Kinetic approach to solution of evaporation-condensation problems taking into account multi-particle interactions in liquid

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Abstract. The presented work is devoted to the study of heat-mass transfer in vapor and liquid, taking into account multi-particle interactions in the condensed phase. An appropriate numerical procedure is proposed to solve the kinetic equation, both in the vapor and in the liquid. Using this approach, the problems of thermal conductivity in liquid argon, as well as the problem of evaporation-condensation, are solved.

1. Introduction
The description of the evaporation and condensation processes is most correct with a through-flow vapor-liquid solution of the problem [1,2]. This approach eliminates the need to set the values of evaporation and condensation coefficients on the interfacial surfaces, as well as the distribution function of molecules moving from the interface, which are needed as boundary conditions for solving the Boltzmann kinetic equation in the vapor region. The presented work is devoted to the study of heat-mass transfer in vapor and liquid, taking into account multi-particle interactions in the condensed phase.

2. Description of the method
The essence of the method is as follows. We isolate in the liquid a group of $M$ particles located in close proximity to each other. Suppose that the selected group can be considered as a single system in which all atoms simultaneously interact with all. The state of this system can be described using a vector $P$ whose components are $3M$ components of the velocities of atoms (molecules). The interaction between all particles of the selected group is reduced to a change in the state of the system: $P \rightarrow P'$, which is mathematically modeled as a rotation $P$ in multidimensional space with a dimension of $3M$. At the same time, the length of the vector $|P| = |P'|$ will remain unchanged by virtue of the law of energy conservation.

After finding the vector $P'$ all components of the particle velocities after the interaction are known. The proposed approach makes it possible to find the distribution function directly from the computational procedure itself without resorting to recording a complex multi-particle collision integral.

In the presented work, the kinetic equation is solved both in the vapor region and in the condensed phase.
For vapor, this is the Boltzmann kinetic equation with the integral of paired collisions $J$:

$$\frac{\partial f}{\partial t} + \xi \frac{\partial f}{\partial \mathbf{r}} = J.$$  

(1)

The kinetic equation in the liquid region has a similar form:

$$\frac{\partial f}{\partial t} + \xi \frac{\partial f}{\partial \mathbf{r}} = Z_M.$$  

(2)

The value $Z_M$ on the right side is intended to take into account the simultaneous interaction of atoms (molecules) of the condensed phase. In this paper, it is replaced by the computational procedure described above. This method allows the use of a single numerical algorithm to determine macro parameters both inside the liquid and vapor.

3. Estimate of the number of interacting particles

It can be assumed that the system will strive for an equilibrium state the faster the more particles collide simultaneously. This circumstance cannot but affect the third order fineness of the distribution function moment such as heat flux. Its value decreases when striving for Maxwell and, conversely, grows if the system moves away from equilibrium. Therefore, the principle point in implementing the proposed approach will be the choice of the number of interacting particles.

For the initial evaluation of $M$, we represent the element of the condensed phase in the form of a block consisting of $M = 27$ particles (Figure 1), the interaction between which is described using the Lennard-Jones potential.

![Figure 1. Model of interaction of a particle with its immediate environment.](image)

The central particle is shown in black in Figure 1 and is placed at the origin. It is surrounded by 26 adjacent particles, with which it interacts directly. The potential energy of the central particle will be determined as follows:

$$U_{sum} = \sum_{i=1}^{M} 4\varepsilon \left[ \left( \frac{\sigma}{r_i} \right)^{12} - \left( \frac{\sigma}{r_i} \right)^{6} \right],$$  

(3)
where $\varepsilon, \sigma$ is the parameters of the Lennard-Jones potential, $r_i$ is the distance between the central particle and the $i$-th of its surroundings. It is assumed that all particles are located in the nodes of the cubic lattice with the side $d = \sqrt{2}\sigma$.

From Figure 1 you can determine that the 6 particles are at a distance $r = d$ from the center, 12 – at a distance $r = \sqrt{2}d$ and 8 – at a distance $d = \sqrt{2}\sigma$. Then, using the formula (3), the total potential energy of the central particle can be calculated: $U_{\text{sum}} = 9.36\varepsilon$. Thus, from the viewpoint of interaction energy, a model of 27 fixed particles arranged at different distances can be replaced by surrounding the central particle with about nine neighbors located at a distance $d$.

