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Shear viscosity of molten sodium chloride

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The shear viscosity of molten sodium chloride is determined under a wide range of strain rates using nonequilibrium molecular dynamics (NEMD) simulations in the canonical (N,V,T) ensemble. Questions have been recently raised on the use of kinetic temperature thermostats, based on the equipartition principle, in simulations of nonequilibrium fluids and using a configurational temperature thermostat has been suggested to be more realistic. To further ascertain the results obtained in this work, we study molten NaCl with both kinetic and configurational temperature thermostats. Since configurational thermostats have been so far restricted to simple fluids or alkanes, we first apply configurational expressions for the temperature to molten NaCl, test the values so obtained in equilibrium molecular dynamics simulation for various system sizes and state points and finally use them to thermostat molten NaCl under shear. NEMD results obtained for both thermostats show that except for the so-called normal stress coefficients, molten salt under shear exhibits mostly the same features as a simple fluid under shear, i.e., features in agreement with the mode-coupling theory. The choice of the thermostating method is found to have little influence on the results for the range of shear rates investigated. © 2003 American Institute of Physics.
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I. INTRODUCTION

Nonequilibrium molecular dynamics (NEMD) simulation^{1–5} has been often used over recent years to understand and characterize the rheological properties of fluids undergoing shear flow. The homogeneous SLLOD algorithm,⁵ in which the strain rate is introduced in the equations of motion as a mechanical perturbation, is now a standard method to determine shear viscosities and to study the effect of shear on internal rotation and conformation of molecules.^{5–7} This method has been extensively applied to simple fluids and alkanes and much more rarely to polar liquids^{8,9} or polar liquids mixtures.¹⁰ To our knowledge, it has not yet been applied to study the properties of a molten salt under shear.

In homogeneous NEMD, a thermostating mechanism is required to mimic the natural ways by which heat is dissipated, such as conduction, convection and radiation. The methods most commonly used to eliminate viscous heating in the SLLOD algorithm, the Gauss constraint method and the Nosé–Hoover integral feedback method,⁵ are based on the kinetic definition of temperature. With this definition, motion relative (i.e., “peculiar”) to the flow is thermostatted using the equipartition principle. However, the flow velocity is often difficult to determine. The two “profile biased” thermostats mentioned above solve this problem by assuming a linear streaming velocity profile in the direction of applied shear. This assumption had been tested by simulation of an atomic fluid sheared between two thermostatted atomic

walls, and it was shown that it gives a satisfactory description for low and moderate strain rates.⁶

The need for knowledge of the actual streaming velocity profile can be completely bypassed by using a thermostat based on a configurational expression for the temperature.^{11–18} The profile biased kinetic thermostats and the configurational temperature thermostat give different descriptions of strongly sheared simple liquids and of nonequilibrium molecular liquids where different types of degrees of freedom (translation, rotation, and vibration) are involved. For the latter systems, studies^{17,18} suggest that the “configurational” thermostat is more realistic since it takes into account all degrees of freedom on an equal footing.

On the other hand, one has to be careful when using configurational expressions for the temperature. Previous work on simple fluids has shown that these expressions could depend strongly on the density and on the size of the system simulated.^{13,15} Preliminary studies on the influence of density and system size on the value taken by configurational expressions for the temperature of ionic fluids are thus required before these expressions can be reliably used to evaluate and thermostat such fluids.

Our aim in this work is twofold: First, we assess the suitability of the configurational expressions for the temperature and the efficiency of a configurational thermostat for systems with electrostatic interactions in and out of equilibrium. Second, we apply the SLLOD algorithm to molten NaCl, as an archetypal ionic system, in order to study the influence of shear on its transport and structural properties. We study the influence of the thermostating method on the NEMD simulation in ionic systems by comparing results ob-

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tained with a Gaussian isokinetic and a configurational temperature thermostat.

The paper is organized as follows: First, we briefly present the configurational expressions for the temperature used in this work. Since configurational expressions have been so far mostly applied to simple fluids or alkanes (with the exception of Refs. 19 and 20 where they were used to estimate the temperature in polar fluids), we first test the density and number dependence of these expressions for molten NaCl. In equilibrium, the values given by the configurational expressions should match the kinetic values obtained by applying the equipartition principle. Comparisons of the results obtained with the two thermostats will allow us to assess the density dependence as well as the finite size effect of the simulated system. We subsequently apply these conclusions to the study of molten NaCl under shear, using the SLLOD algorithm with either a kinetic temperature thermostat or a configurational temperature thermostat. Results so obtained are then compared to those obtained for a simple fluid. Finally, we discuss the influence of the thermostating mechanisms on the results.

