

# Combining Berendsen Thermostat with Dissipative Particle Dynamics (DPD) for Polymer Simulation

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*In this article we present a new thermostat – theory and simulation results – obtained by combining two thermostats – Berendsen and DPD types. The new thermostat provides a predictable behavior with temperatures that do not deviate from the reference and with thermal rate constant agreement between simulations and theory. The presented work can be used for the study of polymer properties.*

*Keywords: molecular dynamics, polymers, thermostats*

Molecular dynamics has become an important tool in the study of dynamical properties of molecular solutions, liquids, macro-molecules [1]. They are also used nowadays as an alternative (or in parallel) to the laboratory experiments to study the properties of polymers [2]. In engineering, computer science, mathematics, physics and molecular dynamics, multiscaling is a field of solving physical problems which have important features at multiple scales. The concept of molecular dynamics multiscaling [3] are tightly connected to the dual thermostat scheme developed here because the new algorithms in the field of molecular dynamics multiscaling have required the development of new thermostats.

The purpose of this article is to present a simple and efficient algorithm for a combined scheme of Dissipative Particle Dynamics (DPD) thermostat and Berendsen (B) thermostat. In a previous article [4] we presented an algorithm for the combination of the SD (Stochastic Dynamics) thermostat and Berendsen thermostat. Also an overview of the properties of new thermostats was underlined [4]. Now, a complementary method is applied, the SD thermostat is replaced with the DPD thermostat. An overview of the DPD influence on the molecular dynamic properties will be discussed at the end of this paper.

Global thermostat algorithms lead to a so-called ice-cube effect, in which the energy of high-frequency modes is drained into low-frequency modes, particularly into zero-frequency motions such as overall translation. Our work in multiscaling led us encountering an ice-cube effect. Our attempts for solving this problem included the use of Dissipative Particle Dynamics (DPD) thermostats [5]: we developed thermostating schemes that, while more efficient than the ones from the literature, still displayed the shortcomings of the stochastic thermostat - even though the dynamic properties were to some extent better preserved. Our intention is to use the new thermostat presented in this paper for eliminating the ice-cube effect in multiscaling simulation. The algorithms presented in this article will be also used for studying the properties of polymers with the scope of improving their characteristics and the materials based on them. This is future work.

This article is organized as follows: first a theoretical background is presented in the next section, then simulation results of the combined thermostat will be described in the experimental part. At the end we will draw the conclusions.

## *Theoretical part*

In this section, we will discuss the theoretical background of DPD and Berendsen combined thermostat. The first subsection outlines the global Berendsen thermostat. The second subsection gives the theory for the dissipative particle dynamics (DPD) thermostat in combination with the global Berendsen thermostat. Then a thermostat behaviour for the DPD case is described. The last subsection presents the combination of the two thermostats.

## *Berendsen thermostat*

In this section we will present a short outline of the theory for global Berendsen. A detailed presentation can be found in [6, 7]. First we consider a coupling between a molecular system – with temperature  $T$  – and a bath – with temperature  $T_{ref}$ . This can be done by inserting extra terms for friction and noise in the equation of motion, which will result in a Langevin equation of the following form:

$$m_i v_i' = F_i - m_i \gamma_i v_i + R(t), \quad (1)$$

where  $R_i$  is a stochastic Gaussian variable with null mean and with intensity

$$\langle R_i(t) R_j(t + \tau) \rangle = 2m_i \gamma_i k_B T_{ref} \delta(\tau) \delta_{ij}. \quad (2)$$

and  $F_i$  is the systematic force,  $\gamma_i$  is the friction rate,  $v_i$  is the velocity and  $m_i$  the mass of the particle.

Through the Langevin equation the system is locally subject to random noise and couples globally to a heat bath. In order to impose global coupling with minimal local disturbance we should modify (1) so that only the global coupling influence remains.

