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Molecular Dynamics implementation of BN2D or ‘Mercedes Benz’ water model[☆]



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ABSTRACT

Two-dimensional ‘Mercedes Benz’ (MB) or BN2D water model (Naim, 1971) is implemented in Molecular Dynamics. It is known that the MB model can capture abnormal properties of real water (high heat capacity, minima of pressure and isothermal compressibility, negative thermal expansion coefficient) (Silverstein et al., 1998). In this work formulas for calculating the thermodynamic, structural and dynamic properties in microcanonical (NVE) and isothermal–isobaric (NPT) ensembles for the model from Molecular Dynamics simulation are derived and verified against known Monte Carlo results. The convergence of the thermodynamic properties and the system’s numerical stability are investigated. The results qualitatively reproduce the peculiarities of real water making the model a visually convenient tool that also requires less computational resources, thus allowing simulations of large (hydrodynamic scale) molecular systems.

We provide the open source code written in C/C++ for the BN2D water model implementation using Molecular Dynamics.

Program summary

Program title: BN2DMD

Catalogue identifier: AEVJ_v1_0

Program summary URL: http://cpc.cs.qub.ac.uk/summaries/AEVJ_v1_0.html

Program obtainable from: CPC Program Library, Queen’s University, Belfast, N. Ireland

Licensing provisions: Standard CPC licence, <http://cpc.cs.qub.ac.uk/licence/licence.html>

No. of lines in distributed program, including test data, etc.: 3120

No. of bytes in distributed program, including test data, etc.: 274895

Distribution format: tar.gz

Programming language: C/C++.

Computer: Workstation.

Operating system: Linux, Unix.

Classification: 16.9.

Nature of problem: Molecular dynamics simulation of BN2D or ‘Mercedes Benz’ water model.

Solution method: A BN2D water model [2], microcanonical (NVE) and isothermal–isobaric (NPT) ensembles with velocity–Verlet and Predictor–Corrector integration [1] respectively. Rotational degree of freedom is treated differently in NVE and NPT ensembles due to the nature of the model.

Restrictions: Memory and CPU time limits the size of simulations.

Running time: Depends on the size of system.

[☆] This paper and its associated computer program are available via the Computer Physics Communication homepage on ScienceDirect (<http://www.sciencedirect.com/science/journal/00104655>).

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- [1] A. B. Naim, “Statistical mechanics of ‘waterlike’ particles in two dimensions. i. physical model and application of the Percus–Yevick equation”, J. Chem. Phys. vol. 54, p. 3682, 1971.
 [2] K. A. T. Silverstein, A. D. J. Haymet, and K. A. Dill, “A simple model of water and the hydrophobic effect”, J. Am. Chem. Soc. vol. 120, pp. 3166–3175, 1998.

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1. Introduction

Two dimensional models in Molecular Dynamics (MD) simulations have the advantage of quadratic scaling of the number of particles with the system size. This can be critical for nano- and meso-scale modelling when the system approaches hydrodynamic sizes. When simulating water it is important to capture abnormal properties such as the minimum of pressure, the negative thermal expansion coefficient at low temperatures, high heat capacity, and the minimum of isothermal compressibility. These properties are attributed to hydrogen bonding, an important feature of water. Three dimensional water models are in good quantitative agreement with the experiment, however, a qualitative agreement can also be achieved for two dimensional (2D) models. A 2D water model that mimics real water properties is the ‘Mercedes Benz’ (BN2D) water model [1]. This model was mainly studied in the past using Monte Carlo methods [2], which lacks dynamical properties. An extended version of the BN2D model, three-dimensional ‘Mercedes Benz’ was studied in [3]. However, the authors did not provide detailed results on the physical chemistry of the model and only NPT ensemble, which is common for MC simulations was used.

The BN2D water model was successfully implemented in MD by the authors [4,5], who studied the properties of a protein and a limited number of the water model properties. MB water model was also used for the study of hydrophobic effects and cold denaturation [6]. In our work we focus on the BN2D water model detailed implementation using Molecular Dynamics. We derive formulas for physical chemical characteristics of the model in the NVE ensembles and equations of motion for the NPT ensemble.

2. The model

The MB or BN2D [7] model is a two dimensional water model, where molecules interact pairwise through the Lennard-Jones and orientation dependent (which depends on the respective orientation of the arms) potentials Fig. 1, that is sufficient to reproduce thermodynamic properties of real water. The total potential is

$$\Phi = \Phi_{LJ} + \Phi_{HB}, \quad (1)$$

where the Lennard-Jones potential Φ_{LJ} is defined in the usual fashion

$$\Phi_{LJ} = 4 \epsilon_{LJ} \left(\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right) \quad (2)$$

and Φ_{HB} is the explicit hydrogen bonding term defined as

$$\Phi_{HB} = \epsilon_{HB} \cdot G(r_{ij} - r_{HB}) \sum_{ij} G(\vec{i}_k \cdot \vec{u}_{ij} - 1) G(\vec{j}_l \cdot \vec{u}_{ij} + 1), \quad (3)$$

where G is the Gaussian function

$$G(x) = e^{-\frac{x^2}{2\sigma^2}},$$

\vec{u}_{ij} is a unit vector that connects the particle centres, \vec{i}_k and \vec{j}_l are the unit vectors of the orientation of the arms, r_{ij} is the distance between the particles, and the angle between a molecule’s arms is 120° .

3. Thermodynamics in NVE ensemble

Since MD simulations are performed in the microcanonical ensemble, where entropy $S(N, V, E)$ depends on the number of particles (N), volume (V), and energy (E), the thermodynamic properties have to be written in terms of time averages of the parameters that can be evaluated during the simulation.

Using the first law of thermodynamics

$$dE = TdS - PdV + \mu dN, \quad (4)$$

and the chain rule for the entropy

$$dS = \frac{dS}{dE} dE + \frac{dS}{dV} dV + \frac{dS}{dN} dN,$$

the following relationships are obtained for temperature (T) and pressure (P):

$$\left(\frac{dS}{dE} \right)_{V,N} = \frac{1}{T}, \quad (5)$$

$$\left(\frac{dS}{dV} \right)_{E,N} = \frac{P}{T}. \quad (6)$$

Isochoric heat capacity is defined as

$$C_V = \left(\frac{dE}{dT} \right)_{V,N} = \left[\left(\frac{\partial^2 S}{\partial E^2} \right)_{V,N} \right]^{-1}, \quad (7)$$

isothermal compressibility as

$$\begin{aligned} \beta_T &= -V \left(\frac{\partial P}{\partial V} \right)_{T,N} \\ &= -V \left[\left(\frac{\partial P}{\partial V} \right)_{V,N} + \frac{T}{C_V} \left(\frac{\partial P}{\partial T} \right)_{V,N}^2 \right], \end{aligned} \quad (8)$$

thermal expansion coefficient as

$$\begin{aligned} \alpha_P &= \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_{P,N} = -V \left(\frac{\partial P}{\partial V} \right)_{T,N} \left(\frac{dP}{dT} \right)_{V,N} \\ &= \beta_T \left(\frac{dP}{dT} \right)_{V,N}, \end{aligned} \quad (9)$$

where $\frac{dP}{dT}$ can be calculated numerically using (5) and (6).

