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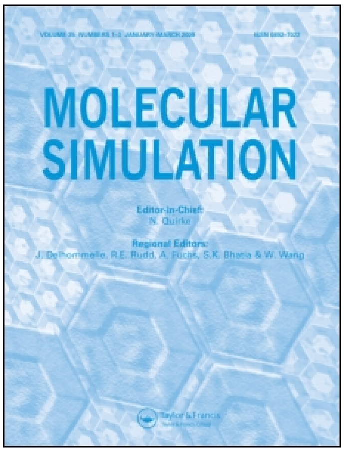

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On The Berendsen Thermostat

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ON THE BERENDSEN THERMOSTAT

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The behaviour of the total momentum of a system immersed in the Berendsen thermostat is analyzed. It has been found that under certain conditions the kinetic energy of the system can be transformed from internal degrees of freedom to the external ones, and conversely. A concrete example of such a transformation is presented. The results of molecular dynamics simulations of the $Fe_4S_4(SH)_4$ complex coupled to different external heat baths are discussed.

KEY WORDS: Molecular dynamics, heat bath, Berendsen thermostat, collisional dynamics

1 INTRODUCTION

Molecular dynamics simulation methods have become an important technique for the study of the dynamical properties of liquids, molecular solutions, and macromolecules. There are a number of situations where the system under simulation is not isolated and exchanges energy with the external bath. One widely used method to couple a system to a heat bath is the so called method of "*weak coupling to an external bath*" (WCEB), which has been proposed by Berendsen *et al.* [1]. This method is also referred to as the Berendsen thermostat. Sometimes the Berendsen thermostat is considered to correspond to the canonical ensemble, but simulation by the WCEB method does not correspond exactly to any of the standard thermodynamic ensembles. This work presents another peculiarity of the Berendsen thermostat. It is demonstrated that coupling to a bath by the WCEB method can induce a redistribution of the kinetic energy of the system between external and internal degrees of freedom during the simulation. As a result two extreme positions can be achieved:

1) Nearly the whole kinetic energy of the system is concentrated in the internal degrees of freedom;
2) A considerable part of the kinetic energy has been transformed to external degrees of freedom, corresponding to a motion of the system as a whole.

In the second position the temperature, calculated from the velocities of internal degrees of freedom, is found to be below its prescribed value. The way in which the kinetic energy is shared by internal and external motions is "*a priori*" unknown. The first situation is likely to be the typical one. An example, when the second situation is realized is given below.

In the present work we also give the results of molecular dynamics (MD) simulation of a $Fe_4S_4(SH)_4$ complex immersed in a bath. This simulation appeared interesting due to the following circumstances. In reference [2] MD simulation at constant temperature of the protein ferredoxin is performed. This low molecular weight protein contains two Fe_4S_4 clusters. Each cluster is attached to the protein matrix through the four Fe-S_γ bonds, where S_γ are sulfur atoms of the cysteine residues. The following question arises here: in what way does the protein matrix influence the internal dynamics of $Fe_4S_4(S_\gamma)_4$ complexes? If the proper MD trajectory of the complex immersed in a heat bath is obtained, a comparison of this trajectory with the one in the protein could reveal a specificity of the protein influence. The results of such comparison will be reported elsewhere. Here we outline the results of computer experiments that concern the obtaining of the proper MD trajectory of the complex coupled to a bath. A trajectory is considered to be the proper one if energy exchange between the complex and the thermostat along the trajectory is the same as in the case when the complex is immersed in the protein. The energy exchange can be characterized by the value of r.m.s. fluctuations of the complex energy and the energy autocorrelation function. Our attempts to obtain the proper MD trajectory of the complex using the WCEB method have failed. The aim has been attained when an alternative method to couple the complex to a bath was used. This alternative method, called in reference [3] collisional dynamics (CD), is a modification of Andersen's one [4].

2 MODEL AND DETAILS OF SIMULATION

Valence structure of the $FE_4S_4(SH)_4$ complex is shown in figure 1. A heavy atoms model of the complex consists of 12 atoms of three types. The potential energy of the complex includes only the deformation energy of valence bond lengths and valence angles. The parameters for quadratic functions of the stretching and bending were taken as in reference [2].

