_0)$. In particular, when $\gamma=1$ (the case of the Andersen's method) the spectrum consists of only one point $\nu_1=\lambda_0$. When the particle is coupled to a bath by the BD method, the relaxation spectrum is given by Equation (11). This spectrum $\{\nu_n^B\}$ is not bounded by any finite interval as it is in the case of the CD method, but is disposed in the infinite interval $[\eta, \infty)$. Note that both sets of the eigenvalues $\{\nu_n\}$ and $\{\nu_n^B\}$ are ordered according to their increasing values. Taking into account the relation (12) we see that the minimum eigenvalue for any $0<\gamma<1$ in the CD spectrum is the same as in the BD one: $\nu_1=\nu_1^B=\lambda_0\alpha$, whereas other corresponding eigenvalues differ from one another: $\nu_n\neq\nu_n^B$ for $n>1$. Comparison of the spectra $\{\nu_n\}$ and $\{\nu_n^B\}$ in the long time behavior domain gives some idea about the quality of the diffusional approximation of the collisional dynamics by the Brownian dynamics. In Figure 1 the ratio ν_n/ν_n^B is depicted. Note that $\nu_n\rightarrow\nu_n^B$ for $n>1$ in the limit $\alpha\rightarrow 0$, and $\lambda_0\rightarrow\infty$ with the proviso that $\lambda_0\alpha=\eta$ is constant.

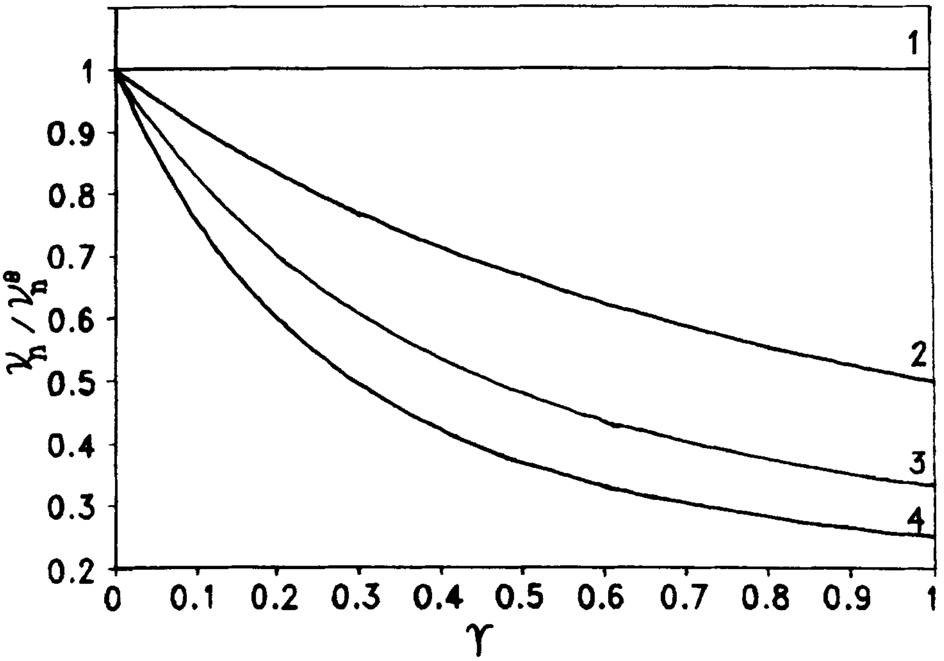

Figure 1 Comparison of the velocity relaxation spectra $\{\nu_n\}$ (Eq. 9) and $\{\nu_n^B\}$ (Eq. 11) using relation (12). The ratios ν_n/ν_n^B for $n = 1,2,3,4$ (lines 1, 2, 3, 4 accordingly) are shown as a function of the mass ratio $\gamma = m_0/m$.

5 CONCLUDING REMARKS

The problem of how the influence of solvent particles upon the solute can be approximated in MD calculations is of fundamental importance, because very often the needed computer resources for explicit simulation of all particles constituting a system are very expensive. In particular, this problem arises in the studies of dilute polymer solutions. For example, if a single chain molecule consisting of only a 100 monomer units is simulated, the required number of solvent molecules is of order of 10^6. Otherwise, the polymer molecule in an extended state will interact with its own images in the neighboring boxes.