Previously, we used [2] an approximation for the dependence of the potential energy of the liquid particle on the surface on the temperature $T$ of the condensed phase:

$$
\varepsilon(T) = kT \frac{\varepsilon_{s0}}{\varepsilon} \cos \left(\frac{\pi T}{2k}\right),
$$

(4)

Here $\varepsilon_{s0} = 9.36\varepsilon$ is the total potential energy taking into account the surrounding particles in the absence of thermal motion, $\varepsilon$ is the Lennard-Jones potential parameter, $T_k = 1.07T_{cr}$, $T_{cr}$ is the critical temperature, $k$ is the Boltzmann constant. This formula will be true for a particle in the depth of a liquid, but at a different value $\varepsilon_{s0}$, since there are more neighboring particles.

Take, for example, the boiling point of argon, neon, krypton and xenon and substitute in the approximation formula. We calculate $(\varepsilon_sT)^{-s}$ and find the relation value $(\varepsilon_sT)^{-s} = 1$. By analogy with stationary particles, this number will show how many particles interact in terms of potential energy. That is, the interaction of 27 atoms $(26 + 1)$ will be equivalent to $s$ the interaction of particles in the presence of thermal motion. Such numbers are obtained: $s_{Ar} = 4.26$, $s_{Ne} = 4.83$, $s_{Kr} = 4.18$, $s_{Xe} = 4.48$. Thus, a preliminary evaluation indicates that the number of particles interacting in the liquid simultaneously will be 4-5.

Further, the quantity of liquid atoms involved in the multi-particle interactions is specified when solving the test problem of thermal conductivity through a flat wall is made. The comparison the value of the heat flux found by the method discussed above with calculation in accordance with the Fourier's law at the known table empirical value of the thermal conductivity coefficient for various substances is done. As result of this comparison the quantity of liquid atoms involved in the multi-particle interactions is defined. Monatomic argon (Ar), neon (Ne), krypton (Kr) and xenon (Xe) were considered.

4. Test the method using an example of a thermal conductivity problem

Statement of this problem is as follows. Thin layer of specified substance with thickness $L$ is limited by impermeable surfaces having temperatures $T_1$ and $T_2$. The problem was solved for $T_1/T_2 = 1.1$. The lower temperature $T_2$ is taken as the base $T_0 = T_2$, the length of the area $L = 1$ is taken as one.

To determine thermal conductivity coefficients for different temperatures and substances, kinetic equation (2) was solved. The heat flux in the direction $x$ was defined as the third moment of the distribution function:

$$
q_x = \frac{1}{2} m \int (\xi - u)^2 (\xi_x - u_x) f \, d\xi,
$$

(5)

where $d\xi = d\xi_x d\xi_y d\xi_z$, $u(x, y, z)$ is the mean velocity vector of the gas, $m$ is the mass of the molecule. Further, thermal conductivity coefficients $\lambda$ were calculated by the formula:
\[ \lambda = \frac{q_s L}{T_1 - T_2}. \]  

(6)

At the first stage of work, the boundary conditions for the Boltzmann equation on surfaces were given in the form of semimaxvellians with temperatures \( T_1 \) and \( T_2 \), respectively. When solving the Boltzmann equation (3), the largest heat flux that can be obtained is limited by the free molecular limit. The distribution function is maximally different from the equilibrium one. Any collision operator brings the function closer to equilibrium and reduces heat flow. Figure 2 shows an example \( f(\xi_x) \) for \( \xi_y = 0, \xi_z = 0 \) the thermal conductivity problem in the free molecular flow mode for argon. The calculations showed that with the boundary conditions given in the form of semimaxvellians, the obtained heat flux in the liquid is several times less than that observed experimentally, even in the free molecular limit. However, further calculations show that for vapor (gas), the results are well consistent with the experiment at \( M = 2 \) for enough rarefied gas or 3 in the case of a dense gas.

To solve the problem of heat flux in the liquid, the Chapman-Enskog function [3] was taken as boundary conditions:

\[ f_i = f_M \left[ 1 - \frac{q_s}{p \frac{c_s}{R T}} \left( 1 - \frac{1}{5} \frac{c^2}{R T} \right) \right], \]

(7)

where \( f_M \) is the Maxwell distribution function calculated at temperature \( T = T_1 \) or \( T = T_2 \) and density determined from the condition of impermeability of surfaces; \( c_s = \xi_x - u_x \); \( c^2 = (\xi - u)^2 \); \( p \) is pressure.

Figure 3 shows an example of the cross section of the distribution function \( f(\xi_x) \) within the condensed phase, similar to Figure 2. However, unlike the free molecular regime with boundary conditions in the form of semimaxvellians (Figure 2), Figure 3 illustrates a solution with non-equilibrium Chapman-Enskog boundary conditions in the presence of intermolecular interaction with \( M = 4 \) for argon. If you compare Figure 2 and Figure 3 visually, the function in the last figure may appear closer to equilibrium. In fact, the distribution function with non-equilibrium boundary conditions is further from Maxwell in the sense that the heat flux (5) calculated by it is about five times higher \( q \) for free-molecular \( f \), which in fact is only the sum of two semimaxvellians.

