Conductivity of molten sodium chloride and its supercritical vapor in strong dc electric fields

Janka Petrávic and Jérôme Delhommelle

Citation: *The Journal of Chemical Physics* **118**, 7477 (2003); doi: 10.1063/1.1562612

View online: <http://dx.doi.org/10.1063/1.1562612>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/118/16?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Conductivity of molten sodium chloride in an arbitrarily weak dc electric field](#)

J. Chem. Phys. **123**, 114505 (2005); 10.1063/1.2035085

[Conductivity of molten sodium chloride in an alternating electric field](#)

J. Chem. Phys. **119**, 8511 (2003); 10.1063/1.1613256

[Shear viscosity of molten sodium chloride](#)

J. Chem. Phys. **118**, 2783 (2003); 10.1063/1.1535213

[Translational dynamics of a cold water cluster in the presence of an external uniform electric field](#)

J. Chem. Phys. **116**, 8786 (2002); 10.1063/1.1473657

[Molecular dynamics simulations of sodium chloride solutions in water–dimethyl sulphoxide mixtures: Potentials of mean force and solvation structures](#)

J. Chem. Phys. **111**, 7526 (1999); 10.1063/1.480079

APL Photonics is pleased to announce
Benjamin Eggleton as its Editor-in-Chief

Conductivity of molten sodium chloride and its supercritical vapor in strong dc electric fields

Janka Petravica^{a)}

Research School of Chemistry, The Australian National University, Canberra ACT 0200, Australia

Jérôme Delhommelle

Équipe de Chimie et Biochimie Théoriques, UMR 7565, Université Henri Poincaré, BP 239, F-54506 Vandœuvre-lès-Nancy Cedex, France

(Received 2 December 2002; accepted 29 January 2003)

We investigate the influence of thermostating methods on the electrical conductivity and structure of molten and supercritical sodium chloride obtained in nonequilibrium molecular dynamics simulations in strong constant (dc) electric fields. The strong dependence of the results on the type of thermostat employed in simulations becomes apparent only at extremely high fields ($>0.5 \times 10^9$ V/m). For this range of fields, quantitative differences of unexpected size can be seen in the melt. In the supercritical fluid, different thermostats predict qualitatively very different behavior and structure. While the kinetic-type thermostats predict increased association of ions in the field, configurational thermostat predicts enhanced dissociation. © 2003 American Institute of Physics. [DOI: 10.1063/1.1562612]

I. INTRODUCTION

Electric conductivity and diffusion coefficients of different models of ionic liquids were investigated using molecular dynamics methods^{1–3} from the early days of molecular simulations. The results were applied to study the collective dynamical properties of molten salts, such as longitudinal and transverse optical modes,^{2,3} and to assess the validity of the Nernst–Einstein relation and the importance of the velocity cross-correlations of distinct ions.^{2,4,5} Recently, an extensive study of electrical conductivity of molten sodium chloride by means of equilibrium molecular dynamics⁶ was performed over a very large range of thermodynamical conditions, i.e., in gas, liquid, and supercritical fluid states. The large differences in conductivity were linked to the structural differences in these states.^{6,7} Until now, nonequilibrium molecular dynamics (NEMD) has been used to calculate the field-dependent electrical conductivity only for a model monovalent ionic liquid with ions of equal mass and size.⁸

The aim of the present paper is to calculate the field-dependent dc conductivity of molten NaCl, and in particular to determine the influence of thermostating (and of temperature expression) on the transient and steady state currents in strong dc fields. We chose to do our simulation on a model representing molten NaCl because it is hard to estimate the importance of difference in mass and size in binary mixtures, and we want our conclusions to be applicable to simulation of real ionic systems.

In an NEMD simulation, the adiabatic application of an external field causes a monotonic increase of internal energy. The system heats up and there is no well-defined final steady state from which transport coefficients can be calculated. In reality, this heat would be transmitted to the environment.

The mechanisms of heat exchange with the environment are in NEMD simulations substituted by “thermostating” terms in equations of motion, which ensure that the temperature of the system stays constant. Most of them conserve the “kinetic” temperature, defined from the equipartition law.^{9–11} However, an external field acting on a fluid creates a flow, i.e., an anisotropic distribution of particle velocities. Thermal motion is defined in terms of fluctuations with respect to this flow. In an ionic liquid in an electric field, positive and negative ions move in opposite directions, but the center-of-mass velocity stays constant and there is no net mass flow. Therefore there is an ambiguity in the definition of the flow velocity that should be chosen as a reference for the kinetic temperature definition. From one point of view all motion in the barycentric reference frame should be thermostatted. On the other hand, electric current is precisely the response we want to measure. If a thermostat is applied to the total velocity (including the flow velocity of each type of ion) from the moment when field is switched on, it could prevent relaxation to the correct steady-state electric current. From this point of view, the thermal motion defining kinetic temperature to be controlled by a thermostat is the motion of ions relative to the flow velocity of each type.

