Molecular dynamics simulation of thermal diffusion processes in non-isothermal flow of the medium

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Abstract. The article presents a brief information on the discovery and experimental study of a new thermoelectrokinetic effect consisting in the formation of thermoelectrokinetic EMF in viscous conductive media in the presence of mass transfer (particles) and the action of a temperature gradient. On the basis of the molecular dynamics method, a mathematical model is developed and a numerical simulation of the non-isothermal flow of the Lennard-Jones fluid under the conditions of thermoelectrokinetic effect formation is carried out. As a result of the simulation the microscopic regularities of its formation are established.

1. Introduction

Previously, the authors theoretically predicted [1] and experimentally discovered [2] the thermoelectrokinetic effect which belongs to the cross-transport phenomena of a special class and occurs in viscous electroconductive media under the influence of three thermodynamic forces. Kinetic heterogeneity is a necessary condition for the appearance of this effect. It is formed in a viscous moving electrically conductive medium, on which temperature perturbation is imposed. For example, fluid flow is directed along a temperature gradient in one of the knees, in the other one against, when a conductive fluid flows at a speed $v$ along a U-shaped tube, which is influenced by a vertical temperature gradient. (figure 1).

As a result, the internal electric field is formed in the liquid. In the case of an electrically open circuit, this field can be experimentally detected as a potential difference called thermoelectrokinetic EMF. The method of measuring thermoelectrokinetic EMF in aqueous solutions of electrolytes is shown in figure 2.

Along the U-shaped tube (1) through which the solution of the aqueous ionic compound moves, the vertical temperature gradient is created, which leads to the formation of kinetic heterogeneity. Shortly thereafter, the electric potential difference is formed, which is recorded by the electrodes (3) and corresponds to thermoelectrokinetic EMF. The electric heater (2) is designed to equalize the temperature of the aqueous electrolyte at the inlet and outlet of the system in order to minimize the associated thermoelectric effect.
The paper uses approaches based on molecular dynamics methods to analyze the known experimental laws of the thermoelectrokinetic effect.

2. Experimental regularities of the thermoelectrokinetic effect
The papers [2, 3] establish main experimental regularities of the thermoelectrokinetic effect in aqueous solutions of electrolytes.

The absolute value of thermoelectrokinetic EMF depends on the difference in the mobility of electrolyte ions. The highest value of thermoelectrokinetic EMF is characteristic of electrolyte solutions that decompose into ions which differ greatly in their mobility: strong acids and alkalis. The value of the corresponding EMF is tenths of a millivolt with extremes of temperature between the elbows of the $U$-shaped tube and its bend equal to $10^{-15}$ K. The sign of thermoelectrokinetic EMF is determined by the sign of the coefficient of thermoelectric EMF, its magnitude directly proportional to the concentration of the electrolyte solution, the temperature difference and the flow rate of the medium at its small value.

The sign of the thermoelectrokinetic EMF does not depend on the sign of the temperature gradient and changes to the opposite when the direction of the flow rate changes and the previous temperature gradient direction stays the same.

The obtained experimental results allowed to conclude that the thermoelectrokinetic effect refers to cross-transport phenomena, and the thermoelectrokinetic EMF value is proportional to the product of two thermodynamic forces $\varepsilon_1 \sim \text{grad}(T) \cdot \text{grad}(P)$, where the pressure gradient $P$ is proportional to the flow velocity of the medium $v$. This conclusion is a generalization of Onsager thermodynamics on the action of three thermodynamic forces. At the same time, microscopic mechanisms of the thermoelectrokinetic EMF formation require additional research and are the objective of this paper. To that end, the first-principle approach of the molecular dynamics method was chosen, which allows us to trace the evolution of a many-particle system in the smallest details.

3. Molecular dynamics model formulation
The paper [4] justifies the possibility of using the molecular dynamics method for simulation of nonequilibrium phenomena occurring under the influence of three thermodynamic forces. As a simulated system, a two-dimensional system of disks interacting with each other through Lennard-Jones truncated potential is considered. Algorithms that simulate the application of spatially inhomogeneous temperature perturbations to the medium and make it possible to calculate the averaged macroscopic characteristics of a system of interacting particles are tested.