II. CONFIGURATIONAL EXPRESSIONS FOR TEMPERATURE IN IONIC FLUIDS

Let us consider an N -particle system. We denote a phase space vector by $\Gamma = (\mathbf{q}_1, \dots, \mathbf{q}_N, \mathbf{p}_1, \dots, \mathbf{p}_N)$, where $\mathbf{q}_i$ is the position coordinate of particle i and $\mathbf{p}_i$ is its momentum. The energy of the system is given by the Hamiltonian,

$$H(\Gamma) = \sum \frac{\mathbf{p}_i^2}{m_i} + V(\{\mathbf{q}_j\}), \quad (1)$$

where V stands for the potential energy. Extending Rugh's result,¹¹ Jepps *et al.*¹³ showed that the temperature can be evaluated through

$$k_B T = \frac{\langle \nabla H \cdot \mathbf{B}(\Gamma) \rangle}{\langle \nabla \cdot \mathbf{B}(\Gamma) \rangle}, \quad (2)$$

where $\mathbf{B}(\Gamma)$ is an arbitrary phase space vector [$\mathbf{B}(\Gamma)$ must be such that $0 < \langle \nabla \cdot \mathbf{B} \rangle < \infty$, $0 < \langle \nabla H \cdot \mathbf{B} \rangle < \infty$, where the triangular brackets represent an ensemble average and $\langle \nabla H \cdot \mathbf{B} \rangle$ grows more slowly than e^N in the thermodynamic limit]. This expression has been shown to hold in the (N,V,E) microcanonical ensemble and in the (N,V,T) canonical ensemble.

We can choose the vector $\mathbf{B}(\Gamma)$ such that temperature can be expressed only in terms of first and second spatial derivatives of the Hamiltonian. If we choose $\mathbf{B} = \mathbf{G} \cdot \nabla H$, where $g_{ij} = \delta_{ij}$ if i and j refer to coordinates and 0 otherwise, we have the following expression for temperature:

$$k_B T_{\text{conf}} = \frac{\langle \sum_{i=1}^N \mathbf{F}_i^2 \rangle}{\langle -\sum_{i=1}^N \nabla_i \cdot \mathbf{F}_i \rangle}, \quad (3)$$

where $\mathbf{F}_i$ is the total force exerted on particle i and the index conf denotes that the expression so obtained is a fraction of averages.

Another choice can be made $\mathbf{B} = (\mathbf{G} \cdot \nabla H) / (\nabla H \cdot \mathbf{G} \cdot \nabla H)$, where $g_{ij} = \delta_{ij}$ if i and j refer to coordinate and 0 otherwise, leading to the following expression for temperature,

$$\frac{1}{k_B T} = \left\langle \frac{-\sum_{i=1}^N \nabla_i \cdot \mathbf{F}_i}{\sum_{i=1}^N \mathbf{F}_i^2} - \frac{2 \sum_{i,j=1}^N \mathbf{F}_i \mathbf{F}_j : \nabla_i \nabla_j}{(\sum_{i=1}^N \mathbf{F}_i^2)^2} \right\rangle. \quad (4)$$

As pointed out by Jepps *et al.*,¹³ the second term on the right-hand side of (4) vanishes in the thermodynamic limit for a short-ranged potential. Thus one can define an order 1 configurational expression for the temperature noted as T_{conf1} ,

$$\frac{1}{k_B T_{\text{conf1}}} = \left\langle \frac{-\sum_{i=1}^N \nabla_i \cdot \mathbf{F}_i}{\sum_{i=1}^N \mathbf{F}_i^2} \right\rangle. \quad (5)$$

It is interesting to point out that since $\Delta(1/r) = 0$, the electrostatic interactions do not contribute to the denominator on the right-hand side of Eq. (3) and the numerators in (4). A consequence of this fact is that configurational temperature diverges for purely $1/r$ potentials, such as, e.g., gravitational systems of point particles or a one-component plasma. In force fields used in molecular dynamics simulations, electrostatic interactions are always accompanied by at least a short-ranged repulsive term which falls off with a higher power of $1/r$, and therefore the values taken by Eqs. (3) and (4) are always finite. While in this case only the short-ranged interactions directly contribute to the denominator of the right-hand side of Eq. (3), all types of interactions contribute to the numerator.