Another way to control the kinetic temperature of a system, without any interference with the development of current, is to impose a thermostat only on motion perpendicular to the electric field direction.

Recently, an alternative definition of “configurational” temperature, in terms of positions only, has been proposed.^{12–14} In equilibrium, both kinetic and configurational definitions are equivalent and can be derived from the thermodynamic temperature definition as inverse rate of change of entropy with internal energy at constant volume, using the Gibbs’ microscopic expression for entropy. Far from equilibrium, temperature is not a well-defined quantity.

^{a)}Author to whom correspondence should be addressed. Electronic mail: janka@rsc.anu.edu.au

Extending both kinetic and configurational definitions to systems out of equilibrium implies the approximation that the phase space probability distribution stays equal to the equilibrium probability distribution. This approximation is assumed in both types of temperature definitions when used out of equilibrium. However, the configurational expression does not contain the additional error of incorrect estimate of flow velocity. Therefore we consider the configurational expression as “more correct” and use it to resolve the kinetic temperature ambiguity.

The expressions for configurational temperature are complex and hard to interpret. Our other aim is to gain further understanding of their physical meaning by calculating them in different systems and under different conditions.

The paper is organized as follows: In Sec. II we give the parameters for the ion interaction potential, list the expressions for temperature and the equations of motion used in the computation, and give the technical details of the simulations. In Sec. III we show the results of equilibrium electric conductivity calculations for the two investigated state points. These will serve as references for field-dependent conductivities. In Sec. IV we show how electric field, applied adiabatically, heats up the system. Thermostatted responses for four different thermostats are compared in Sec. V. There we also discuss the differences in steady-state temperature values of different temperature definitions, and explain them in terms of structural differences resulting from different thermostating methods. Section VI contains our concluding remarks.

II. MICROSCOPIC DESCRIPTION

A. Model

We used the Born–Huggins–Mayer potential to describe the pair interactions,

$$\Phi_{ij}(r_{ij}) = z_i z_j \frac{e^2}{r_{ij}} + A_{ij} \exp[B(\sigma_i + \sigma_j - r_{ij})] - \frac{C_{ij}}{r_{ij}^6} - \frac{D_{ij}}{r_{ij}^8}, \quad (1)$$

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 determined by Fumi and Tosi¹⁵ from properties of solid alkali halides. This model has been widely used in simulations and despite its simplicity accounts for the main structural features and thermodynamical and transport properties of molten alkali halides.

B. Expressions for temperature

In this work we compared two kinetic and two configurational definitions of temperature. The first is the conventional kinetic temperature T_{KIN} defined from the equipartition theorem applied to the motion in the barycentric frame,

$$\frac{3}{2} N k_B T_{\text{KIN}} = \left\langle \sum_{i=1}^N \frac{p_i^2}{2m_i} \right\rangle. \quad (2)$$

Here N is the total number of positive and negative ions, k_B is the Boltzmann constant, and $\mathbf{p}_i$ and m_i are the momentum and mass of ion i , respectively.

Flow velocity $\mathbf{u}_\nu$ of each type is

$$\mathbf{u}_\nu = \frac{2}{N m_\nu} \sum_{i_\nu=1}^{N/2} \mathbf{p}_{i_\nu}, \quad (3)$$

where $\nu = +, -$ denotes positive and negative ions, m_ν is mass of the ion of type ν , and the index i_ν goes over ions of type ν only. It is assumed that there are equal numbers of ions of each type.

The “flow kinetic temperature” T_{FLOW} is defined from the equipartition theorem, but using the momenta relative to the flow velocity of each species,

$$\frac{3}{2} N k_B T_{\text{FLOW}} = \sum_{\nu=+,-} \frac{1}{2 m_\nu} \left\langle \sum_{i_\nu=1}^N (\mathbf{p}_{i_\nu} - m_\nu \mathbf{u}_\nu)^2 \right\rangle. \quad (4)$$

In all cases, we also calculate the flow kinetic temperatures in the direction of the field (T_x) and perpendicular to it (T_{yz}).

The two configurational expressions, arising from two different choices of purely spatial displacement directions in phase space when calculating the entropy change, are

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

and

$$\frac{1}{k_B T} = \left\langle - \frac{\sum_{i=1}^N \nabla_i \cdot \mathbf{F}_i}{\sum_{i=1}^N \mathbf{F}_i^2} - \frac{2 \sum_{i,j=1}^N \mathbf{F}_i \mathbf{F}_j : \nabla_i \mathbf{F}_j}{(\sum_{i=1}^N \mathbf{F}_i^2)^2} \right\rangle. \quad (6)$$

The indices i and j refer to all ions in the melt, and $\mathbf{F}_i$ is the total force acting on the ion i . In Eq. (6), the second term on the right-hand side vanishes in the thermodynamic limit for short-ranged potentials and exactly for electrostatic ($\sim 1/r$) potential. Therefore we define the first order configurational temperature T_{C1} as

$$\frac{1}{k_B T_{\text{C1}}} = \left\langle - \frac{\sum_{i=1}^N \nabla_i \cdot \mathbf{F}_i}{\sum_{i=1}^N \mathbf{F}_i^2} \right\rangle. \quad (7)$$

In all our simulations, the temperature values calculated from the definitions (5) and (7) agree to <0.1% deviations.