The article carries out the development of the emerging model, which includes algorithms that simulate the hydrodynamic flow of the medium. The model itself becomes more complex and represents a two-dimensional system of particles of two different types that interact with each other through the Lennard-Jones potential. In such a medium, cross-transport phenomena are already possible. For example, thermal diffusion phenomenon, at which in an initially homogeneous system of
particles of different types, when a temperature gradient is imposed, their partial separation occurs, i.e. a concentration gradient is formed. The simulated system is a two-dimensional region containing Berendsen thermostats in the center -1 and at the boundaries of the simulation cell -2,3, which maintain different constant temperatures in these areas by rescaling the particle velocities. Thus, a temperature gradient is created in the simulation cell (figure 3).

![Figure 3](image)

Figure 3. A two-dimensional molecular-dynamic cell that simulates a non-equilibrium system with temperature inhomogeneity.

In such a formulation, the molecular dynamics computing simulations corresponds to the modeling technique, which in English scientific publications is called “Boundary-driven non-equilibrium molecular dynamics” [5, 6] and, in fact, corresponds to the direct measurement of the transport coefficients as in the experiment. For a system of identical particles in this way it is possible to measure the coefficient of thermal conductivity as, for example, in the paper [7], in which the authors thus calculated the coefficient of thermal conductivity of a thin argon film. If a system consists of particles of different types, then this method allows to calculate the dimensionless thermal diffusion factor $\alpha_T$, for example, for a binary system [8]

$$\alpha_T = \frac{D_T}{D_{x_1 x_2}}$$

where $D_T$ is the thermal diffusion coefficient, $D$ is the concentration diffusion coefficient, $x_1, x_2$ are the mole fractions of components 1 and 2 of the binary system. In the steady state in the absence of convection and chemical reactions, the temperature gradient imposed on the system causes the formation of time-independent concentration gradients of both components

$$\frac{1}{x_1 x_2} \text{grad}(x_2) = \alpha_T \text{grad}(T).$$

As follows from (2), the thermal diffusion factor $\alpha_T$ for a system in the steady state is

$$\alpha_T = \frac{T \text{grad}(x_2)}{x_1 x_2 \text{grad}(T)}.$$  

(3)

All the values in (3) can be easily calculated in accordance with the results of the molecular-dynamics simulations. This method of determining the thermal diffusion coefficient is used to calculate the factor and thermal diffusion coefficient in such media as zeolites [9], polymers [10] and various liquid systems [11, 12]. All these and many other examples demonstrate that the molecular dynamics method can be successfully used to analyze cross-thermodynamic phenomena in various media and allows to calculate transport coefficients with the accuracy of a natural experiment. Moreover, it enables to reveal microscopic mechanisms of the phenomena under study.

Let us consider a more general, than in the paper [4] model of particles of two types, which are located in a square area with a side $L$, which interact with each other by means of the Lennard-Jones parameterized potential

$$u(r_{ij}) = \begin{cases} 
4\epsilon_{ij} \left[ \frac{(\sigma_{ij}/r_{ij})^{12}}{(\sigma_{ij}/r_{ij})^6} - 1 \right] + \epsilon_{ij}, & r_{ij} < r_c \\
0, & r_{ij} > r_c
\end{cases},$$

(4)

where $r_{ij}$ is the distance between particles, $r_c$ is the potential cutoff radius. The parameters of $\epsilon_{ii}, \sigma_{ii}$ potential determine the interaction between identical particles. The parameters for different particles $\epsilon_{ij}, \sigma_{ij}$ are defines in the Lorentz-Berthelot rule [13]

$$\sigma_{ij} = 0.5(\sigma_i + \sigma_j), \quad \epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}.$$  

(5)
The zone is divided into a number of subzones $i=1\ldots13$ (figure 4). In zones $i=1, 13$ temperature $T_C$ is maintained, in area $i=7$, temperature $T_H > T_C$.