III. MODEL AND SIMULATION METHODS

A. Interionic pair potential

We used the well-known Born–Huggins–Mayer potential to describe the interionic pair interactions:²¹

$$\phi_{ij}(r) = z_i z_j \frac{e^2}{r_{ij}} + A_{ij} \exp[B(\sigma_i + \sigma_j - r_{ij})] - \frac{C_{ij}}{r_{ij}^6} - \frac{D_{ij}}{r_{ij}^8}, \quad (6)$$

where z_i and z_j are the formal charges of ions i and j , respectively, and A_{ij} , B , $(\sigma_i + \sigma_j)$, C_{ij} and D_{ij} are parameters deduced by Fumi and Tosi²² from the properties of solid alkali halides. This model has been extensively studied in the literature. Though certainly too simplistic because it neglects polarization effects,²³ this pair potential yields a reasonably good description of thermodynamics,²⁴ structure and transport properties^{25–27} of molten salts.

B. Simulation methods

All equilibrium molecular dynamics (EMD) and non-equilibrium molecular dynamics (NEMD) simulations are performed in the constant temperature (N,V,T) ensemble. EMD simulations were performed using a Gaussian thermostat,⁵ which holds fixed the total peculiar kinetic energy and hence the temperature. Long-range interactions were handled using the Ewald sum technique (real space electrostatic interactions are cut off at $L/2$, where L is the boxlength, the

reciprocal space wave vector cutoff is $k_{\max}=6\cdot(2\pi)/L$, the convergence acceleration factor was chosen as $k=1.8\pi/L$ and conducting boundary conditions were used). NEMD simulations of NaCl undergoing shear flow were performed by integrating the SLLOD equations of motion,⁵

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i} + \gamma y_i \cdot \mathbf{e}_x, \quad (7a)$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i^N - \gamma p_{y_i} \mathbf{e}_x, \quad (7b)$$

where $\mathbf{r}_i(\mathbf{p}_i)$ stands for the position (momentum) of the center of ion i , $\mathbf{F}_i^N$ is the Newtonian force acting on i , m_i the mass of i , γ the imposed strain rate, $\mathbf{e}_x$ is a unit vector, parallel to the direction of the flow, y_i (p_{y_i}) the coordinate (component of the momentum) along the y axis, $\mathbf{p}_i$ the momentum of i . In Eqs. (7a) and (7b), $\mathbf{p}_i$ is in fact the peculiar momentum of the ion i with respect to the linear velocity profile of slope γ (the peculiar kinetic energy is obtained by summing the squares of the peculiar momenta for all i).

This algorithm requires the use of the Lees–Edwards “sliding brick” periodic boundary conditions¹ consistent with the strain rate γ . As pointed out in previous work,^{9,10} these nonorthogonal periodic boundary conditions cannot be used in conjunction with the usual form of the Ewald sum, which is specific to an orthogonal lattice of simple cubic simulation cells.²⁸ A similar conclusion was drawn by Balasubramian *et al.* who performed NEMD simulations of shear flow with deforming box boundary conditions.⁸ In this work, we use the generalized Ewald sum proposed by Wheeler *et al.*^{9,10} in conjunction with the SLLOD algorithm.

Two types of thermostats were used in the NEMD simulations performed in this work. First, a Gaussian isokinetic thermostat was used to fix the total peculiar kinetic energy. In this case, the NVT-SLLOD equations of motion are⁵

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i} + \gamma y_i \cdot \mathbf{e}_x, \quad (8a)$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i^N - \gamma p_{y_i} \mathbf{e}_x - \xi \mathbf{p}_i, \quad (8b)$$

where ξ is the thermostat multiplier, determined by applying Gauss’ principle of least constraint.⁵

Second, we applied a thermostat based on the configurational expression for temperature presented in Sec. II. This thermostat is devised in analogy with the Nosé–Hoover thermostat:²⁹ an extended system, with an additional degree of freedom s , is considered and the configurational temperature is maintained using integral feedback. However, since the configurational temperature is evaluated from the positions and not from the momenta, the thermostatting term is included in the position equations instead of the momentum equations. We have the following NVT-SLLOD equations of motion:^{16–18}

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i} + \gamma y_i \cdot \mathbf{e}_x + \frac{s}{T_0} \cdot \frac{\partial T_{\text{con1}}}{\partial \mathbf{r}_i}, \quad (9a)$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i^N - \gamma p_{y_i} \mathbf{e}_x, \quad (9b)$$

FIG. 1. Influence of the system size (N is the number of NaCl molecules) on the value taken by the configurational expressions T_{con1} (squares) and T_{conF} (circles) for NaCl and for a modified NaCl—with electrostatic interactions turned off (triangles and diamonds, respectively) in EMD simulations at ($T=2060$ K, $\rho=1.55$ g cm⁻³).

$$\dot{s} = -Q_{Tc} \cdot \frac{(T_{\text{con1}} - T_0)}{T_0}, \quad (9c)$$

where T_0 is the input temperature and Q_{Tc} a damping constant ($Q_{Tc} = \sigma^2/\tau_{Tc}^2$ with τ_{Tc} the response time of the feedback mechanism). T_{con1} is evaluated at each timestep through the order 1 expression given in Eq. (5). The value of the damping constant for the configurational temperature thermostat Q_{Tc} is set to 100.0.