For making the analytical computation easier we chose the friction constant to be the same for all particles:  $\gamma_i = \gamma$ . This is a matter of choice; different classes of degrees of

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freedom can be coupled to the bath with different friction constants. From the derivation of the kinetic energy  $E_k$  we can see the time dependence of  $T$ :

$$\frac{dE_k}{dt} = \lim_{\Delta t \rightarrow 0} \frac{\sum_{i=1}^{3N} \frac{1}{2} m_i v_i^2(t + \Delta t) - \sum_{i=1}^{3N} \frac{1}{2} m_i v_i^2(t)}{\Delta t}, \quad (3)$$

where  $N$  is the number of particles, and

$$\Delta v_i = v_i(t + \Delta t) - v_i(t) = \frac{1}{m_i} \int_t^{t+\Delta t} [F_i(t') - m_i \gamma v_i(t') + R_i(t')] dt \quad (4)$$

Using the relation (2)

$$\sum_{i=1}^{3N} \int_t^{t+\Delta t} \int_t^{t+\Delta t} dt'' R_i(t') R_i(t'') = 6N m_i \gamma k_B T_{ref} \Delta t, \quad (5)$$

and the fact that  $R_i(t')$  is uncorrelated with  $v_i(t)$  and  $R_i(t)$  for  $t' > t$ , we obtain

$$\frac{dE_k}{dt} = \sum_{i=1}^{3N} v_i F_i + 2\gamma \left( \frac{3N}{2} k_B T_{ref} - E_k \right). \quad (6)$$

In terms of temperature we have the following equation

$$\left( \frac{dT}{dt} \right)_{bath} = 2\gamma (T_{ref} - T). \quad (7)$$

We can remark that the time constant  $\tau_T$  equals  $(2\gamma)^{-1}$ . Looking at equation (1) and (7), it can be noted that the global additional temperature coupling equation (7) is accomplished by the equation:

$$m_i v_i' = F_i + m_i \gamma \left( \frac{T_{ref}}{T} - 1 \right) v_i \quad (8)$$

Without adding local stochastic terms, according to (8) it follows that:

$$\frac{dE_k}{dt} = \sum m_i v_i v_i' = \sum_{i=1}^{3N} v_i F_i + 3N \gamma k_B (T_{ref} - T), \quad (9)$$

which is equivalent to (6). In this way we come to (8) as the new equation of motion. This represents a proportional scaling of the velocities from  $v$  to  $\lambda v$  with

$$\lambda = 1 + \frac{\Delta t}{2\tau_T} \left( \frac{T_{ref}}{T} - 1 \right) v_i. \quad (10)$$

The change in temperature can also be made equal to  $\frac{(T_{ref} - T)\Delta t}{\tau_T}$ , yielding

$$\lambda^2 - 1 = \frac{\Delta t}{k_{Ber}} \left( \frac{T_{ref}}{T} - 1 \right), \quad (11)$$

$$\text{where } k_{Ber} = \frac{0.5 * 3N k_B}{C_V \tau_T} \quad (12)$$

and  $C_V = N * c_V$  is the heat capacity of the system. (13)

The rate constant  $k_{Ber}$  can be rewritten using equation (12) and (13) as:

$$k_{Ber} = \frac{1.5 k_B}{c_V \tau_T} \quad (14)$$

### Dissipative Particle Dynamics

The main idea of the DPD-like friction and noise is that it is applied to relative velocities between pairs of particles. Theoretically, if the pairwise application is well resolved it should ensure the conservation of total linear momentum. The friction and noise can be applied isotropically to the velocity difference vector. Also, between two particles the velocity vector can be split into a component perpendicular to the inter-particle vector and a component parallel to it. This results in a three dimensional vector: because the parallel component has one dimension and the perpendicular component has two dimensions - from its definition in a plane.

In pure DPD [9] only the parallel component is used. The perpendicular form has been introduced by Junghans et al. [10] and the isotropic three dimensional form is in fact a combination of both. We will consider all three possibilities. In all three cases there is a velocity reduction factor  $f = 1 - \exp(-\gamma \Delta t)$  and a damping rate factor  $\gamma$ . These factors depend on the inter-particle distance: a cutoff distance beyond which the impulsive friction and noise is not applied ( $f = 0$ ) should be chosen.

For determining the inter-particle distance, usually one uses the short range pair particle list that is already constructed for the computation of forces. In DPD the dumping factor is scaled with a factor which depends on the distance between two pairs of particles; the original DPD chooses a linear bound between 1 ( $r = 0$ ) and 0 ( $r = r_c$ ).

A first sub-step is the selection of a pair of particle that will be subject to the impulsive friction and noise. This pair selection can be done in several ways. We consider the selection of one neighbor per particle. The selection can be made at random, but it can also be based on a distance-

weighted probability, e.g. proportional to  $1 - \frac{r_{ij}}{r_c}$ . A selected pair can be subject to friction and corresponding noise, with the friction either:

- isotropically in the direction of the velocity itself (iso)
- parallel to  $r_{ij}$  (par)
- perpendicular on  $r_{ij}$  (perp)

In the following we will chose one of the three possibilities or one combination of them. Each choice can be applied to one or more pairs, also different choices can be applied to the same particle pair.