C. Equations of motion and expressions for thermostats

We used the Gauss minimal constraint method^{9,10} to make the desired kinetic temperature an exact constant of motion. The electric field was applied in the x -direction. The equations of motion are in this case of the form,

$$\begin{aligned} \dot{\mathbf{r}}_i &= \mathbf{p}_i / m_i \\ \dot{\mathbf{p}}_i &= \mathbf{F}_i + i z_i e E_{\text{EL}} - \alpha \mathbf{p}_i, \end{aligned} \quad (8)$$

where $\mathbf{r}_i$ is the position of ion i , $\mathbf{F}_i$ is the total force on ion i resulting from the interaction potential (1), E_{EL} is the magnitude of electric field, $\mathbf{i}$ is the unit vector in the x -direction,

and α is the thermostat multiplier. If the kinetic temperature (2) is constrained, the thermostat multiplier α is given by the expression,

$$\alpha = \frac{\sum_{j=1}^N \mathbf{p}_j \cdot \mathbf{F}_j / m_j + e E_{\text{EL}} \sum_{j=1}^N z_j p_{xj} / m_j}{\sum_{j=1}^N \mathbf{p}_j^2 / m_j}. \quad (9)$$

The “flow kinetic temperature” T_{FLOW} is constrained by the thermostat multiplier α of the form¹⁶

$$\alpha = \frac{\sum_{\nu=+,-} \frac{1}{m_\nu} \sum_{j=1}^{N/2} (\pi_{xj\nu} \varphi_{xj\nu} + p_{yj\nu} F_{yj\nu} + p_{zj\nu} F_{zj\nu})}{\sum_{\nu=+,-} \frac{1}{m_\nu} \sum_{j=1}^{N/2} (\pi_{xj\nu}^2 + p_{yj\nu}^2 + p_{zj\nu}^2)}, \quad (10)$$

where $\nu=+,-$ is the ion type, $\pi_{xj\nu}$ is the x -component of momentum of ion j of type ν relative to the flow, $\pi_{xj\nu} = p_{xj\nu} - m_\nu u_\nu$, and the flow velocity has only an x -component in this geometry, $\mathbf{u}_\nu = \mathbf{i} u_\nu$. The “peculiar” form of the interaction force $\varphi_{xj\nu}$ appearing in Eq. (10) is $\varphi_{xj\nu} = F_{xj\nu} - F_\nu$, where $F_\nu = 2 \sum_{j=1}^{N/2} F_{xj\nu} / N$. The flow velocities u_ν , and the peculiar quantities $\pi_{xj\nu}$ and $\varphi_{xj\nu}$ are evaluated at each time step in the simulation.

When only the degrees of freedom perpendicular to the field are controlled, the thermostat multiplier α is

$$\alpha = \frac{\sum_{j=1}^N (p_{yj} F_{yj} + p_{zj} F_{zj}) / m_j}{\sum_{j=1}^N (p_{yj}^2 + p_{zj}^2) / m_j}. \quad (11)$$

We shall sometimes call this a “yz” thermostat for brevity.

When $\alpha=0$ in Eq. (8), there is no heat exchange with the environment and all the work done by the external field is completely converted into internal energy. This describes the adiabatic process presented in Sec. IV, in which a system continuously heats up.

The “configurational” thermostat is introduced using the Nosé–Hoover integral type of feedback.^{13,14} The thermostat multiplier is in the position equations of motion because configurational temperature is defined in terms of positions,

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i} + \frac{\xi}{T_0} \frac{\partial T_{\text{Cl}}}{\partial \mathbf{r}_i}, \quad (12a)$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i + \mathbf{i} z_i e E_{\text{EL}}, \quad (12b)$$

$$\dot{\xi} = -Q_{\text{TC}} \frac{(T_{\text{Cl}} - T_0)}{T_0}. \quad (12c)$$

Because $\Delta(1/r)=0$, electrostatic interactions do not contribute directly either to the thermostat terms in Eq. (12a) or to the denominator of Eq. (5).

In equilibrium, when $E_{\text{EL}}=0$, all thermostats give the same statistics in the thermodynamic limit. We have chosen to perform equilibrium simulations with constant conventional kinetic temperature (2) and the Gauss kinetic thermostat of the form (9).

