

## On the centre of mass velocity in molecular dynamics simulations

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Molecular dynamics simulations are performed on a fluid at supercritical conditions to analyze the effect that the velocity of centre of mass (VCOM) of the system has on temperature and phase stability. Standard rescaling velocities and Nosé-Hoover chains of thermostats methods are used to carry out simulations on Square Well, Lennard-Jones and Soft Primitive potential models. Removing the VCOM at the beginning or during the simulation is not required for the Nosé-Hoover chain of thermostats to keep the correct temperature of the system, however, it is fundamental to keep null the VCOM when the traditional rescaling velocity scheme is used. It is shown that if the VCOM is removed only at the beginning of the simulation the internal and external temperatures are not the same for very long simulations and the fluid becomes a solid. The temperatures and physical properties obtained using the Nosé-Hoover chain method are the same as those obtained by removing the VCOM during the simulation in the rescaling velocity procedure.

*Keywords:* Molecular dynamics; scaling velocities; Nosé-Hoover chains; centre of mass velocity.

Realizamos simulaciones de dinámica molecular en fluidos a condiciones supercríticas para analizar el efecto que la velocidad del centro de masa (VCM) del sistema tiene sobre la temperatura y la estabilidad de fases. Escalamiento estándar de velocidades y cadenas de Nosé-Hoover son usados como métodos de termostato para realizar simulaciones en modelos de potencial de pozo cuadrado, Lennard-Jones y el modelo primitivo suave. Remover la VCM al inicio o durante la simulación no es requerido para que el termostato de cadenas de Nosé-Hoover mantenga la temperatura correcta del sistema, sin embargo es fundamental mantener nula la VCM cuando se usa el esquema tradicional de escalamiento de velocidades. Se muestra que si la VCM es removida sólo al inicio de la simulación las temperaturas interna y externa no son iguales para tiempos de simulación muy grandes y el sistema se solidifica. La temperatura y las propiedades físicas obtenidas usando el método de cadenas de Nosé-Hoover son iguales a aquellas obtenidas usando escalamiento de velocidades donde se remueve la VCM durante la simulación.

*Descriptores:* Dinámica molecular; escalamiento de velocidades; cadenas de Nosé-Hoover; velocidad del centro de masa.

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### 1. Introduction

In molecular dynamics simulations is useful to keep the temperature constant to systematically study the effect on physical properties at the same thermal conditions. It is also important to directly compare the predictions with experimental data. The microcanonical equations of motion have to be modified in order the system follows an isothermal trajectory [1, 2] with energy fluctuations. Different schemes to control the temperature have been proposed on the literature. The so-called “rescaling velocities” method [3], where the instantaneous kinetic energy corresponds to an external temperature, has been widely used by the simulation community [1, 2] because is easy to code into a molecular dynamics program. The main concern of that method is that it does

not give the canonical distribution but it has been suggested that can be used to equilibrate the system [4]. Other routes to change the velocities with additional parameters than the external temperature are the Andersen [5], the Berendsen [6] methods and the Langevin dynamics presented by Adelman *et al.* [7]. These methods do not produce also the canonical ensemble either but produce a sampling of the canonical phase space distribution from which equilibrium properties can be computed [4]. It has been shown that Nosé-Hoover chains (NHC) method gives the correct velocity distribution on the canonical ensemble [8]. That method is based on dynamical extended variables and it is an extension of that proposed by Nosé-Hoover with one thermostat [9]. The thermodynamic properties on molecular systems using different methods to control temperature have been analyzed [10]. It is

not well established which properties depend on the thermostat parameter value, however the self-diffusion coefficient of water decreases to the half value when the parameter used in the Langevin dynamics is increased by a factor of 10 [11].

The idea of rescaling velocities is to fix the kinetic energy of the system to achieve a constant temperature along the time. In this procedure, it is usual to measure the velocity of particles respect to the VCOM of the system such that the total linear momentum is zero, *i.e.*, to translate the origin of the reference system to the centre of mass. Although results of physical properties using different approaches to control the temperature have been compared [10], we were unable to find a systematic study that analyzes the effect that the VCOM of the system has on thermodynamic properties when the traditional “rescaling velocity” method is applied to keep the temperature constant.