To couple the complex to an external heat bath without explicitly simulating solvent molecules, two different algorithms are used: an algorithm of the WCEB method and an algorithm of the collisional dynamics. In the WCEB method at each time step all atomic velocities are rescaled with the relaxation time τ_T if the temperature of the system T(t), calculated from velocities, deviates from the prescribed value T_0 [1]. In this case the equations of motion are given by

$$m_\alpha \frac{d^2\vec{r}_\alpha}{dt^2} = -\frac{\partial}{\partial \vec{r}_\alpha} U(\mathbf{r}(t)) + \frac{m_\alpha}{2\tau_T}\left(\frac{T_0}{T(t)} - 1\right)\cdot \vec{v}_\alpha, \quad \alpha = 1, \ldots, N \tag{1}$$

with

$$T(t) = \frac{1}{3Nk_B}\sum_1^N m_\alpha \vec{v}_\alpha^2$$

In the collisional dynamics the coupling to a bath is simulated by collisions with virtual bath particles. The collisions occur in accordance with a Poisson process and the time moments at which different atoms suffer collisions are statistically uncorrelated. Between the stochastic collisions the system evolves in accordance with Hamilton's equations as in the usual molecular dynamics. Each stochastic collision is an instantaneous event that affects the velocities. The values of the velocities after

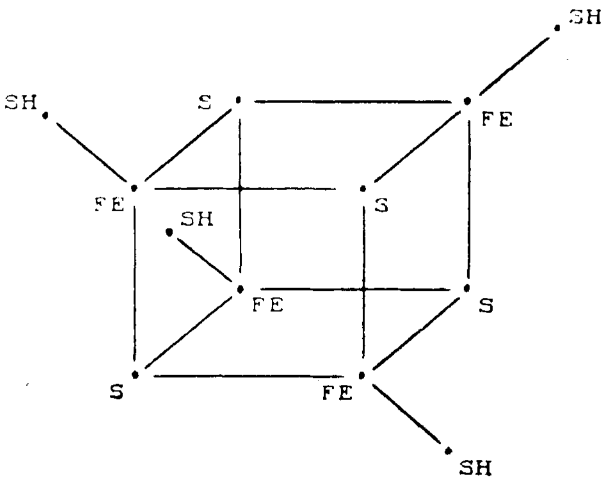

Figure 1 The heavy atoms model of (FE_4S_4) $(SH)_4$ complex.

collision are found by solving a collisional problem. In this problem the velocity $\vec{v}_0$ of the bath particle is chosen at random from a Maxwellian distribution.

$$P_M(\vec{v}_0) = \left(\frac{m_0}{2\pi k_B T_0}\right)^{\frac{3}{2}} \exp\left(-\frac{m_0 v_0^2}{2k_B T_0}\right)$$

To carry out collisional dynamics simulation numerical values should be chosen for the bath temperature T_0, the mass of the bath particle m_0, and the collision frequency λ.

All simulations were started from the same initial conditions. The time step was chosen as 0.001 ps. Each run was carried out during 100 ps. Coordinates were stored at every 10 time steps. Temperature of the bath T_0 was used as 300 K. In WCEB simulations several values of the coupling time constant τ_T were chosen. In CD simulations we took $m_0 = 15$ atomic mass unit, and a few values of collision frequency λ.

We also took the trajectories of (FE_4S_4) $(S_\gamma)_4$ complexes extracted from the MD trajectory of the protein ferredoxin [2] to compare with our simulations.

3 ENERGY FLUCTUATIONS

For thermodynamical characterization of the system studied under different conditions, the mean values of the total E_{tot}, the kinetic E_{kin}, and the potential E_{pot} energies of the complex and their r.m.s. fluctuations were calculated and are presented in table 1 for various coupling to the heat bath and for coupling to protein environment. For a canonical ensemble system of 12 atoms at 300 K one would expect the mean value of the kinetic energy $\langle E_{kin} \rangle = 44.89$ kJ/mol and its r.m.s. fluctuations $\delta E_{kin} = 10.59$ kJ/mol. If we imply that the potential energy is a

Table 1 Mean values and r.m.s. deviations*) of the total, kinetic and potential energies of $(FE_4S_4)(SH)_4$ complex for various coupling of the cluster to the environment.