D. Technical details

We selected two state points, one at a density of $\rho = 1500 \text{ kg/m}^3$ and at temperature of $T = 1500 \text{ K}$, in the middle of the liquid region of the phase diagram,⁶ and the

second in the supercritical region above the critical point, at a density of $\rho = 200 \text{ kg/m}^3$ and at a temperature of $T = 3200 \text{ K}$, in order to estimate the effect of density on thermostating. The first state point will be referred to as “liquid” in further text, while the second will be called “fluid.” Molecular dynamics simulations were performed on systems consisting of 512 ions (256 ions of each type), a system size which has been shown in previous studies^{1–8} to be sufficient in order for the number dependence of results not to be important. The set of first order equations of motion were solved using the fifth order Gear predictor–corrector scheme. Electrostatic interactions were treated using the Ewald summation technique with the conducting boundary at infinity.¹⁷ The nonelectrostatic and the real space electrostatic interactions were cut off at half the box length, $L/2$, the reciprocal space wave-vector cut-off was at $k_{\text{max}} = 6(2\pi/L)$, and the convergence acceleration factor was chosen as $\kappa = 1.8\pi/L$. The pressure tensor was evaluated using the representation of Nosé and Klein.¹⁸ Beyond the cut-off, the long-range corrections to the nonelectrostatic contribution to potential energy and hydrostatic pressure were included in order to account for the truncation effects.¹⁹ The system was started off as an fcc lattice at the correct density and first equilibrated for 0.5 ns at each state point.

The equilibrium conductivities σ were computed using the Green–Kubo expression,²⁰

$$\sigma = \frac{V}{3k_B T} \int_0^\infty \langle \mathbf{j}(t) \cdot \mathbf{j}(0) \rangle dt. \quad (13)$$

In Eq. (13), V is the volume of the system, k_B is the Boltzmann constant, T is the temperature, and $\mathbf{j}$ is the electric current density,

$$\mathbf{j} = \frac{e}{V} \sum_{i=1}^N z_i \mathbf{v}_i, \quad (14)$$

where $\mathbf{v}_i$ is the velocity of the ion i . For both systems, the production runs started from the equilibrated configuration and lasted for 2 ns, with a time window of 5 ps. The time step was 1 fs for the liquid and 0.5 fs for the fluid.

For adiabatic [Eqs. (8) with $\alpha=0$] and transient response simulations, field-dependent trajectories were started every picosecond from an equilibrium trajectory. For each initial equilibrium microstate, additional starting microstates of the same equilibrium probability were created by applying time-reversal mapping, i.e., reversal of the signs of all momenta, and mirror symmetry of all positions with respect to $y=0$ and $z=0$, in order to reduce systematic error. The time steps were the same as in equilibrium runs. The averages were taken every 0.5 fs over 2000 nonequilibrium trajectories.

For the calculation of thermostatted steady-state averages, the system was first brought to the steady state with the field and the appropriate thermostat, in runs that varied in length from 0.5 ns for the lowest field, to 0.25 ns for the highest field. The averages were collected in production runs that were twice the length of the preparation runs. For the kinetic-type thermostats (9), (10), and (11), the time step was

of the same length as for equilibrium and adiabatic simulations, except for the highest field (1.2×10^{10} V/m), in which case it had to be halved for the fluid.

In simulations with the configurational thermostat, the constant Q_{TC} in Eq. (12) was chosen to be 100. For the liquid, time step of 1 fs could be used for all fields except the highest, where it had to be reduced drastically to 0.05 fs. The instability of the configurational thermostat was more noticeable for the fluid, where the time step of 0.5 fs could be used only for the fields up to 0.73×10^{10} V/m. For the field of 0.85×10^{10} V/m it had to be reduced to 0.01 fs, for 0.98×10^{10} V/m it was 0.001 fs, and the equations were too unstable for integration at the two highest fields.

III. EQUILIBRIUM RESULTS

The electric fields accessible to molecular dynamics simulations are very large (of the order of $\sim 10^8$ to $\sim 10^9$ V/m). Therefore we first computed equilibrium electric conductivities at the two investigated state points, in order to have reference values, estimate the response times and see if a linear response region still exists at such large fields.

For both systems, the integrals (13) reached a plateau value within 5 ps. The resulting conductivities are $\sigma = 4.53 \pm 0.05$ mho/cm for the liquid and $\sigma = 0.332 \pm 0.006$ mho/cm for the fluid. These results are in good agreement with the results obtained by Guissani and Guillot⁶ in nearby states. The fluid conductivity is much lower because at such low density the system is not fully dissociated.