The temperature in a simulation is related with the kinetic energy of the system. When the system is isolated the total energy should be constant but in practice the energy fluctuates around an average value. For the square well potential the trajectory of particles is obtained analytically, therefore the simulation error is expected to be small. For Lennard-Jones and soft primitive models, continuous potentials, the equations of motion are solved numerically and the fluctuations of the total energy depend on the size of the time step used to perform the simulations. It is a common practice to choose the largest time step such that the fluctuations of energy are stable, *i.e.*, there is not a drift in energy as a function of time. The total energy is *constant* within a numerical error. The temperature in the isolated system is adjusted by the kinetic energy of the molecules and it can not be controlled by external sources. For many reasons, it is desirable to perform simulations at constant temperature and the particle velocities have to be modified to allow energy fluctuations. The temperature of the system does not have to include kinetic energy contributions from the centre of mass, that is why the VCOM has to be removed. In addition to the numerical errors observed in the simulation of isolated systems there is a new source of error if during the rescaling procedure the final velocities include also contributions due to the centre of mass.

The VCOM can be removed at the beginning of the simulation and should remain null during the simulation if there are not external forces. Nowadays is easy to perform large simulations and accumulative round-off errors might modify the VCOM affecting the temperature when the rescaling velocity method is applied. The evaluation of many properties require very long simulations, such as the calculation of surface tension in interface simulations, it is therefore useful to know if the VCOM is drift from the initial value of zero and which is the effect on the particles temperature and phase stability of the system. The main goal of this work is to show that when the standard rescaling method is applied and the VCOM is removed only at the beginning of the simulation, there is a drift of temperature that drives the system to an unphysical fluid-solid phase transition due to an increase of

the VCOM. In order to keep the internal and external temperatures equal it is required to remove the VCOM not just at the beginning but also during the simulation. The results using that latter procedure are in good agreement with those calculated in this work using the NHC method.

The rest of this work is organized as follows: The potential models used to perform the simulations are presented in Sec. 2, technical details about simulations are given in Sec. 3. Results are discussed in Sec. 4 and finally Concluding remarks and References are given.

## 2. Potential models

Three potential models for the interaction between pairs of particles are used to study the effect that VCOM has on the properties of the system.

The first one is the square well (SW) potential,

$$U_{SW}(r) = \begin{cases} \infty, & r < \sigma \\ -\epsilon, & \sigma \leq r \leq \lambda\sigma \\ 0, & r > \lambda\sigma \end{cases}$$

where  $\sigma$  is the hard sphere diameter,  $\epsilon$  is the well depth and  $\lambda = 1.5$  is the interaction range and  $r$  is the separation distance between two particles.

The second potential is the Lennard-Jones (LJ) model,

$$U_{LJ}(r) = \begin{cases} 4\epsilon \left[ \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right], & r \leq r_c \\ U_{lrc}, & r > r_c \end{cases}$$

where  $\sigma$  is the distance at which  $U_{LJ}(r) = 0$ ,  $\epsilon$  is the well depth,  $r_c = 4.7\sigma$  is the cut-off distance and  $U_{lrc}$  is the long-range correction [1].

The third potential is the soft primitive model (SPM) used to study a two-dimensional equimolar mixture of ions of diameter  $\sigma$ , carrying opposite charges [12],

$$U_{SPM}(r) = A_s \left(\frac{\sigma}{r}\right)^n + \frac{1}{4\pi\epsilon_0\epsilon_s} \frac{z_i z_j e^2}{r} \quad (1)$$

where  $z_i$  is the valence of ion  $i$ ,  $e$  is the electron charge,  $\epsilon_0$  is the vacuum permittivity and  $\epsilon_s = 1$ . The condition  $U_{SPM+-}(\sigma) = 0$  for unlike ions is applied to find the constant  $A_s$ ,