![Figure 2. Free molecular flow distribution function.](image1)

![Figure 3. Distribution function within the liquid region using Chapman-Enskog boundary functions.](image2)
The results of calculations of thermal conductivity coefficients for argon are presented in Table 1. The last columns of all tables contain values $\lambda_{tabl}$ taken from reference literature [4].

| $T_0$, K | $M$ | $\lambda \times 10^3$, W/mK | $\lambda_{tabl} \times 10^3$, W/mK |
|----------|-----|----------------------------|---------------------------------|
| Liquid argon |
| 84       | 3   | 131.7                      |                                 |
|          | 4   | 114.3                      |                                 |
|          | 5   | 92.94                      |                                 |
| 87       | 3   | 134.1                      |                                 |
|          | 4   | 116.4                      | 130.                            |
|          | 5   | 93.57                      |                                 |
| 90       | 3   | 136.4                      |                                 |
|          | 4   | 118.3                      | 124.7                           |
|          | 5   | 95.17                      |                                 |
| 100 (p=1MPa) | 4 | 124.8                      | 110.9                           |
|          | 5   | 100.3                      |                                 |
| 110 (p=1MPa) | 5 | 105.2                      | 97.6                            |
|          | 6   | 72.17                      |                                 |
| 120 (p=2MPa) | 5 | 109.9                      | 85.5                            |
|          | 6   | 75.38                      |                                 |
| 130 (p=3MPa) | 5 | 114.4                      | 73.6                            |
|          | 6   | 78.46                      |                                 |
|          | 7   | 62.77                      |                                 |
| Gas argon |
| 100      | 2   | 9.79                       | 6.6                             |
|          | 3   | 7.65                       |                                 |
|          | 4   | 5.81                       |                                 |
| 200      | 2   | 13.84                      | 12.6                            |
|          | 3   | 10.81                      |                                 |
| 300      | 2   | 16.95                      | 17.7                            |
|          | 3   | 13.24                      |                                 |

It is important to note that the non-equilibrium Chapman-Enskog boundary functions for liquid and Maxwell functions for gas were used to obtain the data in Table 1. It can be seen that the experimental data $\lambda_{tabl}$ are well consistent with the calculation results at $M=3–5$ for liquids and $M=2–3$ for gases of different densities. It can also be seen from Table 1 that at elevated pressures the number of reacting particles for argon can tend to $5–7$. Under normal conditions for all gases $M$ is close to 2.

5. Solution of evaporation-condensation problem

In the vapor region, the Boltzmann kinetic equation with the usual collision integral $J (1)$ is solved. In the liquid, the above procedure (2) is used instead of $J$. As an illustration of the application of the method discussed, the process of evaporation-condensation of argon was investigated. The setting of the problem is shown in Figure 4. The central region filled with vapor is bordered by two layers of condensed phase. Initial values of vapor density and temperature are $n_0 = 33.49$ kg/m$^3$ and $T_0 = 110$ K. The temperatures of the liquid layers are also equal $T_0$.

At the initial time, the temperature of the surface bounding the study area on the left changes and becomes $T_1 = 120$ K, the temperature on the right remains unchanged. Over time, the temperature of
the condensed phase layers also begins to change, which leads to a change in the conditions on the interface surfaces and, therefore, the intensity of evaporation. Density $n_0$ and temperature $T_0$ are taken as basic parameters. The mean free run path of argon $l_0$ is calculated at $n_0$ and $T_0$.

Density, temperature and mass flux dependencies are obtained for $x$ for different quantity of simultaneously interacting particles in liquid $M = 5$, 9 and 20. Examples of the solution results are shown in Figures 5 and 6. It can be seen from Figure 5 that the temperature is very weakly dependent on the number of interacting particles. For density (Figure 6), the difference for $M = 5$ and $M = 20$ is about 5%. This is due to the small differences in the steady state temperatures of the interfacial surface and, as a result, the different evaporation intensity.

![Figure 4. The setting of evaporation-condensation problem](image)

![Figure 5. Dependence of vapor and liquid temperature on $x$](image)

![Figure 6. Dependence of vapor density on $x$](image)

6. Conclusion
An approach is presented for the conjugate solving of liquid-vapor taking into account the multi-particle interaction in the condensed phase. Using the proposed approach, the problem of thermal conductivity and the problem of evaporation-condensation of argon between two layers of liquid are
solved. Thermal conductivity values for argon consistent with experimental data were obtained. The distributions of macro parameters along the $x$ coordinate are presented.

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