IV. ADIABATIC HEATING

If an isolated system is placed in an external field, its internal energy will grow and it will keep heating up indefinitely. The way in which adiabatic heating proceeds in a molten salt depends on system density and field strength. In the liquid and in the fluid, and for two fields, 2.4×10^9 V/m and 6.1×10^9 V/m, we monitored the adiabatic current and temperatures as a function of time. The observation interval was 2.5 ps for the higher field and 3.75 ps for the lower field. The relatively high fields were chosen because the effects had to be seen in a short time interval; otherwise the simulation would be too costly in computer time.

In all cases, current is established instantly with a “switching peak,” due to the first collision and recoil of opposite charges, after approximately the same time as the peak in the current autocorrelation integral in equilibrium. This peak is more prominent when density is low. For the higher field, the build-up of the two currents in time is shown in Fig. 1. In the liquid, the current growth rate decreases in time, while in the fluid the increase of current is faster as the time progresses. In the latter case it is not only a consequence of acceleration in the field, but is also due to higher degree of dissociation as the system heats up. The current growth rate would probably slow down after the fluid is fully dissociated.

The heating of the two systems was measured by the increase in temperature defined by Eqs. (2), (4), and (5). The evolution of different temperatures in the higher field is pre-

FIG. 1. Adiabatic growth of current with time in electric field of 6.1×10^9 V/m, for molten NaCl in (a) liquid and (b) supercritical state.

sented in Fig. 2. We first observe that the differences between temperatures are minute. As the current develops, thermal motion increases too, and flow velocity of ions is never very important. Nevertheless, flow temperature (4) is always lower than kinetic temperature (2). The flow definition seems more natural and therefore we expect configurational temperature to be closer to it than to the kinetic definition. This is the case in the fluid, where configurational temperature is the lowest. However, in the liquid, configurational temperature is the highest and therefore closer to the kinetic definition.

In a lower field, the heating rate is much lower and nearly linear. All definitions of temperature agree for the liquid, which heats up about three times faster than the fluid. In the fluid, the differences in temperature are nevertheless quite noticeable, and temperatures are in the same order as in the higher field. The growth of current is nearly linear after the “switching peak” and especially slow in the fluid, showing that the field is not strong enough to increase the degree of dissociation after ~ 4 ps.

FIG. 2. Increase of three definitions of temperature with time in isolated molten liquid and supercritical NaCl with time in an electric field of 6.1×10^9 V/m.

FIG. 3. Dependence of the current density (a) and electrical conductivity (b) of molten NaCl on the electric field with four types of thermostats. The open circle represents the equilibrium result. The legend shows the definition of temperature controlled by the thermostat.

V. THERMOSTATED RESPONSE

A. Liquid

In a steady state in an external electric field, oppositely charged ions, flow in opposite directions parallel to the field. Irrespective of the type of thermostat used, the average flow velocities (3) satisfy the Sundheim rule,²¹ $|u_+/u_-| = m_-/m_+$, because of momentum conservation and charge neutrality.

Field-dependent current densities and conductivities computed with the four thermostats (9)–(12) are presented in Figs. 3(a) and 3(b), respectively. For fields up to 0.5×10^9 V/m, conductivities computed with different thermostats agree with the equilibrium result to within the statistical error and the response is linear. After that, flow velocities, currents and conductivities increase with the field, but agree with each other for fields up to approximately 2.5×10^9 V/m. This is the range of fields for which flow velocities $u_{\pm}$ are small enough compared to average ion velocities obtained from equipartition at this temperature (2). For higher fields, differences become noticeable.

The smallest response at the same field strength is consistently obtained with the kinetic thermostat (9), because it suppresses the development of flow velocities by interpreting

FIG. 4. Dependence of potential energy of molten NaCl on the electric field with four types of thermostats. The type of controlled temperature is shown in the legend.

them as thermal motion and therefore imposes an absolute limit to the maximum possible value of current. The flow (10) and “yz” (11) thermostats give similar results, but the response is somewhat larger for the “yz” thermostat. Currents obtained with the configurational thermostat show the fastest growth with the field by far.

Potential energy (Fig. 4) and pressure grow steadily as the field increases in all cases. The differences in pressure between systems with different thermostats are the consequence of different rates of growth of both kinetic and potential parts. The potential part in particular increases from a negative value of -1.25 kbar to positive values at high fields. It is equal in all directions except at the highest fields ($>8 \times 10^9$ V/m) with the configurational thermostat, where the potential part of pressure is somewhat greater in the field (x) direction. This increase is the fastest, and nearly the same, for the configurational thermostat, which makes no assumptions whatsoever about velocities, and the “yz” thermostat, which makes no assumptions about velocity fluctuations in the direction of the field. The similarities between various properties under these two thermostats are an indication of the important role velocity fluctuations play in the formation of the current.