![Figure 4. Splitting the simulation cell into equal subareas with numbers $i = 1\ldots13$.](image)

The flow of the medium is simulated as follows: at each time step, a constant is added to the projection of each particle velocity along the $ox$ axis, thereby a constant flow in the system is maintained artificially. This allows not to pay attention to the influence of boundaries and to simulate an infinite medium. Periodic boundary conditions are used at the boundaries. If an atom leaves the cell through one of the faces, then, at the same time, it returns through the opposite face. Since the presence of a constant flow along the $ox$ axis removes symmetry, then the used boundary conditions topologically mean that the faces $i=1$ и $i=13$ close up and the infinite plane closes into an infinitely long ring along the $oy$ axis (figure 5).

![Figure 5. Molecular dynamics cell, on which periodic boundary conditions are imposed.](image)

The interaction force between particles $i,j$ is calculated from the potential (4):

$$f_{ij} = -\nabla u(r_{ij}).$$

At the next time step, the position and velocity of the particles are calculated from classical equations of motion

$$m_i \ddot{r}_i = f_i = \sum_{j=1, j \neq i}^{N_m} f_{ij}.$$ 

A special system of units is used in the calculation: $\sigma_{ij}$ is chosen as the unit of length, atomic mass $m_i$ is chosen as the unit of mass, and $\varepsilon_{ij}$ of the potential parameters (4) of particles of class $i$ is chosen as the unit of energy. The Boltzmann constant is assumed to be equal to one. Then the temperature is determined as the average total kinetic energy of $N_m$ particles.

$$T = \frac{1}{2N_m} \sum m_i v_i^2.$$
To solve the system of equations (7), “leapfrog method” [19] is used, which has a third order of accuracy in the coordinate and minimum memory requirements

\[ v_{ix}(t + h/2) = v_{ix}(t - h/2) + h a_{ix}(t), \]  
\[ r_{ix}(t + h) = r_{ix}(t) + h v_{ix}(t + h/2). \]  

Here (x=1, 2), h is a time step. To accelerate the calculations, the simulated area is divided into cells with dimensions of the potential cutoff radius \( r_c \). In the calculation of the force acting on an individual atom (6), only atoms belonging to this cell and several neighbouring ones can be taken into account, and the co-ordinate data of the atoms should be organized in the form of the linked-list structure. The cell division method reduces the computational complexity of the problem to an acceptable level \( O(N_m) \), along with the method of the list of nearest neighbors proposed by Verlet [15].

Heating and cooling of cells \( i=7 \) and \( i=1, 13 \) is simulated by special Berendsen thermostat algorithms [16]. In this case, particle velocities are adjusted at each time step by multiplying by a scale factor \( \lambda \) so that the rate of temperature change in the cell with the source or heat sink is proportional to the difference between the current cell temperature \( T \) and the desired one \( T_{fi}=T_h, T_c \).

\[ \frac{dT}{dT} = \frac{T - T_0}{\tau} \]  

where \( \tau \) is the degree of relationship parameter between the system and the thermostat, which determines the characteristic time during which the system reaches the desired temperature. Then the scale factor \( \lambda \) is equal to

\[ \lambda = \sqrt{1 + \frac{h}{\tau} \left( \frac{T}{T_0} - 1 \right)}. \]  

Thus, at each time step cell temperatures \( T_j (j=1, \ldots, 13) \), the number of particles in cells \( N_j \), the projections values of the average velocity of particles of different types \( v_x, v_y \), across the system, algebraic number of particles crossing each of the borders of neighbouring cells, for particles of both types \( N_{ij}^{cross} (i=1,2) \), and the kinetic energy \( E_{ij}^{cross} \) transferred by them are calculated. While calculating, these values are averaged over \( M \) steps, and the values of diffusion particle fluxes \( J_i \) and energy flux \( J_i^Q \) through the boundaries of neighbouring cells are calculated

\[ J_i = \frac{N_{ij}^{cross}}{hML}, \]  
\[ J_i^Q = \frac{E_{ij}^{cross}}{hML}. \]  

4. Molecular dynamics simulations results

4.1. Absence of the flow of the medium

The paper [4] carries out test calculations in an equilibrium and non-equilibrium one-component system, the results of which are qualitatively consistent with the literature data [13].