In most cases, the equations of motion were integrated using a fifth order Gear predictor–corrector algorithm with a time step of 1 fs. When a configurational thermostat is used for shear rates higher than 5 ps⁻¹, the equations of motion are found to be quite stiff and require smaller timesteps to be properly integrated (e.g., the timestep was chosen to be of 0.2 fs for a shear rate of 8 ps⁻¹).

IV. EQUILIBRIUM RESULTS

A. System size dependence of the configurational temperature

We first study molten NaCl at a state point that lies in the liquid phase ($T=2060$ K, $\rho=1.55$ g cm⁻³) according to the phase diagram given by Guissani and Guillot.²⁴ We perform EMD simulations in the (N,V,T) ensemble with an isokinetic Gaussian thermostat for systems of size ranging from 108 ions (54 Na⁺ and 54 Cl⁻) to 864 ions (432 Na⁺ and 432 Cl⁻) and measure the values taken by the configurational expressions T_{con1} and T_{conF} . Since the fluid is at equilibrium, the values of the configurational expressions should match the kinetic value T_{kin} , obtained by applying the equipartition principle. In Fig. 1, we plot the ratios $T_{\text{con1}}/T_{\text{kin}}$ and $T_{\text{conF}}/T_{\text{kin}}$ obtained for the various system sizes of molten NaCl at equilibrium. Results obtained for a “neutral NaCl,” with the electrostatic interactions switched off, are also plotted in Fig. 1. “Neutral NaCl” is very similar to the simple

FIG. 2. Influence of the density on the value taken by the configurational expressions T_{con1} and T_{conF} for NaCl and for a modified NaCl—with electrostatic interactions turned off in the EMD simulation of 432 ions (216 Na^+ and 216 Cl^-) at $T=3500$ K. The same legend as in Fig. 1.

fluids studied so far. We first note that the configurational expressions give an estimate for the temperature in excellent agreement with T_{kin} for all systems sizes (the maximum discrepancy is of 1%). We also observe for both fluids the convergence of the configurational temperatures towards a common value, i.e., the thermodynamic temperature, in the thermodynamic limit. In agreement with previous work^{13,15} on simple fluids, we note that T_{conF} is the most efficient choice of a configurational temperature, since its convergence in the thermodynamic limit is faster than for T_{con1} . Finally, we note that the configurational expressions converge slightly faster for “neutral NaCl” than for NaCl for that particular state point. This is not a general rule but depends on density of the state point studied, as we shall see below.

B. Density dependence of the configurational temperature

Our next study concerns a system of 432 ions (216 Na^+ and 216 Cl^-) at a series of state points situated on the $T=3500$ K isotherm in the supercritical phase, with densities ranging from 0.01 to 1.5 g cm^{-3} . In Fig. 2, the ratios of configurational temperatures to the kinetic temperature obtained for NaCl are compared to those obtained for the “neutral NaCl” at the same kinetic temperature and density. We first observe that, for “neutral NaCl,” T_{con1} is an inefficient measure of temperature at low densities. This is due to the fact that the omitted term in T_{con1} becomes more important as density drops. Since T_{con1} will converge to the thermodynamic temperature in the thermodynamic limit, this result shows that larger systems sizes are required for the same degree of convergence of T_{con1} as the density of the fluid of “neutral NaCl” drops. On the other hand, T_{con1} gives a reliable estimate for the temperature at all densities for NaCl.

FIG. 3. Integrated stress autocorrelation function $\eta(t)$ for molten NaCl at $T=1500$ K and $\rho=1.5 \text{ g cm}^{-3}$.

This is presumably due to the interplay between two factors for NaCl: (1) since there is no cutoff for electrostatic interactions, the denominator in Eq. (4) never vanishes regardless of how low the density is (which occurs in the case of the “neutral NaCl” fluid) and how “small” the system studied is; and (2) since $\Delta(1/r)=0$, electrostatic interactions do not contribute to the omitted term in the T_{con1} expression, which consequently becomes less important. On the other hand, T_{conF} represents an efficient measure of temperature for both systems at all densities.