The N index can be omitted in Eqs. (5)–(9), since μ (the chemical potential) is assumed to be constant.

The phase space volume Ω for the microcanonical ensemble is defined as an integral over all phase space coordinates and momenta (\vec{q} and \vec{p}) [8]:

$$\Omega(N, V, E) = M \int \delta(E - H(\vec{q}, \vec{p})) d\vec{q} d\vec{p}, \quad (10)$$

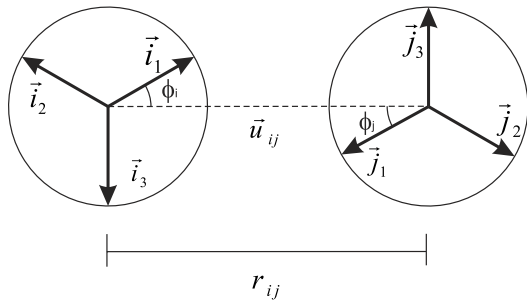


Fig. 1. Mercedes Benz model.

where $H[\vec{q}, \vec{p}]$ is the system's Hamiltonian. The phase space density Σ is defined as [8]

$$\Sigma(N, V, E) = M \int \Theta(E - H[\vec{q}, \vec{p}]) d\vec{q} d\vec{p}, \quad (11)$$

where Θ is the Heaviside step function and then the entropy can be defined as

$$S = k_B \ln \Sigma. \quad (12)$$

The dependence between Ω and Σ is

$$\Omega(N, V, E) = \frac{\partial}{\partial E} \Sigma(N, V, E).$$

The integrals (10) and (11) cannot be evaluated directly due to their 6N and 6N-1 dimensionality.

Assuming the separation of the system's Hamiltonian into the potential and the kinetic energies

$$H[q^N, p^N] = \Phi(q^N) + K(p^N),$$

where q^N and p^N are phase space vector components, the Laplace transform of (10) can be found introducing a normalisation coefficient $M = \frac{E_0}{N!h^{3N}}$:

$$\begin{aligned} L(\Omega) &= M \int dp^N \int dq^N \int dE e^{-\beta E} \delta(E - \Phi(q^N) - K(p^N)) \\ &= M \int dp^N \int dq^N e^{-\beta K(p^N)} e^{-\beta \Phi(q^N)} \\ &= M \int dq^N e^{-\beta \Phi(q^N)} \int dp^N e^{-\beta K(p^N)}, \end{aligned} \quad (13)$$

where h is the Planck constant, E_0 is the thickness of the energy shell.

Assuming the Cartesian coordinate system the MB model's kinetic energy has three components (K_x, K_y, K_ϕ): two translational

$$K_x(p_x) = \frac{p_x^2}{2m},$$

$$K_y(p_y) = \frac{p_y^2}{2m},$$

and one rotational

$$K_\phi(\phi) = \frac{\omega^2}{2I},$$

where p_x, p_y are the momenta along x and y respectively, ω is the rotational velocity.

The parts of the integral (13) are independent, thus can be solved separately by performing the substitution $p^2 = \frac{p'^2}{2m}$, $p = p' \sqrt{2m}$ and $dp = dp' \sqrt{2m}$ (note that $dp^N = dp^1 dp^2 \dots dp^N$).

The kinetic part is

$$\int dp^N e^{-\beta K(p^N)} = (2m\pi)^{3N/2} \beta^{-3N/2},$$

since

$$\int dp' e^{-\beta p'^2} = \sqrt{\frac{\pi}{\beta}},$$

and Laplace transform (13) is simplified to

$$\begin{aligned} L(\Omega) &= M \int dq^N e^{-\beta \Phi(q^N)} (2m\pi)^{3N/2} \beta^{-3N/2} \\ &= M (2m\pi)^{3N/2} \int dq^N e^{-\beta \Phi(q^N)} \beta^{-3N/2}. \end{aligned} \quad (14)$$

Applying the inverse Laplace transform to the integral above

$$\begin{aligned} L^{-1}(L(\Omega)) &= L^{-1} \left(\int dq^N e^{-\beta \Phi(q^N)} \beta^{-3N/2} \right) \\ &= \frac{1}{2\pi i} \int_{-i\infty}^{i\infty} dq^N \beta^{-3N/2} e^{\beta(E - \Phi(q^N))} d\beta, \end{aligned} \quad (15)$$

where

$$\int \frac{1}{p^\nu} e^{-ap} dp = \frac{(E-a)^{\nu-1}}{\Gamma(\nu)}, \quad (16)$$

we obtain

$$\begin{aligned} \Omega(N, V, E) &= M (2m\pi)^{3N/2} \\ &\times \int \frac{(E - \Phi(q^N))^{3N/2-1}}{\Gamma(3N/2)} \Theta(E - \Phi(q^N)) dq^N. \end{aligned} \quad (17)$$

Using the relationship (12), the phase space density becomes

$$\begin{aligned} \Sigma(N, V, E) &= M (2m\pi)^{3N/2} \\ &\times \int \frac{(E - \Phi(q^N))^{3N/2}}{\Gamma(3N/2 + 1)} \Theta(E - \Phi(q^N)) dq^N. \end{aligned} \quad (18)$$

The volume dependence is contained implicitly in the integration limits, thus, by changing variables in the integrals (17) and (18), we render the limits independent of the box size. Using the substitutions for the coordinates and momenta in the phase space

$$q = A^{1/2} q^*$$

and

$$p = A^{1/2} p^*$$

the phase space integrals become

$$\begin{aligned} \Sigma(N, V, E) &= M_1 A^N \int dq^{*N} \frac{(E - \Phi((A^{1/2} q^*)^N))^{3N/2}}{\Gamma(3N/2 + 1)} \\ &\times \Theta(E - \Phi((A^{1/2} q^*)^N)) \end{aligned} \quad (19)$$

and

$$\begin{aligned} \Omega(N, V, E) &= M_1 A^N \int dq^{*N} \frac{(E - \Phi((A^{1/2} q^*)^N))^{3N/2-1}}{\Gamma(3N/2)} \\ &\times \Theta(E - \Phi((A^{1/2} q^*)^N)), \end{aligned} \quad (20)$$

where $M_1 = M(2m\pi)^{3N/2}$.

3.1. Thermodynamic properties

Using the relationships above, the thermodynamic quantities are written in terms of the phase space volume and density.