Coupling	$\langle E_{tot}\rangle$	$\langle E_{kin}\rangle$ 1)	$\langle E_{pot}\rangle$ 2) *(kJ/mol)*	δE_{tot}	δE_{kin}	δE_{pot}
WCEB method:						
$\tau_T = 5.00$ ps	89.58	44.69	44.69	0.07	7.82	7.82
$\tau_T = 0.50$ ps	89.83	44.81	44.81	0.46	7.32	7.32
$\tau_T = 0.10$ ps	89.66	44.85	44.77	1.34	4.31	4.52
$\tau_T = 0.01$ ps	89.66	44.85	44.77	4.81	1.38	5.02
CD method:						
$\lambda = 12\,ps^{-1}$	81.38	44.22	44.35	15.19	10.71	10.67
$\lambda = 24\,ps^{-1}$	84.73	46.07	46.07	11.34	9.83	9.79
$\lambda = 48\,ps^{-1}$	87.49	47.45	47.45	13.18	10.29	10.29
$\lambda = 80\,ps^{-1}$	82.84	45.06	45.19	12.55	9.75	9.75
in PROTEIN:						
complex 1	98.49	46.65	46.65	15.94	10.42	10.42
complex 2	91.63	45.69	45.60	15.06	10.46	10.46

*) All mean values are calculated as a time averages using 100 ps MD trajectories.

1) The value $\langle E_{kin}\rangle = 44.89$ kJ/mol corresponds to the temperature $T = 300$ K.

2) In E_{pot} of the complex in the protein only potential energy of the internal degrees of freedom was included.

quadratic function of atomic displacements, we obtain $\delta E_{pot} = 10.59$ kJ/mol and $\delta E_{tot} = ((\delta E_{kin})^2 + (\delta E_{pot})^2)^{1/2} = 14.94$ kJ/mol. From table 1 it can be concluded that in CD simulations and in the protein the complex behaves as in a canonical ensemble. Moreover, in CD simulations the value of λ does not influence on the mean value of energy fluctuations. In WCEB simulations the values of r.m.s. fluctuations of the energies differ considerably from the canonical ones. In this case the value of r.m.s. fluctuations is influenced by the value of the time constant τ_T. But a suitable agreement with canonical ensemble can not be achieved by the proper choice of τ_T because the value of τ_T influences δE_{kin} and δE_{tot} differently. A decrease in τ_T yields an increase in δE_{tot} and a decrease in δE_{kin} [1]. It is worthy of note that as τ_T increases, the system is clearly moving closer towards the microcanonical ensemble for which $\delta E_{tot} = 0$.

The dynamics of energy fluctuations can be described in terms of the energy autocorrelation function $C_E(\tau) = \langle(E(t) - \langle E\rangle)(E(t + \tau) - \langle E\rangle)\rangle$. Autocorrelation functions obtained from the various trajectories show that the dynamical behaviour of the energy in CD simulations differs from that in WCEB simulations. These autocorrelation functions are shown in figures 2 and 3. Each of them can be interpreted in a traditional way by comparison with the corresponding one for a harmonically bound Brownian particle. In WCEB simulations energy behaves like an underdamped oscillator. In CD simulations autocorrelation functions show overdamped oscillations of energy. An effective damping coefficient is altered by changing λ. Autocorrelation functions show (figure 4) that the behaviour of energy fluctuations of the complex in protein and in the CD simulations seems to agree reasonably well in contrast to the case of the WCEB simulations. Especially, the coincidence of the kinetic energy autocorrelation functions is remarkable.