$$A_s = \frac{|z_+ z_-| e^2}{4\pi\epsilon_0\epsilon_s\sigma}. \quad (2)$$

Reduced units are used in this work for the three potential models. The dimensionless quantities in  $nd$  dimensions are: distance  $r^* = r/\sigma$ , energy  $u^* = u/\epsilon$ , temperature  $T^* = kT/\epsilon$ , density  $\rho^* = \rho\sigma^{nd}$ , time  $\Delta t^* = \Delta t(\epsilon/m\sigma^2)^{1/2}$  and pressure  $p^* = p\sigma^{nd}/\epsilon$ . For the SPM potential  $\epsilon = U_{+-}(r_{\min}) = A_s |[n^{n/(1-n)} - n^{1/(1-n)}]|$ , where the absolute value is indicated by bars, and  $r_{\min} = n^{1/(n-1)}\sigma$ , is the distance at which the potential is minimum [12]. Other parameters are  $n = 225$ ,  $A_s^* = A_s/\epsilon = 1.02905$ , and  $z_{\pm} = \pm 1$ .

### 3. Details about simulations

Several molecular dynamics simulations at supercritical conditions are performed to analyze the effect that the centre of mass velocity has on particles temperature and phase stability in very long simulations. Two short-ranged potentials, SW and LJ, in three dimensions and a long-ranged potential, SPM, in two dimensions are used. The equations of motion for the LJ and SPM models were solved using the velocity Verlet algorithm [1,2]. All the simulations and the results here presented come from double precision calculations.

For the SW potential, the collision time between two colliding particles of mass  $m$  is obtained to determine their trajectories [13]. The procedure to solve the equations of motion is analytic in this case, therefore the simulation error is rather small. This simulation is performed using  $N=256$  particles at  $T^* = 2$  and  $\rho^* = 0.6$ . The critical temperature and density for  $\lambda = 1.5$  are 1.218 and 0.31, respectively [14]. The initial positions are located in a FCC crystalline array and the velocities are randomly distributed. The centre of mass velocity of the system is removed at the beginning of the simulation. The system was followed by 80 blocks of 25 million collisions. Two temperatures are recorded during the simulation, one without removing the VCOM,  $T_{md}$ , and a second,  $T_{VCOM}$ , where the VCOM is removed from the velocity of every particle and the velocities are calculated as ( $\mathbf{v}_i = \mathbf{v}_i - \sum_i \mathbf{v}_i/N$ ). The temperature  $T_{VCOM}$  is not used to change the velocities during the simulation but to follow the temperature of particles as if the VCOM would be removed. In the simulation the velocity of particles is scaled by a factor  $(T/T_{md})^{1/2}$  every collision time, here  $T$  is the imposed temperature and  $T_{md} = 2K/(3N - 3)k_B$  is calculated using the kinetic energy  $K$  of the system, where  $k_B$  is the Boltzmann constant. The number of degrees of freedom is decreased by 3 in view of the VCOM is zero. If the scaling is done every 100 collisions the results are indistinguishable from those where the scaling is done every collision.

For the LJ potential three simulations are performed to keep the temperature constant, two using the traditional “rescaling velocity” method and a second using the Nosé-Hoover chains thermostat [8]. Simulations with  $N = 500$  particles at  $T^* = 2.0$  and  $\rho^* = 0.6$  are carried out. The critical temperature and density of the LJ potential are  $T_c^* = 1.309$  and  $\rho_c^* = 0.307$ , respectively [15]. The initial positions are allocated in a FCC crystalline array and the velocities are assigned according to a Maxwell distribution. The three simulations have the same initial conditions. In the first simulation the centre of mass velocity of the system was removed only at the beginning, and the temperature was controlled by rescaling the velocities of every particle in every step by  $(T/T_{md})^{1/2}$ . During this simulation the VCOM was not removed from the particle velocities. In the second simulation the VCOM was removed from the initial velocities and also at every time step. In the third simulation the Nosé-Hoover chains method was used with a thermostat per particle, length chain of 4 and a thermostat parameter of 0.05. The system in

all cases is followed by 50 blocks of  $5 \times 10^5$  time steps with reduced value of  $\Delta t^* = 0.003$ . The potential energy, pressure and pair distribution functions were calculated during the simulation.