### Algorithm:

I. for  $i, j$  simulation pair step do:

- I.1. choose the velocity reduction factor  $f = f_{iso} f_{dpp} f_{perp}$
- I.2. determine the velocity noise factor  $g$

$$g = \sqrt{f(2-f) k_B T_{ref} / \mu}, \quad (15)$$

$$\text{where } \mu = \frac{m_i m_j}{m_i + m_j} \quad (16)$$

is the reduced mass of the two particles.

I.3. construct the relative velocity vector  $v$

$$v = \lambda_B (v_i - v_j) \quad (17)$$

I.4. if iso:

I.4.a. choose 3 random numbers  $\xi = (\xi_1, \xi_2, \xi_3)$  from a standard normal distribution (mean=1, sd=1).

I.4.b. construct the vector  $\Delta v = -fv + g\xi$ . (18)

Proceed to step I.5.

I.4.c. if par:

I.4.c.a. construct a unit vector  $e_1$  in the interparticle direction:

$$e_1 = \frac{r_{ij}}{|r_{ij}|}, \quad (19)$$

where  $r_{ij} = r_i + r_j$ .

I.4.c.b. determine the component of  $v$  in the interparticle direction:

$$v_{par} = ve_1. \quad (20)$$

I.4.c.c. choose one random number  $\xi$  from a standard normal distribution (mean = 1, sd = 1).

I.4.c.d. construct the vector

$$\Delta v = (-fv_{par} + g\xi)e_1. \quad (21)$$

Proceed to step I.5.

I.4.c.e. if perp:

I.4.c.e.a. Construct a unit vector  $e_1$  in the interparticle direction:

$$e_1 = \frac{r_{ij}}{|r_{ij}|}, \quad (22)$$

where  $r_{ij} = r_j - r_i$ .

I.4.c.e.b. construct the velocity component perpendicular to  $e_1$ :

$$v_{perp} = v - (ve_1)e_1. \quad (23)$$

I.4.c.e.c. construct a unit vector in the direction of  $v_{perp}$ :

$$e_2 = \frac{v_{perp}}{|v_{perp}|}. \quad (24)$$

I.4.c.e.d. construct a unit vector  $e_3$  perpendicular to  $e_1$  and  $e_2$ :

$$e_3 = e_1 \times e_2. \quad (25)$$

I.4.c.e.e. choose two random numbers  $\xi_2$  and  $\xi_3$  from a standard normal distribution (mean=1, sd =1).

I.4.c.e.f. construct the vector

$$\Delta v = -fv_{perp} + g(\xi_2e_2 + \xi_3e_3) \quad (26)$$

I.4.c.e.g. Proceed to step I.5.

I.5. Distribute the relative velocity change over the two particles:

$$v_i \leftarrow \lambda_B v_i + \frac{\mu}{m_i} \Delta v, \quad (27)$$

$$v_j \leftarrow \lambda_B v_j - \frac{\mu}{m_j} \Delta v. \quad (28)$$

In this way the velocities of the particles are updated while the total momentum  $m_i v_i + m_j v_j$  is conserved.

The particle velocities are updated after each impulsive event, not at the end of each step. This is necessary, as a single particle may be involved in more than one pair event.

### Thermostat behaviour

How the total energy changes by the involvement of friction and noise? The total energy leads to a temperature change determined by the specific heat of the system. In the case of pairwise friction and noise the temperature

appears to relax with a first-order process toward the reference temperature. The derivation that follows is valid for the non-constraint case.

The energy change concerns 1, 2 or 3 degrees of freedom; this is related to the relative velocity of two

particles, with reduced mass  $\mu = \frac{m_i m_j}{m_i + m_j}$ . The dimensionality is studied in three cases:

-  $d = 1$  when a component in one direction is considered as in the *par* case (dpd);

-  $d = 2$  when a component in a plane is considered as in the *perp* case;

-  $d = 3$  in the *iso* case.