Temperature

$$T = \frac{1}{k_B} \frac{\Sigma}{\Omega}, \quad (21)$$

pressure

$$P = \frac{1}{\Omega} \frac{\partial \Sigma}{\partial V}, \quad (22)$$

isochoric heat capacity

$$\begin{aligned} \frac{1}{C_V} &= \left(\frac{\partial T}{\partial E} \right)_V = \left(\frac{\partial \left(\frac{1}{k_B} \frac{\Sigma}{\Omega} \right)}{\partial E} \right)_V \\ &= \frac{1}{k_B} \left(\frac{1}{\Omega} \frac{\partial \Sigma}{\partial E} - \frac{\Sigma}{\Omega^2} \frac{\partial \Omega}{\partial E} \right) = \frac{1}{k_B} \left(1 - \frac{\Sigma}{\Omega^2} \frac{\partial \Omega}{\partial E} \right), \end{aligned} \quad (23)$$

isothermal compressibility

$$\begin{aligned} \frac{1}{\beta_T} &= -V \left(\frac{\partial P}{\partial V} \right)_T = -V \left(\frac{\partial \left(\frac{1}{\Omega} \frac{\partial \Sigma}{\partial V} \right)}{\partial V} \right)_T \\ &= -V \left(\frac{1}{\Omega} \frac{\partial^2 \Sigma}{\partial V^2} \right)_T + V \left(\frac{1}{\Omega} \frac{\partial \Sigma}{\partial V} \frac{1}{\Omega} \frac{\partial \Omega}{\partial V} \right)_T. \end{aligned} \quad (24)$$

The ensemble average of an observable A described by a phase space function $a(q^N, p^N)$ is [9]

$$A = \frac{\int a(q^N, p^N) \delta(E - H[q^N, p^N]) dq^N dp^N}{\int \delta(E - H[q^N, p^N]) dq^N}. \quad (25)$$

Using Eqs. (21)–(24) with the Eq. (25) the thermodynamic properties are obtained from the ensemble/time averaged system's parameters:

Temperature

$$k_B T = \frac{\Sigma}{\Omega} = \frac{2}{3N} \langle K \rangle, \quad (26)$$

where $\langle \rangle$ is the ensemble/time average, k_B is the Boltzmann constant.

Pressure

$$P = \frac{1}{\Omega} \frac{\partial \Sigma}{\partial A} = \frac{N}{A} \frac{2}{3N} \langle K \rangle - \left\langle \frac{\partial \Phi}{\partial A} \right\rangle = \rho k_B T - \left\langle \frac{\partial \Phi}{\partial A} \right\rangle, \quad (27)$$

where $\rho = N/A$ is the particles number density.

Isochoric heat capacity

$$\frac{C_V}{Nk_B} = \left(\frac{2}{3} \langle K \rangle \langle K^{-1} \rangle + N (1 - \langle K \rangle \langle K^{-1} \rangle) \right)^{-1}. \quad (28)$$

The first term in the equation for the isothermal compressibility (8) is

$$\begin{aligned} \left(\frac{\partial P}{\partial A} \right)_S &= \left(\frac{N(N-1)}{A^2} k_B T - \left\langle \frac{\partial^2 \Phi}{\partial A^2} \right\rangle - 2\rho \left\langle \frac{\partial \Phi}{\partial A} \right\rangle \right. \\ &\quad \left. + (3N/2 - 1) \left\langle K^{-1} \left(\frac{\partial \Phi}{\partial A} \right)^2 \right\rangle \right) \\ &\quad - \left(\rho - (3N/2 - 1) \left\langle K^{-1} \frac{\partial \Phi}{\partial A} \right\rangle \right) P. \end{aligned} \quad (29)$$

4. Potential derivatives

For integrating MD equations of motion forces acting on each particle should be evaluated. For conservative potential fields the force acting on the i th molecule is calculated as the negative gradient of the potential field. For the MB model in addition to the translational force the derivative with respect to the angle ϕ produces the torque τ :

$$\tau = - \frac{\partial \Phi}{\partial \phi}. \quad (30)$$

The additional degree of freedom ϕ gives rise to the angular velocity ω . A corresponding moment of inertia I should be introduced in order to characterise the rotation of water molecules (I is an equivalent for the mass for rotation), and the time step should be chosen accordingly.

The formulas for thermodynamic properties depend, besides the kinetic energy, on the derivatives of the potential only. The first and the second order derivatives of the potential energy with respect to an area are:

$$\frac{d\Phi}{dA} = \frac{1}{2A} \sum_{i=1}^{N-1} \sum_{j=i+1}^N dx \frac{d\Phi_{ij}}{dx} + dy \frac{d\Phi_{ij}}{dy}, \quad (31)$$

and

$$\begin{aligned} \frac{d^2\Phi}{dA^2} &= \frac{1}{4A^2} \sum_{i=1}^{N-1} \sum_{j=i+1}^N dx^2 \frac{d^2\Phi_{ij}}{dx^2} \\ &\quad + 2 \cdot dx dy \frac{d^2\Phi_{ij}}{dx dy} + dy^2 \frac{d^2\Phi_{ij}}{dy^2}, \end{aligned} \quad (32)$$

where Φ_{ij} is the potential, dx and dy are the distances along x and y direction between the i th and j th particles respectively.

4.1. Lennard-Jones part

The derivatives of the Lennard-Jones (LJ) part of the potential for i th particle leads to:

$$F_{LJ} = -\nabla_q \Phi_{LJ} = - \frac{\Phi_{LJ}}{r_{ij}} \frac{dr_{ij}}{dq}, \quad (33)$$

where $r_{ij} = \sqrt{(x_j - x_i)^2 + (y_j - y_i)^2}$ and q denotes x_i or y_i coordinate, the notation of ∇_q is either $\frac{\partial}{\partial x_i}$ or $\frac{\partial}{\partial y_i}$.

Using Eq. (2) we obtain

$$\frac{d\Phi_{LJ}}{dr_{ij}} = -24 \cdot \epsilon_{LJ} \cdot \sigma^6 (2 \sigma^6 r_{ij}^{-14} - r_{ij}^{-8}) \cdot r_{ij},$$

where the distance derivatives with respect to x_i and y_i are

$$\frac{dr_{ij}}{dx_i} = - \frac{x_j - x_i}{r_{ij}},$$

and

$$\frac{dr_{ij}}{dy_i} = - \frac{y_j - y_i}{r_{ij}}$$

respectively.

The second order derivatives of the LJ potential with respect to x_i and y_i components are

$$\begin{aligned} \frac{d^2\Phi_{LJ}}{dq^2} &= 24 \cdot \epsilon_{LJ} \cdot \sigma^6 \left(\frac{(26 \sigma^6 - 7 r_{ij}^6) \cdot \left(\frac{dr_{ij}}{dq} \right)^2}{r_{ij}^{14}} \right. \\ &\quad \left. + \frac{r_{ij} (-2\sigma^6 + r_{ij}^6) \left(\frac{d^2r_{ij}}{dq^2} \right)}{r_{ij}^{14}} \right), \end{aligned} \quad (34)$$

where

$$\frac{d^2r_{ij}}{dx_i^2} = - \frac{(x_j - x_i)^2}{r_{ij}^3} + \frac{1}{r_{ij}}$$

and

$$\frac{d^2r_{ij}}{dy_i^2} = - \frac{(y_j - y_i)^2}{r_{ij}^3} + \frac{1}{r_{ij}}.$$

The torque of the Lennard-Jones potential is zero.