The increase in potential energy and the potential part of pressure indicate a shift from the largest part of pair interactions being attractive, to a configuration where repulsive interactions give the highest contribution. The reasons for this change can be seen from the change of the local structure of the liquid, as described by the pair distribution function $g(\mathbf{r})$, in a strong electric field. Since $g(\mathbf{r})$ ceases to be isotropic, we plotted the distribution of cations in xy -plane around a central anion in Fig. 5. The concentric circles roughly indicate the spread of the first shell of anions. The shells of opposite charge get displaced in the field direction with respect to the central ion. Aided by the work done by the field, oppositely charged ions can approach the central ion closer from one side. At these positions, the nonelectrostatic repulsion is much stronger, and the result is the increase in potential energy and pressure. The shell of the ions of the same charge is not displaced, since they move with the same average flow velocity as the central ion. There is some barely perceptible

FIG. 5. Distribution of Na^+ ions in the xy -plane through the center of a Cl^- ion in the electric field of 8×10^9 V/m and with (a) the flow kinetic thermostat, (b) the configurational thermostat. The concentric circles indicate the spread of the first anion shell, and the arrow at the bottom of the diagram shows the direction of the field.

deformation because of the difference in screening due to the displacement of the inner shell.

Although the pair distribution functions computed with different thermostats all exhibit the main general features, they differ in detail. The pair distribution functions with the flow thermostat (10) and with the configurational thermostat (11) in the electric field of 8×10^9 V/m are presented in Figs. 5(a) and 5(b), respectively. With the flow kinetic thermostat, the distributions of the same and opposite ions get displaced and deformed, but stay as well defined and of the same average width as in equilibrium. The first shell of opposite ions is markedly more populated in the direction dictated by the field, where “collisions” are more frequent. On the other hand, with the configurational thermostat the spread of both same and opposite ions is larger and the two partial distributions overlap more, while the first shell of oppositely charged ions shows less difference in population between the direction of the field and the direction opposite to it.

The value of configurational temperature (5) depends both on the average local structure and the instantaneous deviations from it.²² In the liquid, the numerator of (5) was found to be much more sensitive to changes in the equations of motion than the denominator, which increased only very slowly with the field. The changes in T_{CONF} generally follow the direction of changes in the numerator. In this case, in the first approximation, constant T_{CONF} means preventing the mean square force of interaction on a particle from changing too much in an external field. The increase in the average force acting on an ion, caused by the displacement of the oppositely charged shells, is partly reduced by the larger allowed overlap and a more uniform population of the first oppositely charged shell. This is achieved by allowing larger velocity fluctuations in all directions, which results in the increase in all kinetic definitions of temperature.

The field dependence of “flow” kinetic temperature in directions parallel and perpendicular to the field with different thermostats is presented in Fig. 6. With the two kinetic-type thermostats (9) and (10) that control velocity fluctuations in all directions, the kinetic temperature in the perpendicular direction decreases in order to allow for the increased temperature in the field direction. If only the “perpendicular” kinetic temperature is controlled, temperature in

FIG. 6. Kinetic temperature in the direction of the field and in the perpendicular direction with four types of thermostat.

the field direction increases at the fastest rate. With the configurational thermostat, velocity fluctuations in all directions increase with the field, and their field dependence is the most similar. Despite the increase in the kinetic temperature, the system stays closest to equipartition, suggesting that it is the least perturbed by thermostating.

If we compare the steady-state currents obtained with different thermostats [Fig. 3(a)] in light of the above discussion, we can conclude that controlling velocity fluctuations in any direction has a retarding effect on the current. Indeed, the form of transient response in the first picosecond after switching on the field (Fig. 7) shows that the current with the configurational thermostat is established in a very different way than with any of the kinetic-type thermostats and that its growth is the least suppressed.

If any of the kinetic temperatures is constrained, configurational temperature increases and vice versa, if we control the configurational temperature, all forms of kinetic temperature increase. This is in agreement with the general expectations that, if we control some degrees of freedom, the others would “heat up.” The size of the difference between configurational temperature and the “streaming” temperature with these two thermostats in particular is about 70% at the highest fields. This suggests that with the configurational thermostat there are additional spatially and temporally dependent flows (e.g., longitudinal and transversal traveling

FIG. 7. Transient response to the electric field of 6.1×10^9 V/m with four thermostats. The legend shows the conserved definitions of temperature.

FIG. 8. Dependence of electric current on field in the supercritical NaCl fluid with four thermostats.

waves), which average to zero over the simulation cell, but are part of the response neglected in the kinetic definitions.