For the two-dimensional ionic fluid modeled through the SPM potential, three simulations are performed using a total number of  $N = 512$  ions at  $T^* = 0.1$  and  $\rho^* = (N_+ + N_-)/A^* = 0.6$ , where  $A^* = A\sigma^2$  is the system area,  $N_+ = 256$  and  $N_- = 256$  are the number of ions with positive and negative charges, respectively. The reduced critical temperature for this potential model is 0.0405 [16]. The particles are initially allocated in a square with velocities given by a Maxwell distribution. The electrostatic interactions were calculated using a 2D version of the Ewald sum [16] with parameters:  $r_c^* = 14.6$ ,  $\eta\sigma = 0.12$ , and reciprocal vectors generated with  $n_x^{\max} = n_y^{\max} = 5$ . The rescaling

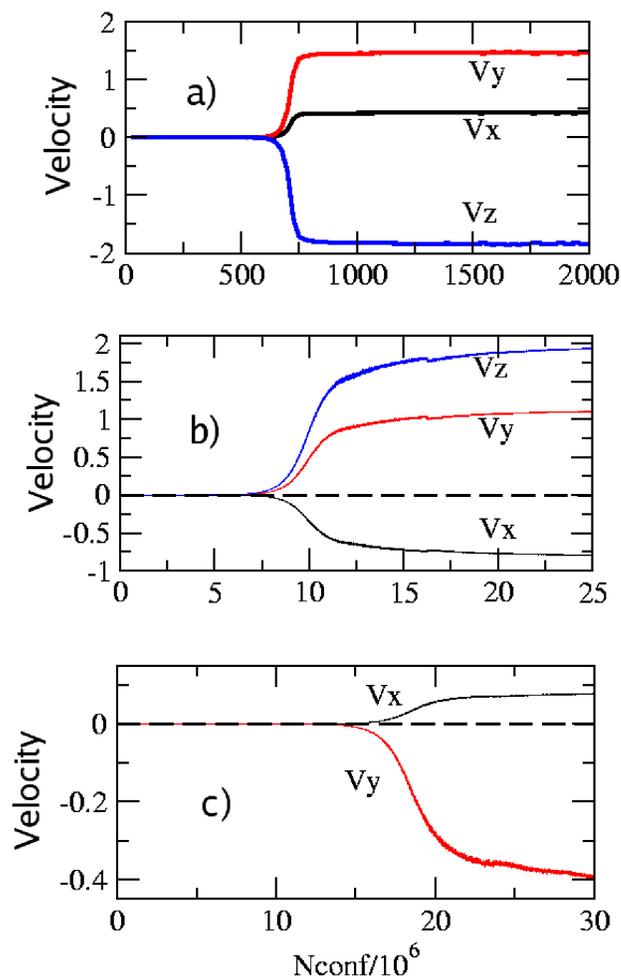


FIGURE 1. Components of the centre of mass velocity of the system as a function of configurations number (Nconf): a) SW, b) LJ, and c) SPM. Labeled lines are results where the VCOM is removed only at the beginning of the simulation in the rescaling procedure. The results where the VCOM is removed during the simulation in the rescaling method are indistinguishable from the NHC values (dashed lines). The results for the NHC are only shown for clarity.