These two series of calculations have allowed us to assess the efficiency and the accuracy of both T_{con1} and T_{conF} expressions that can be reliably used to estimate the temperature in systems of a few hundred molecules of NaCl.

C. Equilibrium viscosity and Maxwell relaxation time

We investigated the system of 512 ions (256 Na^+ and 256 Cl^-) at the state point of $T=1500$ K and $\rho=1.5 \text{ g cm}^{-3}$, which lies well inside the liquid phase. As a test of the non-equilibrium code, we first calculated the equilibrium viscosity at this state point using the Green–Kubo formalism. After initial equilibration of 500 ps, the stress autocorrelation functions were evaluated in five runs of 2 ns each, using a time window of 20 ps, in order to estimate the statistical spread of the results. The integrated autocorrelation function $\eta(t)$ is shown in Fig. 3. Its convergence to the plateau value of $\eta \equiv \eta_\infty = 0.782 \pm 0.015 \text{ mPa s}$ is remarkably fast, within the first 5 ps of the time window. We have not found the experimental data for the viscosity at this state point, but this result corresponds well to the result of 0.87 mPa s obtained by Cicotti *et al.*²⁵ for the same density, but at a lower temperature of 1262 K.

If we plot the logarithm of the difference of $\eta_\infty - \eta(t)$ versus time, it is fairly linear within the first 1 ps, from which we conclude that it is safe to use the Maxwell model of viscoelasticity in order to estimate the relaxation time τ_M of the system. In the Maxwell model, it is assumed that the stress autocorrelation function (i.e., the memory function) decays exponentially. With this assumption, the characteristic decay time τ_M is found as

$$\tau_M = \eta / G_\infty, \quad (10)$$

where G_∞ is the infinite frequency shear modulus, equal to the initial value of the memory function,

$$G_\infty = \frac{V}{k_B T} \langle P_{xy}^2(0) \rangle, \quad (11)$$

and P_{xy} is the shear stress. In our case of molten NaCl at 1500 K and at the density of 1.5 g/cm^3 , the infinite frequency shear modulus is $G_\infty = 0.967 \text{ kbar}$, and the Maxwell time is estimated as 0.081 ps .

It is difficult to compare the properties of molten salts and simple Lennard-Jones liquids. Because the phase diagrams have such different shapes, it is not possible to define the corresponding states or a common system of reduced units. Therefore, in order to compare the dependence of properties on shear in a more quantitative way, we use the dimensionless quantity $\gamma\tau_M$ to characterize the equivalent shear rates.

V. NONEQUILIBRIUM RESULTS

We now turn to the study of molten NaCl under shear using the SLLOD algorithm together with either a Gaussian isokinetic thermostat or a configurational temperature thermostat. All NEMD simulations are carried out for systems of 512 ions (256 Na^+ and 256 Cl^-). The simulated state point lies in the liquid phase ($T=1500 \text{ K}$, $\rho=1.5 \text{ g cm}^{-3}$).

A. Shear viscosity

We first give an account of the variation of shear viscosity with strain rate. Mode-coupling theory^{30,31} suggests a square root dependence of the zero wavevector viscosity with strain rate, in the limit that $\gamma \rightarrow 0$

$$\lim_{\gamma \rightarrow 0} \eta(\gamma) = \eta(0) - b\gamma^{1/2}, \quad (12)$$

where $\eta(0)$ is the equilibrium Navier–Stokes shear viscosity and b is a constant. The shear viscosity is plotted against the square root of the strain rate in Fig. 4. The shear viscosity at zero strain rate was estimated in EMD simulations using Green–Kubo formalism²⁸ and is also plotted in Fig. 4. The shear viscosity obtained using the two types of thermostats is essentially the same for low shear rates ($<0.8 \text{ ps}^{-1}$) and give a very good estimate of the zero strain rate shear viscosity. We observe 3 distinguishable regions for both thermostats: the Newtonian region with a constant viscosity for very low strain rate ($<0.1 \text{ ps}^{-1}$) and two linearly decreasing region of different slopes which intersect at a crossover strain rate of $2.6 \pm 0.1 \text{ ps}^{-1}$ (the crossover strain rate is about the same for both thermostatting mechanisms). These results show that molten salt under shear has qualitatively very similar behavior to that of a sheared simple fluid, as reported in a very detailed and accurate study by Borzsak *et al.*³² In order to compare the features of shear dependence of viscosity in a more quantitative manner, we used the Maxwell model of viscoelasticity to calculate the response time of the system studied in Ref. 32, i.e., the WCA fluid at the Lennard-Jones triple point. In the Lennard-Jones reduced units, a Green–Kubo simulation yielded for the infinite frequency shear modulus $G_\infty=24.9$, shear viscosity $\eta=3.45$ and the Maxwell