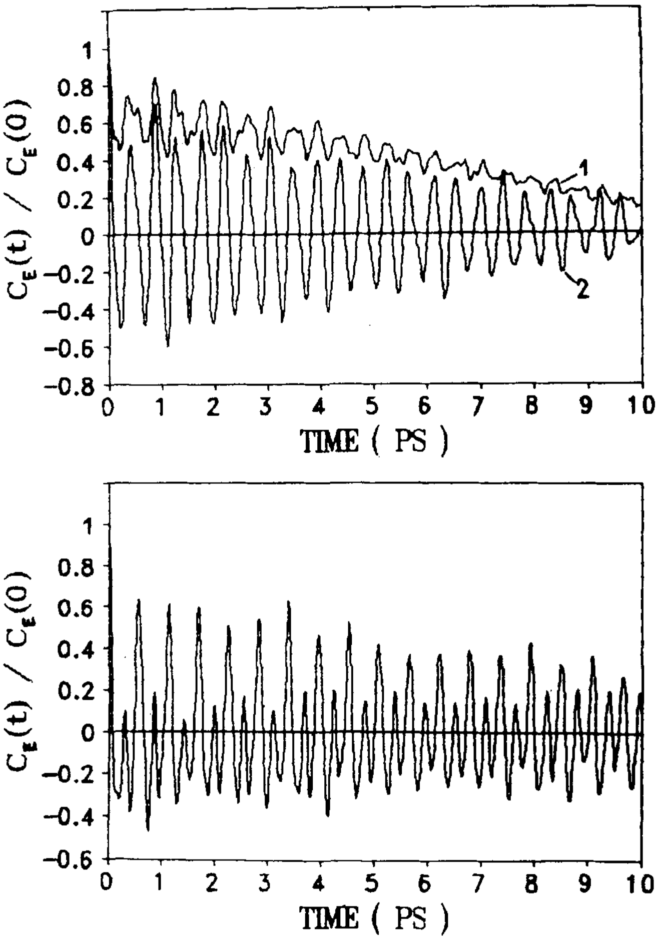

Figure 2 Comparison of the total energy autocorrelation functions $C_E(t)$ of $(FE_4S_4)(SH)_4$ complex obtained from different 100 ps trajectories. Simulation was performed by WCEB method with various values of time constant τ_T. Above: $\tau_T = 5$ ps (line 1), $\tau_T = 0.5$ ps (line 2). Below: $\tau_T = 0.01$ ps.

4 BEHAVIOUR OF TOTAL MOMENTUM IN BERENDSEN THERMOSTAT

The following behaviour of the complex in WCEB simulation with $\tau_T = 0.25$ ps is worthy of note. In this run during the first 300 ps the complex energy fluctuates about 90.0 kJ/mol. This is followed by transition into a new state during 100 ps. In this new state the energy fluctuates about 68.2 kJ/mol with the lesser amplitude. Also the amplitudes of both kinetic energy and potential energy fluctuations have decreased considerably (see figure 5). It means that the energy of internal oscillations has been transformed partly to the energy of a motion of the complex as a whole. That is, internal oscillations have cooled down. The same behaviour of the

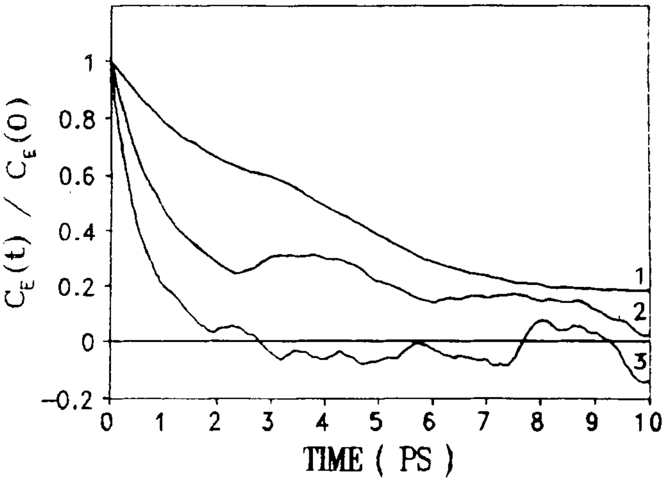

Figure 3 Comparison of the total energy autocorrelation functions $C_E(t)$ of (FE_4S_4) $(SH)_4$ complex obtained from different 100 ps trajectories. Simulation was performed by CD method with various values of collision frequency λ: $\lambda = 12\,ps^{-1}$ (line 1), $\lambda = 24\,ps^{-1}$ (line 2), and $\lambda = 48\,ps^{-1}$ (line 3).

complex was observed when MD trajectory was started from different initial conditions.