Brownian dynamics equations correctly govern the long-time behavior of a macroscopical heavy particle immersed in a low-weight molecular solvent. The BD simulations can hardly be considered reliable in advance in the case of a molecule, which has the same size as solvent molecules, so special investigations are required to analyze it. In this type of investigations the solute properties obtained from the direct MD simulations of the whole system can be used as a model for comparison with those obtained by the BD ones. Such a comparison was made for some special cases [2,11,12]. For a pure liquid krypton it was demonstrated that though the solute structure is reasonably reproduced, marked discrepancies are observed in the dynamical evolution [11,12].

Collisional dynamics offers valid description of strong interactions occurring during collision of the particles, however ignores a great number of weak interactions with solvent molecules, which are not in the immediate vicinity of the solute. Nevertheless, Ref. [13] shows that the CD simulations reasonably reproduce the dynamical behaviour obtained by the direct MD simulations for the case of sulfur-iron cluster, which immersed in protein molecule.

In the present paper a comparison of the dynamics simulated by the BD and the CD methods is performed in the simplest case of one test particle constraint to one dimension. (Restriction to one dimension is not essential, and the main results are valid for the case of three dimensions). It was demonstrated that though both methods generate states in the same canonical ensemble, the relaxation spectra are different. Particularly, if a particle is placed in the solvent constituting of the same particles, the relaxation time for the global energy exchange between the particle and its environment in the CD method is twice as great as in the BD one, provided that average particle velocity at any time is the same in both methods.

In the present work it is shown that the dynamical behavior in the CD simulations does differ noticeably from that in the BD simulations. To find out which method reproduces the dynamics of a real system most adequately, further investigations are required.

Acknowledgments

This work was partly supported by Russian Foundation for Fundamental Researches Grant No. 93-03-4611.

References

[1] D. L. Ermak and J. A. McCammon, "Brownian dynamics with hydrodynamic interactions", *J. Chem. Phys.*, **69**, 1352 (1978).
[2] W. F. van Gunsteren, H. J. C. Berendsen and J. A. C. Rullmann, "Stochastic dynamics for molecules with constraints. Brownian dynamics of *n*-alkanes", *Molec. Phys.*, **44**, 69 (1981).
[3] H. C. Andersen, "Molecular dynamics simulations at constant pressure and/or temperature", *J. Chem. Phys.*, **72**, 2384 (1980).
[4] A. S. Lemak, *Collisional dynamics for molecules with constraints*, Preprint, Research Computing Centre of the Russian Academy of Sciences, Pushchino (1992).
[5] N. K. Balabaev and A. S. Lemak, "Molecular dynamics simulation of a linear polymer in hydrodynamic flow", *Rus. J. Phys. Chem.* **69**, 24 (1995).
[6] J. D. Doll and D. R. Dion, "Generalized Langevin equation approach for atom/solid-surface scattering: Numerical techniques for Gaussian generalized Langevin dynamics", *J. Chem. Phys.*, **65**, 3762 (1976).
[7] G. Ciccotti and J.-P. Ryckaert, "Computer simulation of the generalized brownian motion. I. The scalar case", *Molec. Phys.*, **40**, 141 (1980).
[8] M. R. Hoare and M. Rahman, "On the spectral theory of Rayleigh's piston. I. The discrete spectrum", *J. Phys. A*, **6**, 1461 (1973).
[9] N. G. van Kampen, "A power series expansion of the master equation", *Can. J. Phys.*, **39**, 551 (1961).
[10] R. I. Cukier, K. Lakatos-Lindenberg and K. E. Shuler, "Orthogonal polynomial solutions of the Fokker-Planck equation", *J. Stat. Phys.*, **9**, 137 (1973).
[11] A. Giró, E. Guardia and J. A. Padró, "Langevin and molecular dynamics simulation of Lennard-Jones liquids", *Molec. Phys.*, **55**, 1063 (1985).
[12] J. A. Padró, E. Guardia and A. Giró, "Langevin dynamics simulation of L-J liquids. An analysis of solute concentration influence", *Molec. Phys.*, **57**, 687 (1986).
[13] A. S. Lemak and N. K. Balabaev, "On the Berendsen thermostat", *Molec. Simul.*, **13**, 177 (1994).