4.2. Hydrogen bonding part

The derivative of the HB part of the potential with respect to x_i , y_i , and ϕ_i are derived from Eq. (3) as follows

$$\begin{aligned} \frac{1}{\epsilon_{HB}} \nabla_q \Phi_{HB} &= \nabla_q G(r_{ij} - r_{HB}) \sum_{ij}^N G(\vec{i}_k \cdot \vec{u}_{ij} - 1) G(\vec{j}_l \cdot \vec{u}_{ij} + 1) \\ &+ G(r_{ij} - r_{HB}) \sum_{ij}^N \nabla_q G(\vec{i}_k \cdot \vec{u}_{ij} - 1) G(\vec{j}_l \cdot \vec{u}_{ij} + 1) \\ &+ G(r_{ij} - r_{HB}) \sum_{ij}^N G(\vec{i}_k \cdot \vec{u}_{ij} - 1) \nabla_q G(\vec{j}_l \cdot \vec{u}_{ij} + 1). \end{aligned} \quad (35)$$

Introducing new notation $h_i = \vec{i}_k \cdot \vec{u}_{ij}$ and $h_j = \vec{j}_l \cdot \vec{u}_{ij}$, the scalar products h_i and h_j become

$$h_i = \frac{(x_j - x_i) \cdot \cos \phi_i + (y_j - y_i) \cdot \sin \phi_i}{r_{ij}},$$

and

$$h_j = \frac{(x_j - x_i) \cdot \cos \phi_j + (y_j - y_i) \cdot \sin \phi_j}{r_{ij}}$$

respectively.

Using the notation above we expand the terms in (35) to

$$\nabla_q G(r_{ij} - r_{HB}) = \frac{dG(r_{ij} - r_{HB})}{dr_{ij}} \frac{dr_{ij}}{dq},$$

where

$$\frac{dG(r_{ij} - r_{HB})}{dr_{ij}} = -\frac{(r_{ij} - r_{HB})}{\sigma_{HB}^2} G(r_{ij} - r_{HB}).$$

The orientation dependent terms become

$$\nabla_q G(h_i - 1) = \frac{dG(h_i - 1)}{dh_i} \frac{dh_i}{dq} = -\frac{(h_i - 1)}{\sigma_\theta^2} G(h_i - 1) \frac{dh_i}{dq},$$

and

$$\nabla_q G(h_j + 1) = \frac{dG(h_j + 1)}{dh_j} \frac{dh_j}{dq} = -\frac{(h_j + 1)}{\sigma_\theta^2} G(h_j + 1) \frac{dh_j}{dq},$$

where

$$\frac{dh_i}{dx_i} = -\frac{\cos \phi_i}{r_{ij}} - \frac{(x_j - x_i) \cdot \cos \phi_i + (y_j - y_i) \cdot \sin \phi_i}{r_{ij}^2} \frac{dr_{ij}}{dx_i},$$

$$\frac{dh_j}{dx_i} = -\frac{\cos \phi_j}{r_{ij}} - \frac{(x_j - x_i) \cdot \cos \phi_j + (y_j - y_i) \cdot \sin \phi_j}{r_{ij}^2} \frac{dr_{ij}}{dx_i},$$

$$\frac{dh_i}{dy_i} = -\frac{\sin \phi_i}{r_{ij}} - \frac{(x_j - x_i) \cdot \cos \phi_i + (y_j - y_i) \cdot \sin \phi_i}{r_{ij}^2} \frac{dr_{ij}}{dy_i},$$

$$\frac{dh_j}{dy_i} = -\frac{\sin \phi_j}{r_{ij}} - \frac{(x_j - x_i) \cdot \cos \phi_j + (y_j - y_i) \cdot \sin \phi_j}{r_{ij}^2} \frac{dr_{ij}}{dy_i}.$$

The torque of the HB part for the i th particle is

$$\nabla_{\phi_i} \Phi_{HB} = \epsilon_{HB} \cdot G(r_{ij} - r_{HB}) \cdot \sum_{ij}^N \nabla_{\phi_i} G(h_i - 1) G(h_j + 1),$$

where

$$\frac{dh_i}{d\phi_i} = \frac{-(x_j - x_i) \sin \phi_i + (y_j - y_i) \cos \phi_i}{r_{ij}}.$$

Introducing new notations $A = G(r_{ij} - r_{HB})$, $B = G(h_i - 1)$, $C = G(h_j + 1)$ the second order derivatives of the potential with

respect to the coordinate for HB part are obtained

$$\begin{aligned} \frac{d^2 \Phi_{HB}}{dq^2} &= \frac{d^2 (A \sum B \cdot C)}{dq^2} = \nabla_q^2 A \sum B \cdot C \\ &+ A \sum \nabla_q^2 B \cdot C + A \sum B \cdot \nabla_q^2 C \\ &+ 2 \left(A \sum \nabla_q B \cdot \nabla_q C + \nabla_q A \sum B \cdot \nabla_q C \right. \\ &\left. + \nabla_q A \sum \nabla_q B \cdot C \right). \end{aligned} \quad (36)$$

The second order derivative of the Gauss function $G(f(q)) = e^{-\frac{f(q)^2}{2\sigma^2}}$ is

$$\begin{aligned} \frac{d^2 G(f(q))}{dq^2} &= \frac{G(f(q)) \left((-\sigma^2 + f(q)^2) \cdot \left(\frac{df(q)}{dq} \right)^2 - \sigma^2 \cdot f(q) \cdot \left(\frac{d^2 f(q)}{dq^2} \right) \right)}{\sigma^4}, \end{aligned} \quad (37)$$

while

$$\begin{aligned} \frac{d^2 h_i}{dx^2} &= (y_i - y_j) \left(\frac{\sin(\phi_i) (-2(x_i - x_j)^2 + (y_i - y_j)^2)}{r_{ij}^5} \right. \\ &\left. + \frac{3 \cos(\phi_i) (x_i - x_j) (y_i - y_j)}{r_{ij}^5} \right), \end{aligned} \quad (38)$$

$$\begin{aligned} \frac{d^2 h_i}{dy^2} &= (x_i - x_j) \left(\frac{\cos(\phi_i) ((x_i - x_j)^2 - 2(y_i - y_j)^2)}{r_{ij}^5} \right. \\ &\left. + \frac{+3 \sin(\phi_i) (x_i - x_j) (y_i - y_j)}{r_{ij}^5} \right), \end{aligned} \quad (39)$$

$$\begin{aligned} \frac{d^2 h_j}{dx^2} &= (y_i - y_j) \left(\frac{\sin(\phi_j) (-2(x_i - x_j)^2 + (y_i - y_j)^2)}{r_{ij}^5} \right. \\ &\left. + \frac{+3 \cos(\phi_j) (x_i - x_j) (y_i - y_j)}{r_{ij}^5} \right), \end{aligned} \quad (40)$$

$$\begin{aligned} \frac{d^2 h_j}{dy^2} &= (x_i - x_j) \left(\frac{\cos(\phi_j) ((x_i - x_j)^2 - 2(y_i - y_j)^2)}{r_{ij}^5} \right. \\ &\left. + \frac{+3 \sin(\phi_j) (x_i - x_j) (y_i - y_j)}{r_{ij}^5} \right). \end{aligned} \quad (41)$$

The cross-derivatives of the potentials are calculated using finite differences, due to the cumbersome formulas.