It can be shown from equation (1), that a value of the total momentum of the system $P = \left|\sum_1^N m_\alpha \vec{v}_\alpha\right|$ evolves in WCEB method simulations accordingly to the equation

$$\frac{dP}{dt} = \xi(t)P \tag{2}$$

$$\xi(t) = \left(\frac{K}{E_k(t)} - 1\right) \tag{3}$$

Here the reduced time scaled by $2\tau_T$ is used. The kinetic energy E_k of the system is kept near its mean value $K = \frac{3N}{2} k_B T_0$. This energy is shared by the internal motions and by motion of the system as a whole. The value of P indicates what part of the energy E_k corresponds to translational motion of the system.

To analyze the possible behaviour of P in the WCEB simulation, the equation (2) with $\xi(t)$ is to be considered as a stochastic process. Real stochastic property of the $\xi(t)$ in WCEB simulations are not known and it is rather difficult to establish it. Along the MD trajectory $\xi(t)$ takes both positive and negative values. But its mean value is not necessarily equal to zero. It should be noted, that if $\xi(t)$ is a stochastic process obtained from eq. (3) with $E_k(t)$ assumed to behave as the kinetic energy in canonical ensemble, then $\xi(t)$ is a stationary process the mean value of which can be found by using well known distribution for the E_k. It yields

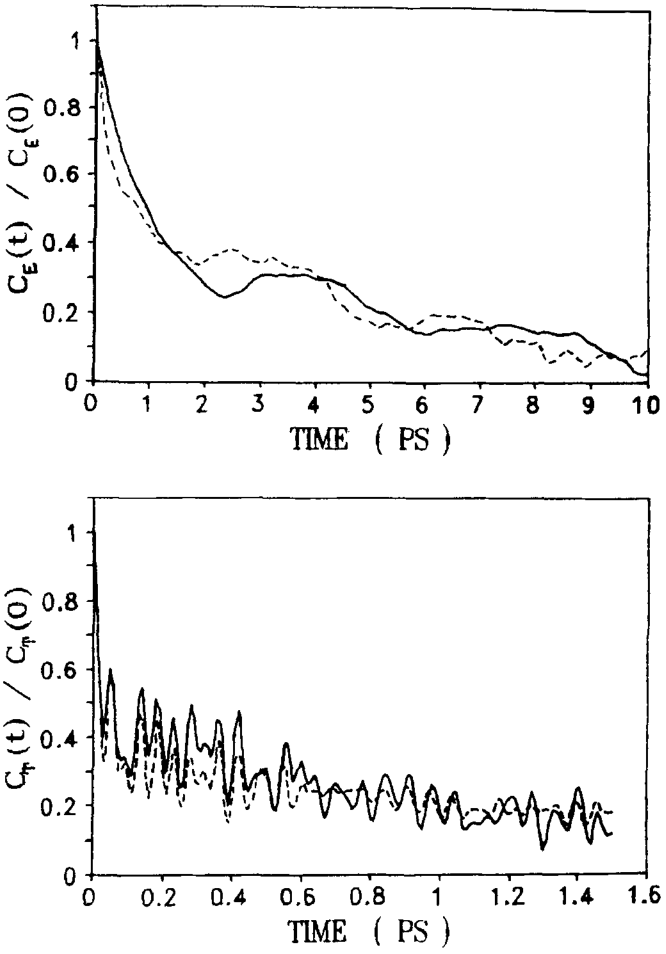

Figure 4 Comparison of the total energy autocorrelators $C_E(t)$ (above) and of the kinetic energy autocorrelators $C_T(t)$ (below) of $(FE_4S_4)(SH)_4$ complex obtained from different 100 ps trajectories. Solid line - trajectory performed by CD method with $\lambda = 24\ ps^{-1}$, dashed line - trajectory of complex 1 in protein ferredoxin [2].

$$\langle \xi(t) \rangle = \frac{1}{3N/2 - 1}$$

Thus, in this case the value of $\langle \xi(t) \rangle$ is strictly positive.