B. Low-density supercritical fluid

The response of supercritical NaCl to strong electric fields is very different than the response of the high-density liquid, and much more sensitive to the type of thermostat employed in the equations of motion. Because of its low density, we expected much higher flow velocities to be attained than in the liquid, and therefore a large difference between electric currents and conductivities obtained with the simple kinetic thermostat and the flow thermostat. Surprisingly, the difference in responses was smaller than in the liquid case; in fact, the current responses with these two thermostats were nearly identical (Fig. 8), as were all the other thermodynamical quantities like internal energy, pressure, and other definitions of temperature. The increase in conductivity was not faster than linear, and was a lot slower than in the liquid. The main difference between fluid and liquid is that the low-density fluid is not fully dissociated, but partly consists of oppositely charged ion pairs and short chains,⁷ so that only free ions contribute to the current. In an electric field with the kinetic thermostats (9) and (10), there are two competing effects, the effect of the field and the effect of the thermostat. The field accelerates the free ions, and allows them to approach each other more closely before backscattering than without field. This contributes to an increase in current, average potential energy per molecule and pressure. The effect of the thermostat is equivalent to continuous rescaling of velocities in order to keep the kinetic energy (total or relative to flow velocities) constant. As oppositely charged ions accelerate towards each other, their potential energy falls, and as a consequence their kinetic energy would grow in a constant energy simulation. The acceleration is interpreted as heating and is suppressed by the thermostats, decreasing the total energy of the accelerating ion. As a consequence, it becomes more probable for it to get caught in the potential well of an oppositely charged ion and form an associated pair. Therefore the thermostats of the type

FIG. 9. Dependence of potential energy in the supercritical NaCl fluid with four thermostats.

(9) and (10) enhance the probability of association and somewhat decrease the number of free ions contributing to the current as the field increases. The result of these two trends is shown in Fig. 9 for the average potential energy per molecule. For potential energy per molecule, the latter effect is more important, and it decreases with field for the whole range of investigated fields. The potential part of pressure has a minimum for the field of approximately 6.1×10^9 V/m. For higher fields, the influence of the field takes over, and pressure increases.

With the configurational thermostat (12) and the kinetic thermostat perpendicular to the field (11), the picture is drastically different. The increase of current with field is faster than linear, and much faster than in the liquid. The reason is that kinetic energy is not directly limited. This allows the ion pairs to dissociate, and the increase in current is the result both of acceleration and the increased number of free ions. As they move faster, they can come closer before recoil, and there are also more particles in the attractive tail of the potential energy. This causes the monotonic increase of the average potential energy (Fig. 9) with the field and the steady decrease of the potential part of the pressure tensor, compensated by the faster increase in the kinetic part, so that the total pressure increases monotonically.

With all thermostats, response is nonlinear even for the lowest field used in simulation (6.1×10^8 V/m). Electrical conductivity is larger than equilibrium but interpolates to the equilibrium value.

For the kinetic thermostat perpendicular to the field (11), for fields larger than 6.1×10^9 V/m, because of low density there is not enough coupling between the motion in the field direction and the motion in the perpendicular plane. Although the kinetic temperature in the perpendicular direction stays constant, the kinetic temperature in the field direction increases without reaching a steady-state value. With the configurational thermostat, the equations of motion (12) become very unstable for fields larger than 7.3×10^9 V/m because of very fast motion of the ions, and the time steps needed to be reduced so much that the simulation becomes too expensive. Therefore our results with these two thermo-

FIG. 10. Decrease of configurational temperature with field in the fluid with streaming kinetic thermostat.

stats include only the fields below these limits. The steady state averages obtained with them are very similar, except that equipartition is again much more closely satisfied with the configurational thermostat.

While all types of kinetic temperature increase in a system with a configurational thermostat in accordance with our intuitive expectations, configurational temperature decreases steadily with the field when the simple (9) or flow (10) kinetic thermostat is used (Fig. 10). Similar behavior was found in sheared ionic liquids with the Gauss kinetic thermostat.²² With an electric field and a kinetic thermostat (9) or (10), the numerator of (5) decreases, while the denominator increases with field (Fig. 11). Both effects can be explained by a lower level of dissociation of the salt vapor. The potential energy (1) of the associated pairs is close to the minimum, where the forces nearly vanish. Associated pairs are neutral (although with a dipole moment) and do not attract shells of alternating charge that are shifted in the field.

FIG. 11. Change of the numerator (triangles) and the denominator (diamonds) of Eq. (5) with field relative to the equilibrium values in the fluid with flow kinetic thermostat (empty symbols) and configurational thermostat (full symbols).

All this contributes to the decrease of the numerator. The highest contribution to the denominator is from the pairs with potential energy close to the minimum, so that greater association also causes it to increase.

When the configurational thermostat is used, both the numerator and the denominator decrease at the same rate with the field. This is different from any other nonequilibrium system investigated so far, where both the numerator and the denominator increased with the field. The decrease in the average force and the denominator is the result of more and more free ions being in the attractive tails of the interaction potential where the forces and their divergences are smaller.

VI. CONCLUSION

The conductivity of molten NaCl is constant for a huge range of electric fields (up to $\sim 10^8$ V/m). For higher fields (up to $\sim 0.5 \times 10^9$ V/m) it increases nearly linearly with field, independent of the thermostating method. In extremely high electric fields above this limit, conductivity of molten sodium chloride and its supercritical vapor is nonlinear and the response depends strongly on the thermostating method for both state points.