FIG. 4. Shear viscosity of molten NaCl against $\gamma^{0.5}$ using a kinetic temperature thermostat (open squares) and a configurational thermostat (open diamonds). The filled circle is an EMD estimate of the shear viscosity using the Green–Kubo formalism. Solid lines are fits to the Cross equation (Eq. 13) and dashed lines are linear fits according to mode-coupling theory.

time of $\tau_M=0.138$. Borzsak *et al.*³² found that the Newtonian regime holds for the product $\gamma\tau_M < 0.0014$, and the second region for $0.0014 < \gamma\tau_M < 0.017$. Of course a much more detailed study of NaCl under a very low strain rate—using transient time correlation function formalism like Borzsak *et al.*³²—would be necessary to clearly identify the Newtonian region. From our results on molten NaCl, the Newtonian regime holds for the product $\gamma\tau_M < 0.008$, and the second region for $0.008 < \gamma\tau_M < 0.16$. This seems to show that molten NaCl have a longer Newtonian region and after that viscosity as a function of the square root of strain rate can be represented by a single line for a larger range.

Fits to an empirical formula, the four parameter Cross equation,³³ are also plotted against the strain rate in Fig. 4,

$$\frac{\eta(\gamma) - \eta_{\text{inf}}}{\eta(0) - \eta_{\text{inf}}} = \frac{1}{1 + (K\gamma)^m}, \quad (13)$$

where $\eta(0)$ and η_{inf} are the asymptotic values of viscosity at very low and very high strain rates, respectively, and K and m are constants. As pointed out by Travis *et al.*,³¹ this equation is not restricted to the vanishing strain rate regime. A great many real materials have flow curves which can be described using this 4-parameter Cross equation. As shown in Fig. 3, the Cross equation fits the data quite well. Results so obtained for $\eta(0)$ (0.791 mPa s with T_{kin} fixed and 0.783 mPa s for T_{conf} fixed) are in good agreement with the Green–Kubo estimate at equilibrium (0.782 mPa s). The two thermostats also give similar results for the infinitely high strain rate value (0.267 mPa s with T_{kin} fixed and 0.271 mPa s for T_{conf} fixed), while the values of the constants K (0.452 ps with T_{kin} fixed and 0.594 ps for T_{conf} fixed) and m (1.24 with T_{kin} fixed and 1.48 for T_{conf} fixed) are significantly different.

FIG. 5. An increase in hydrostatic pressure from the value at equilibrium of molten NaCl against $\gamma^{1.5}$ using a kinetic temperature thermostat (open squares) and a configurational thermostat (open diamonds).

B. Thermodynamic properties

We proceed to study the variation of the thermodynamic properties with shear rate. According to mode-coupling theory,³⁰ hydrostatic pressure and internal energy should vary with strain rate as $\sim \gamma^{3/2}$. Variations of the hydrostatic pressure and internal energy are plotted against $\sim \gamma^{3/2}$ in Figs. 5 and 6, respectively. The results obtained using both thermostats support the mode-coupling result as observed for

FIG. 6. An increase in internal energy from the value at equilibrium of molten NaCl against $\gamma^{1.5}$ using a kinetic temperature thermostat and a configurational thermostat. Same legend as in Fig. 5.

FIG. 7. Normal stress coefficients η_- and η_0 of molten NaCl against $\gamma^{1.5}$ using a kinetic temperature thermostat (open and filled squares, respectively) and a configurational thermostat (open and filled diamonds, respectively).

a simple fluid.^{31,32} However, as can be seen in Figs. 5 and 6, the slopes of the linear fit are strongly affected by the thermostatting method used. While the values taken by the hydrostatic pressure and the internal energy are very similar to each other at low shear rates ($< 0.8 \text{ ps}^{-1}$), they differ more and more as the system gets farther from equilibrium where the estimates given by the kinetic and the configurational temperature differ most. Moreover, when the configurational thermostat is used, we note that as for the shear viscosity, data are best fitted if we use a second linear law to fit the results obtained for shear rates higher than 4 ps^{-1} (this feature can be more clearly seen for the internal energy). We also point out that the difference between the increase rates in internal energy are mostly due to differences between values taken by the kinetic energy for the two thermostats. With a Gaussian thermostat the peculiar kinetic energy is constant, while it increases steadily with strain rate when a configurational thermostat is used.