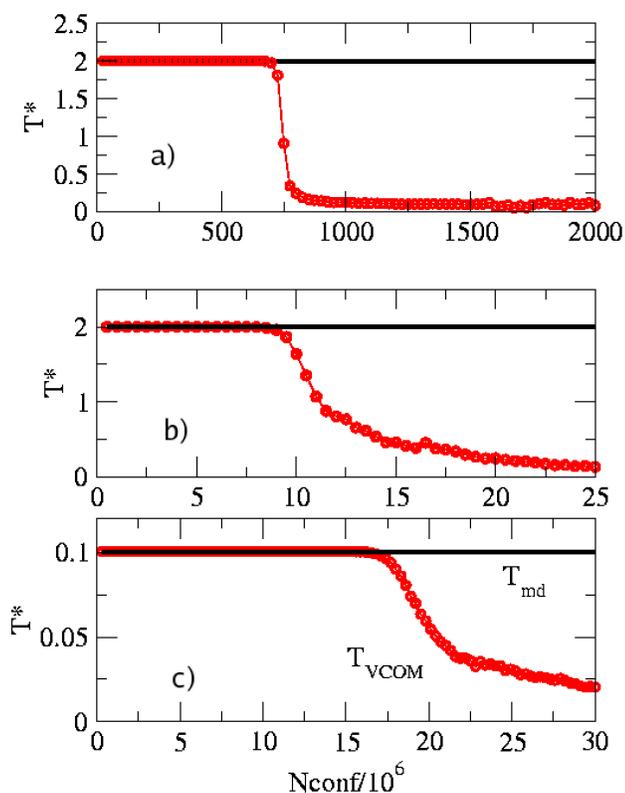


FIGURE 2. Temperature  $T_{md}$  (continuous line) and  $T_{VCOM}$  (open circles) obtained when the rescaling procedure is applied: a) SW, b) LJ and c) SPM. The temperature obtained using the NHC method for the LJ and SPM, parts b) and c), are indistinguishable from those obtained by removing the VCOM during simulations where rescaling is applied. The NHC results are only shown, for clarity, with a continuous line.

method is applied to two simulations, in both cases the VCOM is removed at the beginning but only in one case the VCOM is also removed during the simulation. The temperature of the system was obtained by rescaling the velocities by  $(T/T_{md})^{1/2}$ . The NHC method is applied to a third simulation. A thermostat per particle is used with chain length of 4 and parameter of 0.05. The system is followed for 60 blocks of  $5 \times 10^5$  time steps. The reduced time step is 0.002. The potential energy, pressure and pair distribution functions are followed as a function of time.

#### 4. Results

Molecular dynamics simulations at constant temperature are performed to evaluate the effect that the centre of mass velocity of the system has on temperature, pair distribution functions, pressure and potential energy. The analysis is performed using SW, LJ and SPM potentials.

The components of the VCOM are shown in Fig. 1 for the SW, LJ and SPM models. The results for the rescaling method without removing the VCOM during the simulation are displayed in parts a), b) and c). The results for the rescaling method where the VCOM is removed every time step are

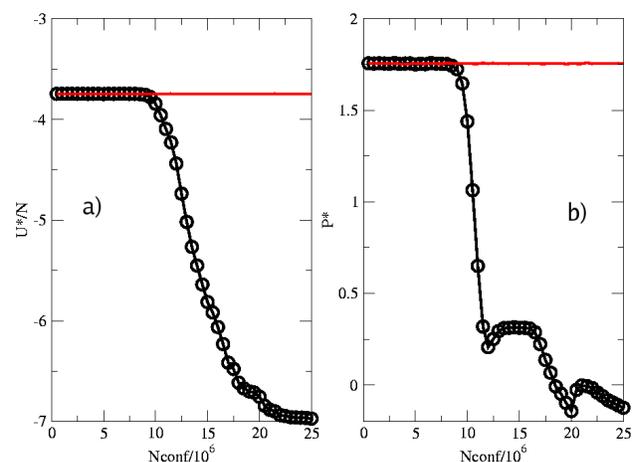


FIGURE 3. Thermodynamic properties of the LJ fluid at supercritical conditions  $T^*=2.0$  and  $\rho^*=0.6$ . a) Potential energy, b) Pressure. Results where the VCOM is removed during the simulation are shown with a continuous line and with open circles those values where the VCOM is not removed during the simulation. The NHC results, not shown, are identical to those given with continuous lines.

shown in parts b) and c). In this case there is not drift of the VCOM for the whole simulation time and the results are identical to those obtained using the NHC method. The components of the VCOM for parts a), b) and c) remain constant and close to zero for a long period of time, however, progressively they start to change reaching a new stable value. The LJ potential results are obtained using the same parameters in both the rescaling and NHC methods, therefore, the different results can not be associated to errors introduced by the potential truncation. When the VCOM is removed at the beginning but not during the simulation the system can change the VCOM due to round-off error and introduce a bias on the particle velocities such that temperature obtained after rescaling the velocities has two components, one due to the particles and a second due to the centre of mass of the system. Figure 1 shows that for the square well model the VCOM components are around zero up to 750 million of collisions while for the LJ and SPM models the velocity components change up to 7 and 15 million of time steps. The numerical error, as expected, affects more the velocity of the continuous models.