Here the model situation is considered. In this model $\xi(t)$ is supposed to be a stationary Gaussian process with

$$\langle \xi(t) \rangle = \varepsilon, \qquad \langle (\xi(t) - \varepsilon)(\xi(t + \tau) - \varepsilon) \rangle = 2\sigma^2 \delta(\tau) \tag{4}$$

In this case the stochastic differential equation (2) can be solved analytically. Integration of both sides of equation (2) yields

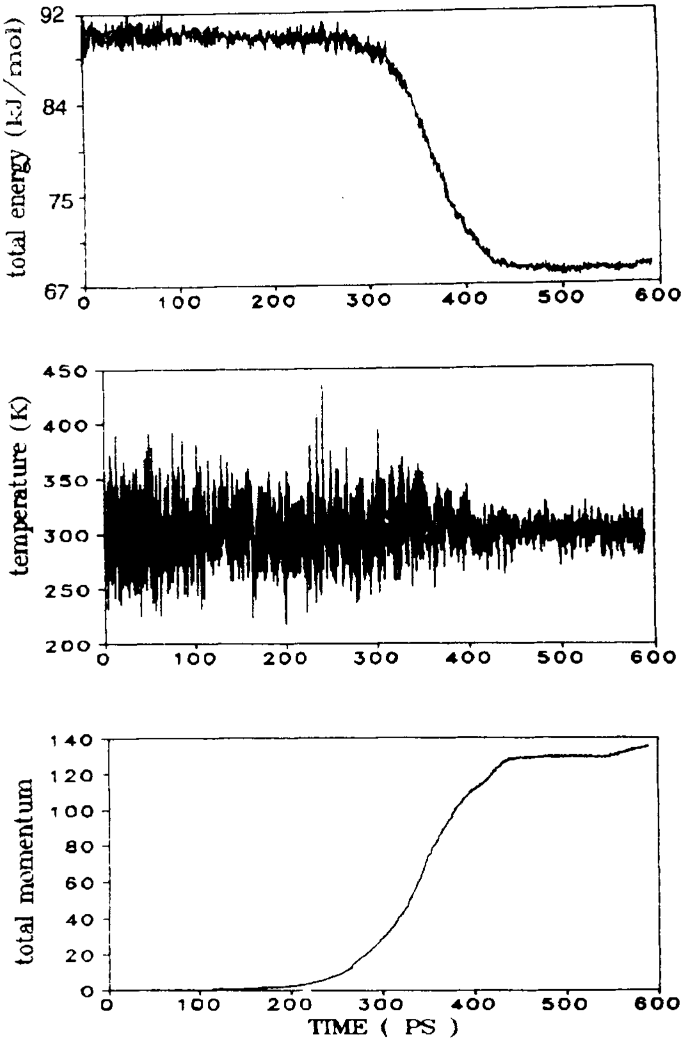

Figure 5 Evolution of the total energy, temperature, and total momentum of (FE_4S_4) $(SH)_4$ complex in the run carried out using WCEB method with time constant $\tau_T = 0.25$ ps. The momentum is given in MD units (a.m.u. Å ps^{-1}).

$$\int_0^t \xi(t')\mathrm{d}t' = \mathrm{Ln}\left(\frac{P}{P_0}\right) \tag{5}$$

Here the initial condition is implied to be $P(0) = P_0 > 0$. The stochastic variable $\nu = \int_0^t \xi(t')\mathrm{d}t'$ is a Gaussian one with the following moments [5]

$$\langle \nu(t) \rangle = \varepsilon t, \qquad \langle (\nu(t) - \varepsilon t)^2 \rangle = 2\sigma^2 t$$

Now, the momentum probability distribution function (p.d.f.) $f(P, t; P_0)$ under the condition $P(0) = P_0$ can be found using (4) and (5). It has at any time t the following form

$$f(P, t; P_0) = \frac{1}{2\sqrt{\pi\sigma^2 t}\,P} \exp\left\{-\frac{[Ln(P/P_0) - \varepsilon t]^2}{4\sigma^2 t}\right\} \tag{6}$$

This distribution takes the value 0 at $P = 0$, ∞ and is one peak shaped. The time evolution of the p.d.f. can be analyzed in terms of two variables. One is the position of the peak $P_m(t)$ and another is its height $f_m(t) = f(P_m, t; P_0)$. It can be found from (6) that

$$P_m(t) = P_0 e^{(\varepsilon - 2\sigma^2)t}, \qquad f_m(t) = \frac{1}{2\sqrt{\pi\sigma^2 t}\,P_0} \exp\{(\sigma^2 - \varepsilon)t\}$$

There are three different types of behaviour for the p.d.f., which are determined by values of ε and σ.