Let us consider a two-component system consisting of \( N_m=2500 \) particles of two types located in the square area \( L \), interacting with each other by means of the Lennard-Jones potential (4). The particles have masses \( m_1, m_2 \), the potential coefficients (4) for them are \( \epsilon_{ij}=1, \sigma_{ij}=1 \), initially orderly distributed in this area, their velocities modulo are identical and correspond to the temperature \( T_0 \). Velocity directions are chosen randomly. In the cells \( j=1, 13 \) the Berendsen thermostats (11), (12) are located, maintaining the temperature \( T_C \), in the cell \( j=7 \), the temperature \( T_H \) is maintained.

As a result, after approximately \( M=20000 \) time steps, equal to \( h=0.01 \) a stationary state with coincident linear temperature profiles for both components is established in the system (figure 6).
In this case, the density of the diffusion particle flux after the given time becomes equal to zero, which indicates that the system reaches a stationary state (figure 7).

Figure 7. Densities of diffusion particle flux $J_i$ of subsystems $m_1=1$, $m_2=0.4$. $T_C=0.4$, $T_{hi}=1$. Dimensionless average density $\rho=0.5$.

Figure 8 shows a spatial profile of the number of particles calculated by averaging over 60 000 time steps after the system reaches a stationary state.
Figure 8. Spatial profiles of the distribution of the number of particles in cells. $T_C=0.4$, $T_H=1$. Dimensionless average density $\rho=0.5$.

The results show the phenomenon of thermal diffusion that occurs in a two-component system and allow to calculate the thermal diffusion factor $\alpha_T$ from the ratio (3). It is equal to $\alpha_T = 0.55$ for the system under study.

It is useful to compare the obtained results with the results of the theory and the real experiment to verify the adequacy of the model used. Molecular kinetic theory allows to obtain an approximate analytical expression for the thermal diffusion factor only in the case of the ideal gas [17]

$$\alpha_T \approx \frac{m_1-m_2}{m_1+m_2} \cdot \frac{n-5}{n-4}$$  \hspace{1cm} (15)

As can be seen from the above expression, the value $\alpha_T$ of the ideal gas depends on the mass difference between the components and the exponent $n$, which is responsible for the repulsion in the expression for the interaction potential (4). This factor is equal to 12 for the Lennard-Jones fluid, that corresponds to the positive thermal diffusion factor $\alpha_T$. In this case, the concentration of the heavier component increases in colder areas compared to the lighter one, which corresponds to the calculated results (figure 8).

The proportionality of the factor $\alpha_T$ of the mass difference $\Delta m=m_1-m_2$ of components is also confirmed by the calculation (figure 9).

As the results of experiments show, in gaseous mixtures the thermal diffusion factor significantly depends on the pressure or density of the mixture. So for an equimolar mixture CO$_2$/H$_2$ at 360 K, it varies from 0.33 to 1.0 with the increase in pressure from 1 to 78 atmospheres [18]. The results of phenomenological thermodynamics of irreversible processes and experiments in dense gases and liquids lead to the conclusion that, when a substance approaches a critical point, the thermodiffusion factor goes to infinity [8]. Figure 10 shows the calculated dependence of the thermal diffusion factor $\alpha_T$ on the dimensionless density of the Lennard-Jones fluid. The dependence obtained is qualitatively consistent with the nature of the change of the thermal diffusion factor during the transition from gaseous to liquid state. This transition apparently occurs in the density range $\rho = 0.6$-$0.7$ for temperature $T = 0.6$. The estimated value of $\alpha_T$ of the ideal gas (formula 15) for masses used in the molecular dynamics calculation of the curve (figure 10) is $\alpha_T = 0.424$. The value of the thermal
diffusion factor for the minimum density $\rho = 0.3$ in the calculation is $\alpha_T = 0.455$, which is close to the theoretical value of the ideal gas.