5. Thermodynamic in NPT ensemble

Thermodynamic properties in the NPT ensemble were evaluated using the following relationships:

$$C_p = \frac{1}{k_B} \left(\frac{\langle H^2 \rangle - \langle H \rangle^2}{NT^2} \right)_p, \quad (42)$$

$$\beta = \frac{\langle V^2 \rangle - \langle V \rangle^2}{\langle V \rangle T}, \quad (43)$$

$$\alpha = \frac{1}{\langle V \rangle} \left(\frac{\partial \langle V \rangle}{\partial T} \right)_p, \quad (44)$$

where $\langle H \rangle = \langle K \rangle + \langle \Phi \rangle + P \cdot \langle V \rangle$ is enthalpy, C_p is heat capacity, α is thermal expansion coefficient, β is isothermal compressibility computed from the fluctuations.

6. NPT ensemble equations of motion

In the NPT ensemble virtual variables (q' , p' , s , V , t') are introduced. These variable can be related to the real variables (q , p , s ,

V, t) when scaling of time and coordinates is performed. Where $'$ denotes virtual variable, q is coordinate, p is impulse or momentum, V is volume, t is time and s is a new variable which is discussed later.

Relationship between these variable can be established if following procedure is done: the time is scaled with the new variable s and the coordinates are scaled with the length, that is defined as $V^{1/d}$, where d stands for dimensionality [9]. In mathematical terms these relationships are expressed as

$$q_i = V^{1/d} q', \quad (45)$$

$$t = \int^t \frac{1}{s} \cdot dt'. \quad (46)$$

The volume V and parameter s are assumed to be new degrees of freedom. As a result, the change in the volume will maintain constant pressure in the system, and the change of the s will keep constant temperature, since MD particle velocities depend on the time rate.

Using the relationships above and statistical mechanics framework, the real momentum is proportional to the virtual momentum and the proportionality coefficient is defined as

$$p = c \cdot p'. \quad (47)$$

The coefficient c is unknown, although it can be derived using classical mechanics concepts. As the momentum is the product of mass m and velocity

$$p = m \cdot \frac{dq}{dt}, \quad (48)$$

where velocity is the derivative of the coordinate with respect to time. Using the relationships (45) and (46) momentum can be expressed in the terms of the virtual variables

$$p = sV^{1/d} m \cdot \frac{dq'}{dt'}. \quad (49)$$

From the statistical mechanics perspective the relationship between the coordinates and momenta is given by

$$\frac{dq'}{dt'} = \frac{dH}{dp'}, \quad (50)$$

where H is the system's Hamiltonian.

The Hamiltonian is the sum of kinetic and potential energies from all degrees of freedom. Therefore, according to the statistical mechanics principles, the full system Hamiltonian is expressed as

$$H = \sum_i \frac{p_i^2}{2m_i} + \sum_i \frac{p_{i\phi}^2}{2I} + \Phi(q, \phi) + \frac{p_s^2}{2M_s} + gkT \ln s + \frac{p_v^2}{2M_v} + P_{ex}V, \quad (51)$$

where p_s and p_v are the conjugate momenta for s and V respectively, I is the moment of inertia, M_s and M_v are proportionality coefficients (generalised masses), the summation is done over all particles. For the virtual time $g = d \cdot N + 1$, where N is the number of particles, and for real time $g = d \cdot N$. For more details see [10].

Now, the derivative $\frac{dq'}{dt'}$ can be substituted in to (49) considering the relationship between the real and virtual momenta

$$p = m \cdot sV^{1/d} \frac{d[c^2 p'^2 / 2m]}{dp'} \quad (52)$$

that can be reduced to

$$p = sV^{1/d} c [c \cdot p'] = sV^{1/d} cp. \quad (53)$$

Eliminating p from both sides, the proportionality parameter is given by

$$c = \frac{1}{sV^{1/d}}. \quad (54)$$

Thus the relationship between the momenta in terms of available parameters is

$$p_i = \frac{p'_i}{sV^{1/d}}. \quad (55)$$

Furthermore, an assumption is made, that the angle between MB arms and x -axis is not scaled, since the angle in the MB model is separated from the spatial space. Thus, the following transformation is true for the angular coordinate

$$\phi_i = \phi'_i. \quad (56)$$

Following similar procedure to the momenta above, a relationship between the real and the virtual rotational momenta is

$$p_\phi = c_\phi \cdot p'_\phi, \quad (57)$$

where c_ϕ is a proportionality coefficient.

As the rotational momenta is the product of the moment of inertia I and the angular velocity

$$p_\phi = I \cdot \frac{d\phi}{dt}, \quad (58)$$

that in terms of the virtual angle and time can be written as

$$p_\phi = s \cdot I \frac{d\phi'}{dt'}. \quad (59)$$

Using statistical mechanics, the virtual angular velocity is defined as the derivative of the system's Hamiltonian with respect to the momentum

$$\frac{d\phi'}{dt'} = \frac{dH}{dp'_\phi}. \quad (60)$$

Substituting the virtual angular velocity in the equation for the virtual angular momentum the following expression is obtained

$$p_\phi = s \cdot I \frac{dH}{dp'_\phi}, \quad (61)$$

that can be simplified to

$$p_\phi = I \cdot s \frac{d[c_\phi^2 p_\phi'^2 / 2I]}{dp'_\phi} \quad (62)$$

and later reduced to

$$p_\phi = s \cdot c_\phi [c_\phi \cdot p'_\phi] = s \cdot c_\phi \cdot p_\phi. \quad (63)$$

Eliminating the angular momenta on both sides, the proportionality coefficient is given by

$$c_\phi = \frac{1}{s}. \quad (64)$$

The relationship between the real and the virtual angular momenta becomes

$$p_\phi = \frac{p'_\phi}{s}. \quad (65)$$

The full system's Hamiltonian in terms of the virtual variables and available parameters is expressed as

$$H = \sum_i V^{-2/d} s^{-2} \frac{p_i'^2}{2m_i} + \sum_i s^{-2} \frac{p_{i\phi}'^2}{2I} + \Phi(V^{1/d} q', \phi') + \frac{p_s^2}{2M_s} + gkT \ln s + \frac{p_v^2}{2M_v} + P_{ex}V. \quad (66)$$

Using statistical mechanics principles together with the obtained relationships above, the set of equations of motion is obtained.