The energy change due to the application of one impulsive friction and noise event in  $d$  dimensions of the relative velocity vector of a selected pair is given by:

$$\Delta E = \frac{1}{2} \mu (v + \Delta v)^2 - \frac{1}{2} \mu v^2 \quad (29)$$

$$\Delta E = \frac{1}{2} df(2-f)k_B(T_{ref} - T), \quad (30)$$

where  $T$  is given by

$$T = \frac{\mu}{k_B} \langle v^2 \rangle. \quad (31)$$

Using

$$\Delta T = \frac{\Delta E}{C_V}, \quad (32)$$

valid for the usual case where the rate constant of the thermostat is smaller than the intrinsic exchange rate between kinetic and potential energy. From (32) we arrive at the rate equation for the temperature:

$$\frac{dT}{dt} = \frac{dk_B}{2C_V} \frac{\sum f(2-f)}{\Delta t} (T_{ref} - T), \quad (33)$$

where the sum is to be taken over all  $d$ -dimensional events per time step. This is a first-order decay towards the reference temperature with rate constant

$$k_{DPD} = \frac{dk_B}{2C_V} \frac{\sum f(2-f)}{\Delta t}. \quad (34)$$

We note that in the case of very strong thermostats  $2 \frac{C_V}{k_B}$  should be replaced by the total number of degrees of freedom.

In the particular case that for all particles in the system one pair is selected in every time step and the velocity reduction factor  $f$  is weighted by a distance-dependent factor, i.e.  $1 - \frac{r}{r_c}$ , where  $r_c$  is a cut-off range used in the neighbor selection, the resulting equation for the time constant of the thermostat is:

$$k_{DPD} = \frac{dk_B}{2c_V} \left( \frac{2f \left\langle \left(1 - \frac{r}{r_c}\right) \right\rangle - f^2 \left\langle \left(1 - \frac{r}{r_c}\right)^2 \right\rangle}{\Delta t} \right), \quad (35)$$

where  $c_V$  is the specific heat per particle and  $d$  is the dimensionality of the applied friction and noise:

- for iso  $d = 3$ ;

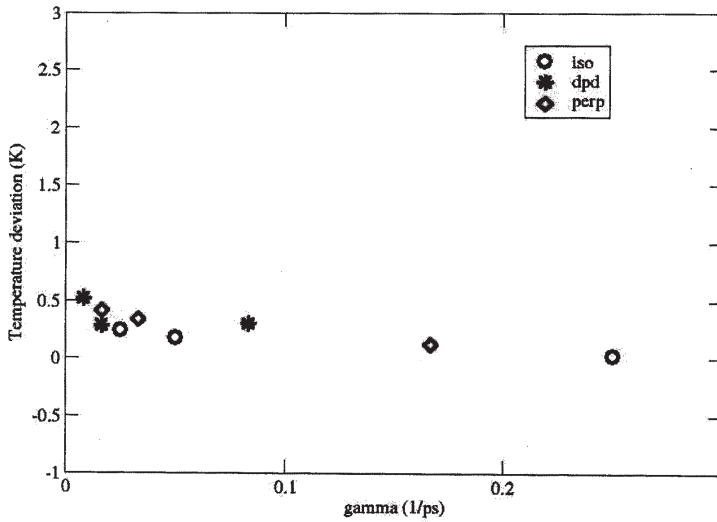


Fig. 1 Deviation from the reference temperature as a function of friction rate  $\gamma$  and  $\tau_r = \{1.0, 1, 10\}$  for MARTINI water; in the DPD – B simulation for the three coupling schemes (*iso*, *dpd*, *perp*). Temperature deviation within expected boundaries. In these simulations, the time step was 2fs.

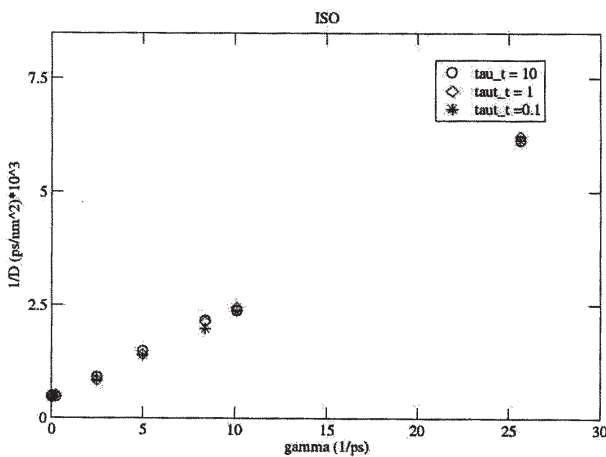


Fig. 2 Inverse diffusion constant versus effective friction rate for „iso” DPD – B simulation coupling scheme used with MARTINI water systems.