Thus, the obtained results are evidence of the adequacy of the molecular dynamics model for the description of cross processes in gas and liquid media.

4.2. Presence of the flow of the medium

At the next stage, calculations take into account the flow of the medium. The calculations are carried out for a two-component system of particles with masses $m_1 = 1, m_2 = 0.2$, with a fixed value of the dimensionless density $\rho = 0.6, T_C = 0.4, T_H = 0.8$ and various values of the flow rate of the medium $v$.

Figure 11 shows the spatial profile of the stationary temperature distribution, averaged over 60 000 time steps, for the flow rate of the medium $v = 0.1$, which is 10% of the average thermal velocity of heavy particles $m_1 = 1$.

The profiles for both subsystems of particles coincide. The presence of the flow of the medium leads to nonlinear spatial distribution of temperature. Next, spatial distribution of local particle concentration $c_i^j = \frac{N_i^j}{S_j}$ is shown, where $S_j$ is the surface area of $j$-th cell, $N_i^j$ is the number of particles of $i$ type in the cell $j$ (figure 12).
In the absence of the flow of the medium similar profiles are symmetric with respect to the central area containing the heat source (figure 8). The presence of the flow removes the indicated symmetry. As a result, the concentration of lighter particles after the hot area in the course of the medium flow increases compared with heavier particles, and before this area the concentration of heavier particles exceeds the concentration of lighter particles (figure 12). Thus, the temperature heterogeneity serves as a barrier, the permeability of which for particles of different masses is not identical.

\[
\Delta \overline{N} = \sum_j \left| \overline{N}^j_1 - \overline{N}^j_2 \right|
\]

can be entered as a quantitative value characterizing this separation effect in a two-component system, where \( \overline{N}^j_1, \overline{N}^j_2 \) are the time-averaged numbers of particles of type 1 and 2 in the cell with the number \( j \). If \( v = 0 \), this value is almost zero. As calculations show, the indicated value substantially depends on the flow rate of the medium (figure 13) and the temperature gradient (figure 14).

The effect of the separation of components by temperature inhomogeneity in the flow of the medium first increases sharply with increasing flow rate. The maximum value \( \Delta \overline{N} \) characterizing the degree of separation of components is achieved in the range of flow rates \( v = 0.04-0.08 \) (3.6% – 7.2% of the average thermal velocity of heavy particles). A further increase in the flow rate leads first to a sharp, then to a smoother decrease of \( \Delta \overline{N} \). The dependence of the magnitude of \( \Delta \overline{N} \) on the temperature difference has a similar character. Thus, based on the analysis of graphs in figure 13 and figure 14, we can conclude that at a fixed average temperature of the medium and its density there are optimal values of the flow rate of the medium and the temperature difference at which the separation effect reaches its maximum.

5. Conclusion

This effect of separation of components leads to the formation of an internal electric field, as in the thermoelectrokinetic effect which the authors discovered and studied in aqueous electrolyte solutions [2] and in colloidal solutions [19] under the condition of a viscous, neutral electroconductive medium, the components of which have an opposite electrical charge (different plasma types, electrolyte solutions and melts, colloid systems).

Based on the results obtained during the simulation of the Lennard-Jones fluid, it can be concluded that the microscopic mechanism for the formation of thermoelectrokinetic EMF is that spatial temperature heterogeneity in the moving electroconductive medium influences particles of the medium with different mobility characteristics, like a potential barrier. The permeability of this barrier for particles is not the same, which leads to their partial separation “before” and “after” temperature
heterogeneity and to the formation of an internal electric field. The simulation shows that this effect depends on the magnitudes of thermodynamic forces: a temperature gradient and a pressure, which is proportional to the flow rate of the medium. For small values of thermodynamic forces, the effect is proportional to the product of two thermodynamic forces, since at a fixed value of one of the thermodynamic forces, the effect is proportional to the other one (initial sections of figure 11, figure 12), which is confirmed by experiments in aqueous solutions of electrolytes. The nonlinearity of this effect is manifested in the case of a strong deviation from thermodynamic equilibrium.

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