The virtual velocities are given by

$$\frac{dq'_i}{dt'} = \frac{\partial H}{\partial p'_i} = V^{-2/d} s^{-2} \frac{p'_i}{m_i}, \quad (67)$$

followed by the virtual forces

$$\frac{dp'_i}{dt'} = -\frac{\partial H}{\partial q'_i} = -\frac{\partial \Phi(V^{1/d} q', \phi')}{\partial q_i} V^{1/d}, \quad (68)$$

the virtual angular velocity is expressed as

$$\frac{d\phi'_i}{dt'} = \frac{\partial H}{\partial p'_{\phi_i}} = s^{-2} \frac{p'_{\phi_i}}{I}, \quad (69)$$

followed by the virtual torque

$$\frac{dp'_{\phi_i}}{dt'} = -\frac{\partial H}{\partial \phi'_i} = -\frac{\partial \Phi(V^{1/d} q', \phi')}{\partial \phi'}, \quad (70)$$

an additional degree of freedom s , the change rate, is given by

$$\frac{ds}{dt'} = \frac{\partial H}{\partial p_s} = \frac{p_s}{M_s}, \quad (71)$$

followed by the conjugate momenta for s

$$\begin{aligned} \frac{dp_s}{dt'} &= -\frac{\partial H}{\partial s} \\ &= \left[V^{-2/d} s^{-2} \sum_i \frac{p'^2_i}{m_i} + s^{-2} \sum_i \frac{p'^2_{\phi_i}}{I} - gkT \right] / s, \end{aligned} \quad (72)$$

the volume change rate is given by

$$\frac{dV}{dt'} = \frac{\partial H}{\partial p_v} = \frac{p_v}{M_v}, \quad (73)$$

followed by the conjugate momenta for the volume change rate

$$\begin{aligned} \frac{dp_v}{dt'} &= -\frac{\partial H}{\partial V} \\ &= \left[V^{-2/d} s^{-2} \sum_i \frac{p'^2_i}{m_i} - \frac{\partial \Phi(q_i)}{\partial q_i} q_i \right] / (d \cdot V) - P_{ex}. \end{aligned} \quad (74)$$

The equations above can be rewritten in terms of the virtual variables, if a derivative of (67)–(74) is taken with respect to the virtual time t' . This yields the following set of equations:

$$\ddot{q}'_i = V^{-1/d} \frac{f_i}{m_i} - \left[\frac{\dot{s}}{s} + \frac{2}{d} \frac{\dot{V}}{V} \right] \dot{q}'_i, \quad (75)$$

$$\ddot{\phi}' = \frac{f_{\phi_i}}{I} - \left[\frac{\dot{s}}{s} \right] \cdot \dot{\phi}'_i, \quad (76)$$

$$\ddot{s} = \frac{\dot{s}^2}{s} + s \left(V^{2/d} \sum_i m_i \dot{q}'_i{}^2 + \sum_i I \dot{\phi}'_i{}^2 - gkT \right) / M_s, \quad (77)$$

$$\begin{aligned} \ddot{V} &= \frac{\dot{s}\dot{V}}{s} + \frac{s^2}{d \cdot M_v \cdot V} \\ &\times \left(\left[V^{2/d} \sum_i m_i \dot{q}'_i{}^2 + V^{1/d} \sum_i F_i \cdot q'_i \right] - P_{ex} \cdot d \cdot V \right). \end{aligned} \quad (78)$$

The set of equations can be expressed in terms of the real variables, if the relationships (45) and (46) are used:

$$\ddot{q} = \frac{f_i}{m_i} - \left[\frac{\dot{s}}{s} \right] \left[\dot{q} - \frac{q}{Vd} \dot{V} \right] + \frac{1}{d} \frac{q\ddot{V}}{V} + q \left(\frac{\dot{V}}{Vd} \right)^2 (1-d), \quad (79)$$

$$\ddot{\phi} = \frac{f_{\phi_i}}{I} - \left[\frac{\dot{s}}{s} \right] \cdot \dot{\phi}_i, \quad (80)$$

$$\ddot{s} = \frac{\dot{s}^2}{s} + s \left(\sum_i m_i \left[\dot{q} - \frac{q}{Vd} \dot{V} \right]^2 + \sum_i I \dot{\phi}_i{}^2 - gkT \right) / M_s, \quad (81)$$

$$\begin{aligned} \ddot{V} &= \frac{\dot{s}\dot{V}}{s} + \frac{s^2}{d \cdot M_v \cdot V} \\ &\times \left(\left[\sum_i m_i \left[\dot{q} - \frac{q}{Vd} \dot{V} \right]^2 + \sum_i F_i \cdot q_i \right] - P_{ex} \cdot d \cdot V \right). \end{aligned} \quad (82)$$

7. Implementation

7.1. NVE ensemble

Common MD simulation is conducted at constant number of molecules, volume, and energy–NVE ensemble. Various integration methods for equations of motion are available. In this work the Verlet method with velocity rescaling algorithm for thermostating [9] was selected. The kinetic energy for MB model is

$$K = \sum_{i=1}^N \frac{m \vec{v}_i^2}{2} + \frac{I \omega_i^2}{2}, \quad (83)$$

where I is the moment of inertia, \vec{v}_i and ω_i are the translational and angle (rotational) velocities.

The structure of the MB water is characterised by the radial distribution function (RDF)

$$g_r^{(2)}(r) = \frac{2V}{N^2} \left\langle \sum_{i < j} \delta(r - |\vec{u}_{ij}|) \right\rangle. \quad (84)$$

The dynamic characteristics are described by the velocity correlation functions that cannot be obtained using Monte Carlo method. The velocity autocorrelation function (VAF) is

$$f_v(\tau) = \langle \vec{v}(t) \cdot \vec{v}(t + \tau) \rangle, \quad (85)$$

where $\vec{v}(t)$ and $\vec{v}(t + \tau)$ are translational velocities at time moments t and $t + \tau$. If the process is stationary f_v is independent of t . The rotational velocity correlation function is defined for the rotational velocity $\omega(t) = \frac{\partial \phi}{\partial t}$:

$$f_\omega(\tau) = \langle \omega(t) \cdot \omega(t + \tau) \rangle. \quad (86)$$

The system of 2500 MB particles was simulated.