Figure 2 shows the calculated temperature  $T_{md}$  as a function of time for the a) SW, b) LJ and c) SPM models. The continuous lines are results for systems where the temperature is obtained by rescaling the velocities by a factor  $(T/T_{md})^{1/2}$ , when the VCOM is removed during simulations  $T_{md}$  is the temperature due to particle velocities only. When the VCOM is not removed during simulations the temperature associated to particles  $T_{VCOM}$ , is estimated by subtracting the VCOM from each particle velocity. The results of  $T_m$  and  $T_{VCOM}$  are shown in Fig. 2 for each model. The temperatures  $T_{md}$  and  $T_{VCOM}$  are the same, within the simulation error, for the first part of the simulation, however, as time evolves  $T_{VCOM}$  starts

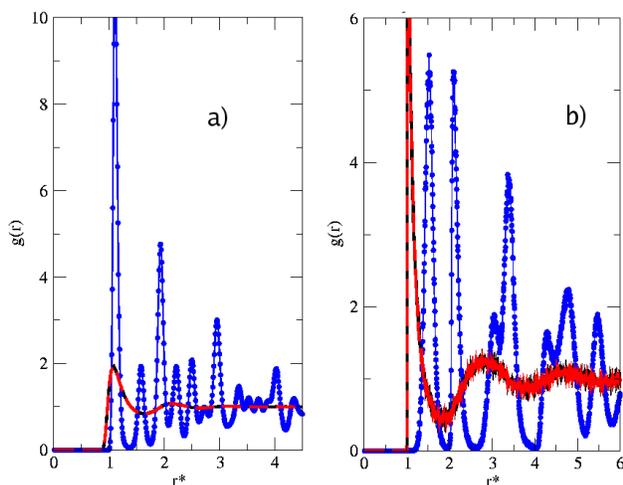


FIGURE 4. Pair distribution functions at supercritical conditions: a) LJ at  $T^*=2.0$  and  $\rho^*=0.6$ . b) SPM at  $T^*=0.1$  and  $\rho^*=0.6$  for species  $+ -$ . The continuous black lines are for results where the VCOM of the system is removed during the simulation. The dashed red lines are for results for the first 2.5 million steps, of a run of 25 millions, where the VCOM is only removed at the beginning of the simulation and the filled circles are for results of the last 1 million steps. The NHC results, not given, are identical to those shown with continuous lines.

to decrease until it reaches a stable value substantially lower than  $T_{md}$ .

The potential energy and pressure for the LJ potential are shown in Fig. 3. The results for systems where the rescaling method combined with removing the VCOM during simulations was applied are the same as those obtained using the NHC method, these results are also in good agreement with those reported by Johnson *et al.* [17] at the same thermodynamic conditions. When the VCOM is not removed during simulation the potential energy decreases to more negative values and the pressure changes from positive to negative values. The same behavior found in these properties for the LJ potential is observed for the SW and SPM models (not shown). The average value of potential energy of LJ model using the NHC and rescaling velocity methods with the VCOM removed every time step are -3.747 and -3.747, respectively. The corresponding values of pressure are 1.754 and 1.755, respectively. The values reported by Johnson *et al.* for these properties are -3.747 and 1.75 [17]. The average value of potential energy of the SPM fluid using the NHC and rescaling velocity methods with VCOM removed every time step are -0.6357 and -0.6355, respectively. The corresponding values of pressure are 0.137 and 0.138, respectively. The energy and pressure reported by Weis [16] for an ionic fluid with hard core repulsions are -0.616 and 0.131, respectively. The differences between the Weis *et al.* results and those from this work are associated to slightly different potential models, hard sphere in their case and soft sphere in this work.