- for dpd (par)  $d = 1$ ;
- for perp  $d = 2$ .

The averages are to be taken over the randomly selected pairs. Given a radial distribution function  $g(r)$  and a cut-off radius  $r_c$ , such averages are determined from

$$\langle h(r) \rangle = \frac{\int_0^{r_c} h(r) g(r) r^2 dr}{\int_0^{r_c} g(r) r^2 dr} \quad (36)$$

When we combine the two thermostats, the rate constant  $k_{thermal}$  is given by:

$$k_{thermal} = k_{Ber} + k_{DPD} \quad (37)$$

where  $k_{Ber}$  is computed with equation (14) and  $k_{DPD}$  with equation (35).

### Experimental part

**Simulation details** The algorithms presented in the previous sections were implemented in the GROMACS program package [11] version 4.0.7, using parallelization [8, 13] based on domain decomposition. In this section, we will present the simulation results of the new algorithms on MARTINI coarse grained water [12]. In future we plan to apply the presented algorithms to more complicated molecular systems, namely to polymers for studying their properties.

All simulations for MARTINI water were performed in a periodic cubic box with dimensions longer than twice the cut-off distance. A cut-off distance was set at 1.2 nm. To minimize cut-off artifacts the potential was modified by a shift function to be zero at the cut-off, the force decaying smoothly to zero from 0.9 nm to the cut-off [14]. In all simulations a time step of 2fs was used. The reference temperature was set to 320K.

The MARTINI water systems consisted of 3200 particles with mass 72u in a cubic box of (7.28856 nm<sup>3</sup>). The initial velocities of the particles were obtained from a Maxwell-Boltzmann distribution corresponding to the chosen initial reference temperature. Simulations were 250000 steps long, for diffusion and thermal rate calculations, respectively.

For the computation of the diffusion constant, we used the mean square displacement (MSD) and applied the  $g_{msd}$  function of Gromacs. This function computes the mean square displacement of atoms from a set of initial positions. This provides an easy way to compute the diffusion constant using the Einstein relation. Thermal rate constants were determined from least-squares fits to a single exponential of the temperature after switching the reference temperature at time  $t = 0$  from 350K to 320K. Each case was repeated 8 times, yielding 8 independent determinations  $k_i$  of the rate constant; we report the averages  $\bar{k}$  with standard uncertainty  $\sigma$  computed from

$$\sigma^2 = \sum_{i=1}^8 \frac{(k_i - \bar{k})^2}{56}.$$

### Results and discussions

Figure 1 covers the temperature deviation for the DPD – B (Dissipative Particle Dynamics – Berendsen thermostat) simulations. Figure 1 shows that for the “iso” coupling scheme the smallest deviation is for  $\tau_r = 0.1$  and also that the temperature is maintained between expected boundaries for all three algorithms.

Figure 2, 3 and 4 shows the inverse of diffusion for the new thermostat (DPD – B) as function of coupling strength. As expected, for different values of the coupling parameter  $\hat{\sigma}_T = \{0.1, 1, 10\}$ , the data points are almost identical; this means that the global Berendsen thermostat did not influence the diffusion. For DPD we observe that the diffusion (a dynamic property) is influenced by the strength of DPD coupling for all three DPD versions, as expected.

In the case of the prediction of the thermal rate we used:

$$c_V = 0.0234(3) \text{ kJ mol}^{-1} \text{ K}^{-1}, \left\langle 1 - \frac{r}{r_c} \right\rangle = 0.24336, \left\langle \left( 1 - \frac{r}{r_c} \right)^2 \right\rangle = 0.089437.$$

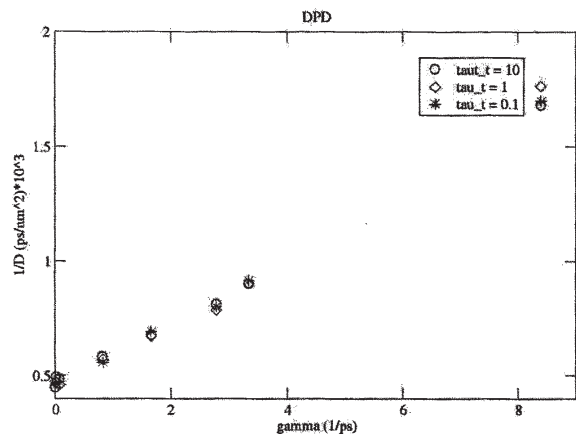


Fig. 3 Inverse diffusion constant versus effective friction rate for „dpd” DPD – B simulation coupling scheme used with MARTINI water systems