7.2. Units

The dimensionless units were used [2]:

$$T = \frac{\epsilon_{HB}}{k_B} T^*, \quad (87)$$

$$r = r_{HB} \cdot r^*, \quad (88)$$

$$m = m_{H_2O} \cdot m^*, \quad (89)$$

$$t = \sqrt{m \cdot r_{HB}^2 / \epsilon_{HB}} \cdot t^*, \quad (90)$$

$$P \cdot V = \epsilon_{HB} \cdot P^* \cdot V^*, \quad (91)$$

where $*$ denotes the dimensionless variables. The time step $dt^* = 0.001$ is small enough to account for the rotation of the molecules which is significantly faster than the translation.

The simulation parameters are listed in Table 1. The value of σ_{HB}^* should be small, such that only one hydrogen bond is formed [2]. Thermodynamic properties are presented in Table 2.

7.3. NPT ensemble

The MB model was also implemented in the NPT ensemble for the same set of conditions as in the NVE ensemble, with variable

Table 1

The variables used in MD simulation. r_{HB} is hydrogen bond length, m_{H_2O} is the water molecule mass, ϵ_{HB} is the hydrogen bond energy, ϵ_{LJ} is the Lennard-Jones energy, σ_{LJ}^* is 0.7 of the r_{HB}^* [2].

Variable	Real values	Units	Dimensionless
m_{H_2O} [11]	$18 \cdot 10^{-3}$	$\frac{kg}{mol}$	1
r_{HB} [11]	2.95	Å	1
ρ [11]	10^3	$\frac{kg}{m^3}$	0.9
ϵ_{HB} [2]	12.742	$\frac{kJ}{mol}$	-1
ϵ_{LJ} [2]	1.274	$\frac{kJ}{mol}$	0.1
σ_{HB} [2]	0.25	Å	0.085
σ_{LJ} [2]	2.065	Å	0.7
I [11]	$2.938 \cdot 10^{-47}$	$kg \cdot m^2$	0.001126
k_B	$1.38 \cdot 10^{-23}$	$\frac{J}{K}$	1

Table 2

Thermodynamic properties obtained in the *NVE* ensemble.

T^*	P^*	C_V^*	α_T^*	β_T^*
0.16	0.17235	2.88919	-1.5966	0.91717
0.165	0.16364	2.87008	-1.803	1.25616
0.17	0.15799	2.84826	-1.0792	1.1471
0.175	0.15423	2.81344	-0.3032	0.92412
0.18	0.15471	2.77659	0.3684	1.23506
0.185	0.15722	2.73583	0.7029	1.02984
0.19	0.16154	2.70603	1.2870	1.32021
0.20	0.1735	2.63204	1.8810	1.299
0.21	0.1893	2.5688	2.6876	1.68253
0.22	0.20621	2.50663	3.6768	2.06904
0.23	0.22417	2.43564	4.8275	2.62353
0.24	0.24302	2.40019	3.8106	2.02395

Table 3

Thermodynamic properties obtained in the *NPT* ensemble.

T^*	V^*/N	C_p^*	α_p^*	β_T^*
0.16	1.07706	7.00561	-1.87581	1.01279
0.165	1.06876	6.7751	-1.5375	1.03558
0.17	1.06063	6.72985	-1.13025	1.034
0.175	1.05677	6.40312	-0.52804	1.02626
0.18	1.05505	6.2048	-0.03696	1.08496
0.185	1.05638	5.98777	0.34555	1.10366
0.19	1.0587	5.75851	0.81742	1.0203
0.20	1.07136	5.51237	1.54385	1.19149
0.21	1.09178	5.30271	2.20864	1.14201
0.22	1.11959	5.1678	2.78091	1.62233
0.23	1.15405	4.90385	3.24432	1.91605
0.24	1.19447	4.74029	3.70994	2.23304

density and constant pressure $P^* = 0.195$. The *NPT* ensemble requires to set parameters M_S and M_V , which contribute to the constant temperature and volume. These quantities must be determined empirically and do not affect the results when the system reaches equilibrium. For this particular case $M_S = 1$ and $M_V = 0.1$.

In the *NPT* simulation the Verlet integrator is replaced with the Predictor–Corrector one as well as a different set of equation of motion is used, Eqs. (79)–(82).

The obtained thermodynamic properties are presented in Table 3.

8. Results and discussion

The MB model is two dimensional, although it has three degrees of freedom (x , y , and ϕ). The derived equations for thermodynamic properties are in agreement with the previous works for a standard 2D problems [8] despite the difference in the third degree of freedom in our model.

As it was shown above the thermodynamic properties in the *NVE* ensemble consist of the combinations of kinetic energy K , the first and second order derivatives of the potential with respect to the area, $\frac{\partial \phi}{\partial A}$ and $\frac{\partial^2 \phi}{\partial A^2}$.

The convergence of the isothermal compressibility is the slowest of all properties analysed. This is due to the fluctuations of the terms involved in Eq. (29), especially the first order derivative of the potential with respect to the area.

The fluctuations of the first order derivative of the potential with respect to area for different system sizes are presented in Fig. 2. For small systems averaging time must be considered long enough to ensure the convergence of the mean value of these fluctuations. For the system of 2500 particles the convergence of $\frac{d\phi}{dA}$ fluctuating term is presented in Fig. 3.

The dynamical properties of water are characterised by the translational (VACF) and rotational (RVACF) autocorrelation functions. The obtained autocorrelation functions, Fig. 4, coincide with the ones from 3D realistic models [12]. The minima on VACF and RVACF are located at approximately correct positions, which confirms the correctness of the values of the moment of inertia and mass.

The structure formed by MB model, Figs. 5 and 6, is similar to realistic water. It also reproduces results by Ben-Naim [7]. The maxima on RDF indicate solvation shells of different order. The maxima roughly correspond to the hexagonal ice structure of water, while a small maximum at ≈ 0.7 is formed by the ‘interstitial’ water molecules (see Fig. 5).

The simulation is stable if the time step is less than $dt^* = 0.01$. As an example, the standard deviation of the rotational velocity rapidly increases with the time step Fig. 7. The translational velocities and other properties are less affected by the time step. Thus the maximal time step is restricted by the rotation of the molecule. For the current simulation the time step was chosen $dt^* = 0.001$, that corresponds to $t = 0.35$ fs.

The thermodynamic properties of both ensembles presented in the Tables 2 and 3 demonstrate that the MB model mimics real water behaviour. The *NPT* ensemble thermodynamics reproduces the MC simulations by other authors [2].

9. Program structure

Our work focuses on the implementation of the BN2D model using Molecular Dynamics, thus corresponding code is uploaded to the CPC library.

Most of the standard routines were used from the book ‘D. C. Rapaport, “The Art of Molecular Dynamics Simulation” (Second Edition), Cambridge University Press, UK, 2004’. That makes it easier to modify and improve the code if the user is familiar with the book, which contains detailed explanations of used and available algorithms, methodology and analysis methods.

The BN2D model parameters were used from Table 1.

The BN2D water model simulation code consists of two header files `macro.h` and `mb_class_defs.h`, the main file `main.cpp` and an input file `input.txt`.