i) In the case $\sigma^2 > \varepsilon$ the initial sharply peaked distribution first broadens up to the time moment $t_1 = 0.5/(\sigma^2 - \varepsilon)$, and then it narrows so that the probability distribution is concentrated at $P_m(t)$, which decays to zero, as $t \to \infty$. Such behaviour of this type is shown in Figure 6.

ii) In the case $\varepsilon/2 \leq \sigma^2 < \varepsilon$ the initial peaked distribution permanently broadens. The position of the peak either remains immobile at $P = P_0$ (only if $\sigma^2 = \varepsilon/2$), or decays to zero.

iii) When $\sigma^2 < \varepsilon/2$, the position of the peak shifts to infinity, as $t \to \infty$, and the distribution subsequently relaxes towards the 'homogeneous' one.

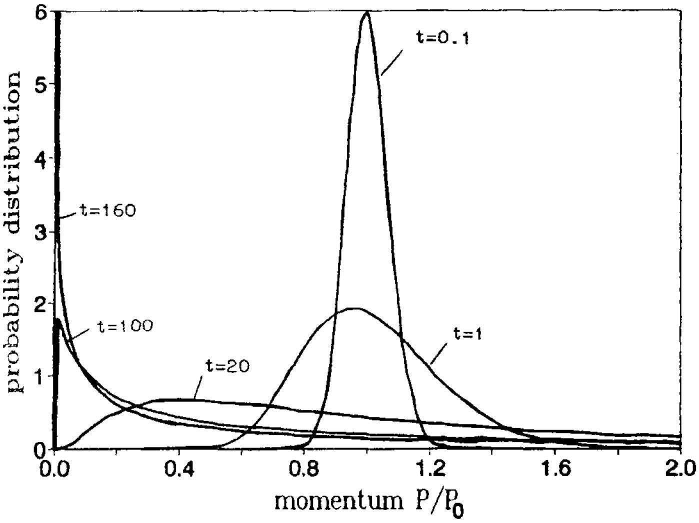

Figure 6 Relaxation of an initial probability distribution according to Eq. 6 with $\varepsilon = 0$, and $\sigma = 0.15$. A reduced time scaled by $2\tau_T$ is used. Initial condition is $P(0) = P_0$.

The right-hand side of equation (2) can be represented by two terms

$$\frac{\mathrm{d}P}{\mathrm{d}t} = \varepsilon P + z(t)P \tag{7}$$

$$\text{with} \quad \langle z(t) \rangle = 0, \qquad \langle z(t)z(t+\tau) \rangle = 2\sigma^2\delta(\tau).$$

The first term in (7) causes the p.d.f. evolution, which is in a way opposite to that caused by the second term. If the first term in (7) exceeds the second one (that is $\varepsilon > 2\sigma^2$), then the value of momentum P increases, as $t \to \infty$, and when the p.d.f. becomes nearly a 'homogeneous' one, there is no well-defined value of P. On the contrary, if the second term in (7) is more then the first one (that is $\sigma^2 > \varepsilon$), then, as $t \to \infty$, the momentum decays to zero, and its fluctuations practically vanish (see figure 6).

Analysis of MD trajectories of the complex shows that the ε and σ vary with time. What is more important, the sign of the expression $(\sigma^2 - \varepsilon)$, which is responsible for the manner in which the momentum evolves, also varies along the trajectory. Thus, along the MD trajectory two terms in equation (7) dominate each other in turn, and this can reasonably lead to the nontrivial behaviour of the momentum, observed in the calculations [6].

5 CONCLUDING REMARKS

The WCEB method of coupling a system to an external heat bath is easy to implement and is widely used. We have used this method to simulate a model system. It has been demonstrated in our study that the coupling to the Berendsen thermostat can drive the system to an undesirable physical state, and that fluctuations of the total energy of the simulated system are unphysical. On the other hand, an alternative method, "collisional dynamics", corresponds to the canonical ensemble, and its parameters have clear physical meaning. We believe that when the dynamics of fluctuations are expected to be relevant, the collisional dynamic method is more appropriate.

Acknowledgements

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[6] As noted by a referee of this article, the effect that total momentum is not conserved in WCEB simulations has been noted by others who use this method. The simple recipe to avoid this is built into the GROMOS program package: reset the center of mass velocity to zero, either each step or at regular intervals.