The kinetic temperature thermostats, either in the barycentric reference frame or with respect to flow velocity of each type of ion, predict a much slower increase in conductivity than the configurational temperature thermostat, which makes no assumption about the nature of the flow. The currents obtained with the two kinetic-type thermostats are surprisingly similar. The reason is that, for the high-density liquid melt, the flow velocities are quite low compared to the average “thermal” velocities obtained from equipartition, while in the supercritical fluid the salt is only partly dissociated.

The kinetic thermostat perpendicular to the field in liquid yields currents similar to the other two kinetic thermostats, while in the supercritical fluid the currents are closer to the results with the configurational thermostat.

In the liquid, a configurational thermostat predicts not only a faster increase of conductivity, but also a different, more centrally symmetric, local structure. The size of the differences between temperatures calculated according to different definitions suggest that in strong electric fields there exists secondary spatially and temporally dependent flows not taken into account in the kinetic definition.

In the supercritical fluid, the structural differences are even more spectacular. Kinetic-type thermostats predict enhanced association, while a configurational thermostat predicts an increase in dissociation of ion pairs and chains.

It is not certain that even experimental measurements, if they were possible at such elevated temperatures and high electric fields, would give a definite answer about transport and structure in these circumstances. An extension of equilibrium definitions of temperature so far from equilibrium is dubious, and it is possible that a unique definition even does not exist for such systems. Different experimental methods of cooling and temperature measurement would possibly give very different results. However, the fact that the configurational expression for temperature does not depend on

velocities and therefore does not rely on any assumed flow characteristic, as well as the fact that the velocity distribution is closest to equipartition with the configurational thermostat and the values of potential energy are similar to the ones obtained with the kinetic thermostat perpendicular to the flow, are the arguments to the advantages of the configurational definition of temperature.

ACKNOWLEDGMENT

The authors wish to thank the National Facility of Australian Partnership for Advanced Computing for a substantial allocation of computer time for this project.

- ¹J. W. E. Lewis and K. Singer, *J. Chem. Faraday Trans.* **71**, 31 (1964).
- ²J. P. Hansen and I. R. McDonald, *Phys. Rev. A* **11**, 2111 (1975).
- ³G. Cicotti, G. Jacucci, and I. R. McDonald, *Phys. Rev. A* **13**, 426 (1976).
- ⁴J. A. Padró, J. Trullàs, and G. Sesé, *Mol. Phys.* **72**, 1035 (1991).
- ⁵J. Trullàs and J. A. Padró, *Phys. Rev. B* **55**, 12210 (1997).
- ⁶Y. Guissani and B. Guillot, *J. Chem. Phys.* **101**, 490 (1994).
- ⁷K. S. Pitzer, *J. Chem. Phys.* **104**, 6724 (1996).
- ⁸I. M. Svishchev and P. G. Kusalik, *Phys. Chem. Liq.* **26**, 237 (1994).
- ⁹D. J. Evans and G. P. Morriss, *Statistical Mechanics of Non-Equilibrium Liquids* (Academic, London, 1990).
- ¹⁰W. G. Hoover, *Computational Statistical Mechanics* (Elsevier, New York, 1991).
- ¹¹W. G. Hoover, K. Aoki, C. G. Hoover, and S. V. De Groot, *Physica D, Proceedings of the International Workshop on Microscopic Chaos and Transport in Many-Particle Systems (CHAOTRAN)*, held in Dresden, Germany 5–25 August 2002 (to be published).
- ¹²H. H. Rugh, *Phys. Rev. Lett.* **78**, 772 (1997); *J. Phys. A* **31**, 7761 (1998).
- ¹³J. Delhommelle and D. J. Evans, *J. Chem. Phys.* **115**, 43 (2001).
- ¹⁴L. Lue, O. G. Jepps, J. Delhommelle, and D. J. Evans, *Mol. Phys.* **100**, 2387 (2002).
- ¹⁵M. P. Tosi and F. G. Fumi, *J. Phys. Chem. Solids* **25**, 31 (1964).
- ¹⁶D. MacGowan and D. J. Evans, *Phys. Rev. A* **34**, 2133 (1986).
- ¹⁷S. W. de Leeuw, J. W. Perram, and E. R. Smith, *Proc. R. Soc. London, Ser. A* **373**, 27 (1980).
- ¹⁸S. Nosé and M. L. Klein, *Mol. Phys.* **50**, 1055 (1983).
- ¹⁹M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Clarendon, Oxford, 1987).
- ²⁰J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic, London, 1986).
- ²¹R. Sundheim, *J. Phys. Chem.* **60**, 1381 (1956).
- ²²J. Delhommelle and J. Petravic, *J. Chem. Phys.* **118**, 2783 (2003).