Five classes are available, the MB class is for MB model, *NVE* and *NPT* for a relevant ensemble respectively, RDF and VACF for the structural and dynamical properties respectively.

Instructions to run the code are available in the readme file.

10. Conclusions

The MB model was implemented using molecular dynamics for a systems of 2500 MB particles. Formulas of thermodynamic properties were derived and implemented for the *NVE* ensemble. Dynamical and structural properties of the model were calculated. A

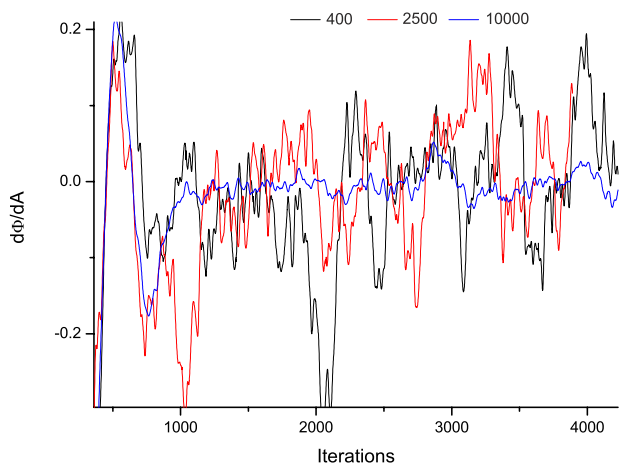


Fig. 2. Fluctuations of the first order derivative with respect to area for different system sizes (the number of molecules is indicated), $T^* = 0.21$.

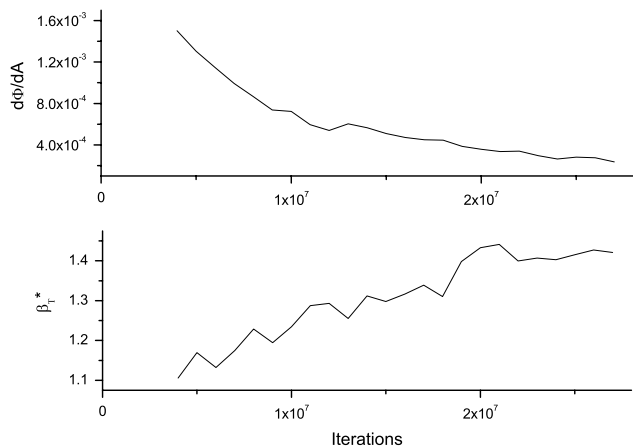


Fig. 3. Convergence of the first order derivative of the MB potential with respect to area and isothermal compressibility, $T^* = 0.21$.

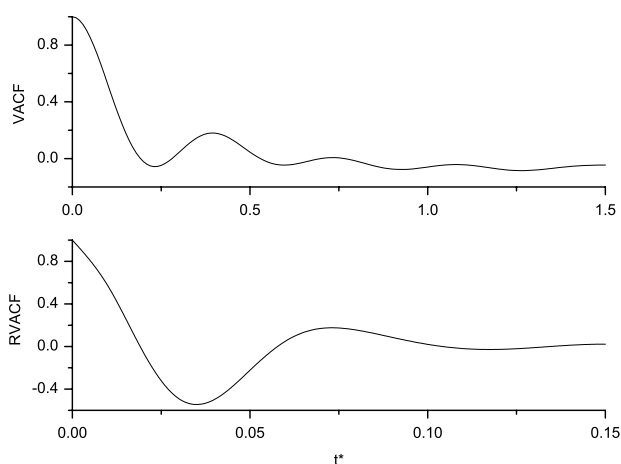


Fig. 4. Translational and rotational velocity autocorrelation functions of MB model.

set of equations of motion in the case of *NPT* ensemble was derived. Upper limit of the time step, virtual masses for the *NPT* ensemble and system size for the thermodynamic properties estimation in the *NVE* ensemble were provided.

The code is uploaded to the CPC library, which allows to conduct BN2D water model simulation using MD in the *NVE* and *NPT*

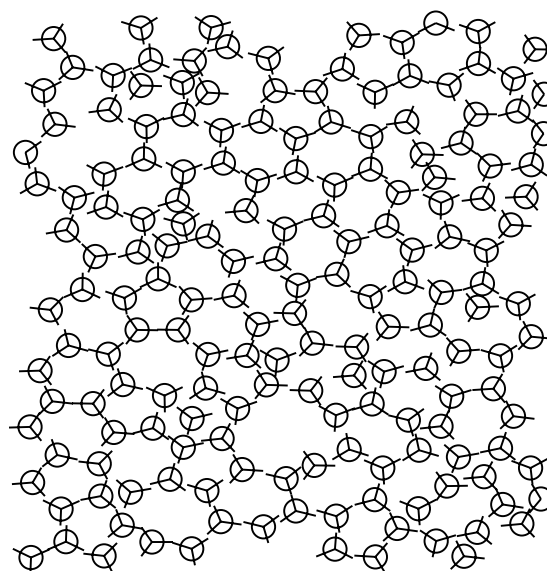


Fig. 5. Snapshot of MB water structures, $T^* = 0.15$.

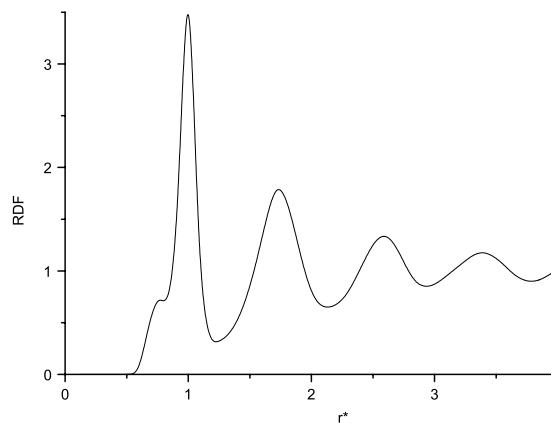


Fig. 6. Radial distribution function of MB water.

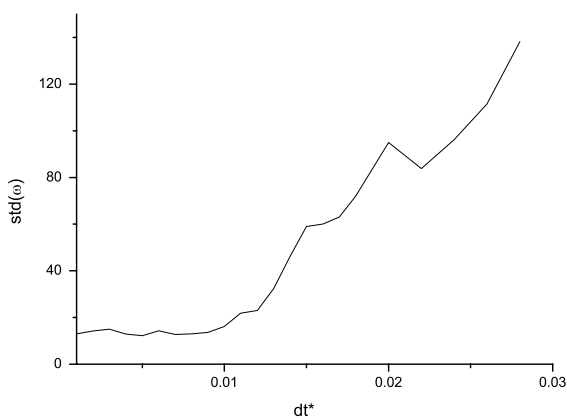


Fig. 7. Standard deviation of rotational velocity with the time step dt^* .

ensembles, calculate thermodynamic properties in *NVE* ensemble and obtain RDF and VACF in both ensembles.

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