The pair distribution functions of LJ and SPM models are shown in Fig. 4. The rescaling method with removing VCOM during simulation and the NHC method give a liquid-like

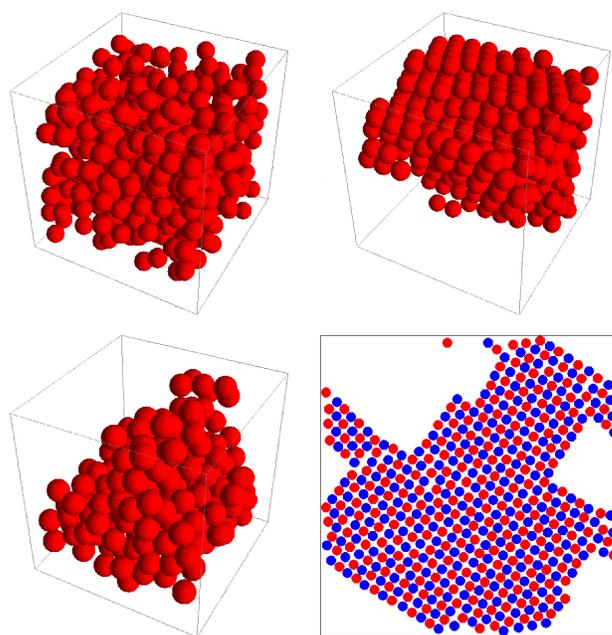


FIGURE 5. Snapshots of systems at supercritical conditions at the end of long simulations: a) LJ (left upper part): The VCOM is removed every time step and the particles fill the simulation cell, the system has a liquid-like structure, b) LJ (right upper part), c) SW (left down part) and d) SPM (right down part). The VCOM is removed just at the beginning of the simulations in parts b), c) and d) and the particles do not fill the simulation cell, the systems have an unphysical solid-like structure.

structure, the results for the SPM compare well with those reported by Weis at the same thermodynamic conditions [16]. When the VCOM is not removed the pair distribution function displays the typical behavior of a fluid for a long lapse of time, about  $10 \times 10^6 \Delta t^*$  for the LJ system and  $30 \times 10^6 \Delta t^*$  for the SPM ionic fluid. After this time the pair distribution function evolves to a solid-like structure in both cases. The systems exhibit an unphysical liquid-solid transition due to an incorrect evaluation of temperature using the rescaling velocity method. The same trend on pair distribution functions is found in the SW potential (not shown). Figure 5 shows snapshots of the final configuration for the LJ in a) and b), c) SW and d) SPM models. The liquid-like structure obtained by using the rescaling procedure and removing the VCOM during simulations or with the NHC is shown in Fig. 5 for the LJ model (upper left part). Large voids within a crystal are observed when the LJ and SPM models are simulated with a no null VCOM (right column) but in the case of the SW model (lower left panel) the system evolves to an amorphous solid.

## 5. Concluding remarks

The role that the VCOM of the system plays in molecular dynamics simulations, where the rescaling velocity and NHC methods are applied has been analyzed. The temperature and properties of the system are the same, within error in the simulation when they are calculated using either the NHC

method or the traditional rescaling method with additional removing of the VCOM during the simulation. The implications of not using the removal can lead to incorrect results, for instance, an unphysical liquid-solid phase transition. In very long runs, it was found that the VCOM behaves as an increasing function of time with a hyperbolic tangent shape. We associate this behavior to a round-off error which results from removing the VCOM only at the beginning but not during the simulation, producing a drift on the system temperature when the rescaling method is applied. The results for the LJ and SPM potential using the NHC and the rescaling methods show that the drift in temperature is not associated to the truncation of the forces.

The simple rescaling method with the corresponding removal of velocity of the centre of mass can be used to obtain accurate results of the thermodynamic and structural properties of the system with the same quality as those obtained using the more sophisticated and computationally expensive Nosé-Hoover chain of thermostats method.

In this work we focus the study on one-phase simulations but the conclusions are also valid for inhomogeneous systems.

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