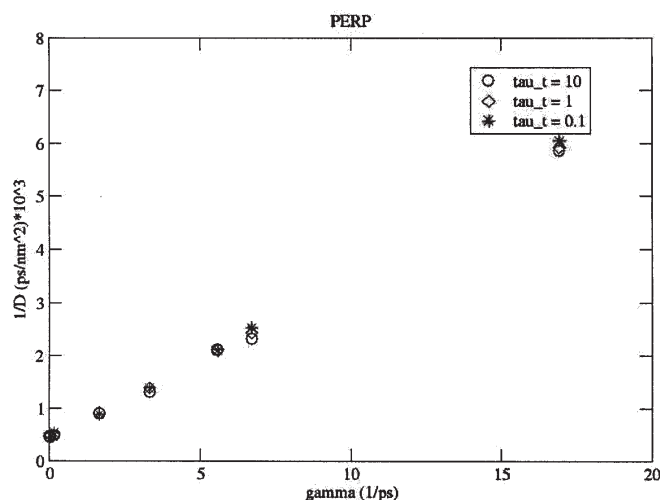


Fig. 4 Inverse diffusion constant versus effective friction rate for „perp” DPD – B simulation coupling scheme used with MARTINI water systems

For the DPD – B thermostat case, the equation for the thermal rate constant  $k_{th}$  is (see equations (14), (35)):

$$k_{thermal} = k_{Ber} + k_{DPD}$$

$$\text{with } k_{Ber} = \frac{1.5k_B}{c_V \tau_T}$$

$$\text{and } k_{DPD} = \frac{d}{3} \left( \frac{2f - f^2 \left\langle \left( 1 - \frac{r}{r_c} \right)^2 \right\rangle}{\Delta t} \right); \text{ with } d = \{1,2,3\} \text{ for the iso, dpd or perp cases.}$$

We observe a match between the theoretical values computed and the values obtained from simulations for all three DPD variants (fig. 5).

### Conclusions

This article describes the theoretical background and simulations results for a new thermostat obtained by combining DPD – Berendsen thermostats. We analyze some properties like: temperature, diffusion or thermal rate constant. The thermostat provides a predictable behaviour with temperatures that do not deviate from the reference and with a good thermal rate constant agreement between simulations and theoretical computation.

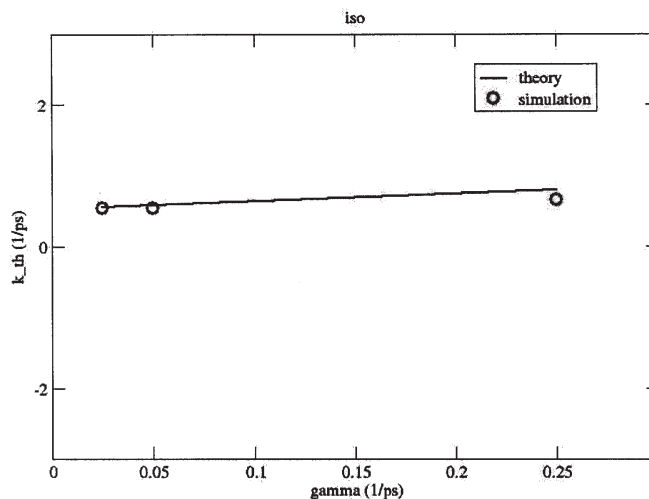


Fig. 5 Thermal relaxation rate versus effective friction rate for the DPD – B simulation in the *iso* case, with a MARTINI water systems and for  $\tau_T = 1$ . We observe a good agreement between the theoretical prediction and obtained simulations values for the *iso* case. Similar conclusions for *dpd* and *perp* cases.

In [2], the global Berendsen thermostat did not influence the diffusion. In this paper, the global Berendsen thermostat has a similar effect for the combined DPD – Berendsen thermostat. The agreement between the theoretical prediction and simulations values for the thermal rate constants is also quite good.

Future work includes applying this algorithm for studying the properties of polymers with the scope of improving materials based on polymers.

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