C. Normal stress coefficients

We also observed dramatic differences in the variations of the diagonal elements of the pressure tensor between molten NaCl and a simple fluid. Though the normal stress coefficients are notoriously difficult to estimate accurately, we found it interesting to plot the out-of-plane normal stress coefficient η_0 and the in-plane normal stress coefficient η_- against the square root of the strain rate:

$$\eta_0 = \frac{-[P_{zz} - \frac{1}{2}(P_{xx} + P_{yy})]}{2\gamma}, \quad (14a)$$

$$\eta_- = \frac{-(P_{xx} - P_{yy})}{2\gamma}. \quad (14b)$$

As shown in Fig. 7, the normal stress coefficients vanish as

FIG. 8. Velocity profile in NaCl for a strain rate of 4 ps^{-1} obtained with (a) a kinetic temperature thermostat and (b) a configurational temperature thermostat.

the strain rate goes to zero, indicating that the fluid becomes Newtonian. Again, both thermostatting methods yield similar results for moderate and low shear rates ($<0.8 \text{ ps}^{-1}$). For higher shear rates ($\geq 2 \text{ ps}^{-1}$), both thermostats yield a qualitatively similar behavior for η_0 . On the other hand, the in-plane coefficient η_- decreased with shear rate when a configurational thermostat was used, while it increased with shear rate when a kinetic thermostat was used.

If we now compare these results to those obtained for the Lennard-Jones fluid, we note several differences: (i) The Lennard-Jones normal stress coefficients were both always positive over the range of strain rates investigated (up to 2 in Lennard-Jones reduced units); (ii) the Lennard-Jones out-of-plane stress coefficient increases monotonically with strain rate; and (iii) the out-of-plane coefficient is always larger than the in-plane coefficient. The Lennard-Jones in-plane stress coefficient does not increase monotonically with shear rate, but has a maximum.³¹ In molten NaCl with a configurational thermostat it also has a maximum and decreases for higher shear rates, but with a kinetic temperature thermostat it increases monotonically.

D. Streaming velocity profile and kinetic temperature

The differences in liquid properties under shear obtained with a “profile biased” kinetic thermostat, and with a “profile unbiased” scheme like a configurational temperature thermostat, can often be related to the incorrect assumptions on the streaming velocity profile by a profile biased thermostat. The Gaussian isokinetic thermostat assumes a perfect linear increase of the x -component of the streaming velocity with the displacement in the y direction. Any deviation from this profile is interpreted as viscous heating and suppressed.

FIG. 9. Variations of the denominator and numerator of the right-hand side of Eq. (3) for NaCl and “neutral NaCl” with strain rate.

In reality, high shear rates lead to instabilities such as “kinks” in the streaming velocity profile, and eventually to the development of turbulence.

For sheared molten salt, deviations of very small amplitude were observed only for the highest shear rates and the time-averaged streaming velocity profile was nearly perfectly linear with both thermostats for the range of investigated shear rates. However, the fluctuations around this profile are noticeably larger with the configurational thermostat (Fig. 8). The larger fluctuations account for the steady increase of kinetic temperature with shear rate when configurational degrees of freedom are thermostatted. This general behavior appears in all configurationally thermostatted sheared systems.

E. Structural changes and configurational temperature

We intuitively expect that nonthermostatted degrees of freedom heat up in an external field. In particular, in a sheared system we expect the numerator of Eq. (3), i.e., the forces on individual particles, to steadily increase with strain rate. For all sheared systems studied until now, configurational temperature increased with strain rate when a kinetic temperature thermostat was used, in accordance with this rule. For molten NaCl, the variation of the configurational temperature with strain rate is not monotonic. T_{conf} first decreases, reaches a minimum (1330 K) at a strain rate of 4 ps^{-1} and then increases steadily. If we switch off the electrostatic interactions and simulate “neutral NaCl,” we observe the expected monotonic behavior. Looking more closely at the variations of the numerator and denominator of Eq. (3) with strain rate, we see that, for both NaCl and “neutral NaCl,” the denominator increases with strain rate. However, for NaCl, the numerator decreases for low strain rates, reaches a minimum at a strain rate of 4 ps^{-1} and then increases for higher strain rates (Fig. 7).

The main difference between a molten salt and a neutral mixture lies in a much more ordered structure of the ionic

FIG. 10. Pair distribution functions of Na^+ around a Cl^- ion in an xy -plane passing through the center (a) at equilibrium and (b) at a strain rate of 4 ps^{-1} .

system. The average pair distribution function around each ion consists of alternating spherical shells of opposite charge. There is no such order in a mixture of neutral sodium and chlorine atoms, where the coordination shells of the two types almost completely overlap. We expect this structural difference to be responsible for the different behavior of configurational temperature.

The change of the numerator in Eq. (3) means the change of the mean-square force on an ion. For both systems, the equilibrium pair distribution function is spherically symmetric. Under shear, the coordination shells deform, but retain a central symmetry (Fig. 9). The mean square force $\langle F^2 \rangle$ reflects the average instantaneous deviation of the local pair distribution around each ion from this average symmetric distribution.

The mean square force can be written as

$$\langle F^2 \rangle = \langle (\mathbf{F}_+ + \mathbf{F}_-)^2 \rangle = \langle F_+^2 \rangle + 2\langle \mathbf{F}_+ \cdot \mathbf{F}_- \rangle + \langle F_-^2 \rangle, \quad (15)$$

where $\mathbf{F}_+$ is the total force exerted by the particles of the same type (Na^+ or Cl^-), and $\mathbf{F}_-$ is the total force exerted by the particles of the opposite type. $\mathbf{F}_+$ and $\mathbf{F}_-$ includes both the repulsion–dispersion and electrostatic terms for NaCl (there is only a dispersion–repulsion term for “neutral NaCl”).

We apply the decomposition of Eq. (12) to both NaCl and “neutral NaCl.” Since splitting the forces in these two contributions would yield very large numbers for $\mathbf{F}_+$ and $\mathbf{F}_-$ with an Ewald sum and cause a loss of precision, we use a cutoff of half the boxlength to evaluate $\mathbf{F}_+$ and $\mathbf{F}_-$. We observed the same qualitative dependence of T_{conf} on the strain rate as before when it was calculated using the Ewald expression. The truncation was only used to evaluate $\mathbf{F}_+$ and $\mathbf{F}_-$ and to interpret the behavior of T_{conf} with increasing strain rate, and not to evaluate the forces which determine the motion of ions.

The results so obtained are shown in Fig. 10. In both systems $\langle F_+^2 \rangle$ and $\langle F_-^2 \rangle$, increase, implying that forces increase because the particles get closer under shear, and maybe local distributions of each type become less symmetric. The scalar product $\langle \mathbf{F}_+ \cdot \mathbf{F}_- \rangle$ is negative in both systems. It reflects how much the total force of one type is balanced by the total force of the other type. The magnitude of this term in the neutral mixture is very small and increases with shear at the same rate as $\langle F_+^2 \rangle$ and $\langle F_-^2 \rangle$. For NaCl, its magnitude is much closer to the magnitude of mean-square forces, and increases with shear faster at low strain rates. The

local deviations of positive and negative shells are highly correlated. For low shear rates, the correlation of local deformations of positive and negative shells is a stronger effect than the increase of mean square forces caused by the closer approach of ions. In this range of shear rates, the correlation between instantaneous local distributions of positive and negative ions is enhanced by the requirement that both types have the same linear streaming velocity profile. This means that the kinetic temperature thermostat artificially changes local structure under shear. For higher shear rates, the increase of mean-square forces dominates. There is of course no possibility for such a correlation to occur in “neutral NaCl.”

VI. CONCLUSIONS

In this work, we performed NEMD simulations of molten NaCl under shear using the SLLOD algorithm in the canonical ensemble using either a kinetic thermostat based on the equipartition principle or a configurational temperature thermostat. As shown in previous work, a configurational temperature thermostat is a more realistic approach (heat is removed from all degrees of freedom and there is no *a priori* assumption on the form of the streaming velocity profile) than a kinetic temperature thermostat. Overall, both series of simulation show that molten NaCl under shear has qualitatively the same behavior as a simple fluid. While the hydrostatic pressure and internal energy vary as $\sim \gamma^{3/2}$ —where γ is the strain rate—as predicted by the mode-coupling theory, the shear viscosity is found to exhibit the same features as for a Lennard-Jones fluid. However, qualitative differences are observed with the Lennard-Jones fluid for the normal stress coefficients and particularly for the out-of-plane normal stress coefficient. We found that the choice of the thermostatting mechanism had little influence on the coefficients computed with the exception of the in-plane normal stress coefficient for high strain rates.

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