Kinetic equation for dense gases and fluids with a multistep potential of interaction

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We analyse new kinetic equation for systems with a multistep potential of interaction proposed by us resently. This potential consists of the hard sphere part and a set of attractive and repulsive walls. Such a model is the unification of many previous semi-phenomenological kinetic theories of dense gases and fluids. For specific parameters of the multistep potential of interaction the obtained results rearrange to those ones of previous kinetic theories by means of the standard Chapman-Enskog method. As a demonstration that our approach allows an accurate reproduction of experimental and MD data for transport coefficients in a wide density-temperature range, we present results of numerical computation for argon along a curve of saturation and their comparison with experimental data available and MD simulations.

In present paper, we consider a new kinetic equation for systems with a multistep potential of interaction (MSPI). This potential consists of the hard sphere part and of a system of attractive and repulsive walls. Such a model is a generalization of SET (RET, MET) [1,2], DRS (RDRS) [3] and KMFT theories [4]. The H-theorem for this equation has been proved in [5], a normal solution has been published in our recent paper [6]. For specific parameters of model interaction potential in shape of the multistep function, the obtained results rearrange to those of the SET (RET, MET), DRS (RDRS) or KMFT theories by means of the standard Chapman-Enskog method [7]. In view of this, new theory can be considered as a generalized one which in some specific cases arrives at the results of previous theories and in such a way displays the connection between of them.

Let us consider a system of N classical particles of mass m enclosed in volume V when $N \to \infty$ and $V \to \infty$, provided $N/V = \text{const}$. Particles interact by means of a multistep potential of interaction (MSPI) $\varphi_{ij} \equiv \varphi(|\vec{r}_i - \vec{r}_j|) \equiv \varphi(|\vec{r}_{ij}|) \equiv \varphi(r_{ij})$ given in a form of a multistep function:

$$\varphi_{ij} = \begin{cases} \infty \ ; & r_{ij} < \sigma_0, \\ \varepsilon_k \ ; \ \sigma_{k-1} < & r_{ij} < \sigma_k; \ k = 1, \ldots, N^*, \\ 0 \ ; \ \sigma_{N^*} < & r_{ij}. \end{cases} \tag{1}$$

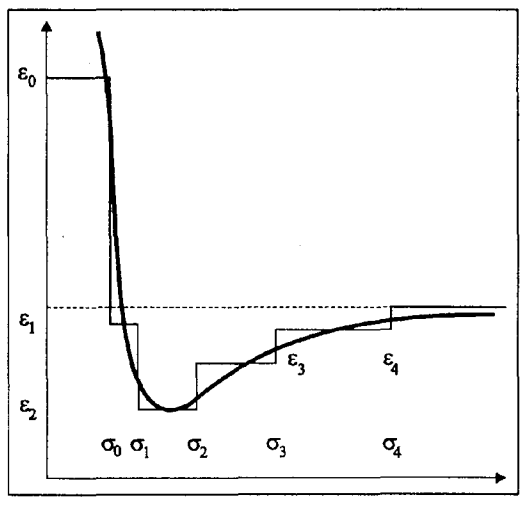

FIG. 1.

Here, N^* is the total number of attractive and repulsive walls except the hard sphere one. For our convenience, we distinguish systems of attractive and repulsive walls, Fig. 1.

Let one has n^* repulsive walls, separated by the distances σ_{ri} and having heights $\Delta\varepsilon_{ri} > 0$, $i = 1, \ldots, n^*$; and m^* attractive walls with the parameters σ_{aj} and $\Delta\varepsilon_{aj} > 0$, $j = 1, \ldots, m^*$, respectively. σ_0 is the location of the hard sphere wall. It is obvious that $n^* + m^* = N^*$, $\Delta\varepsilon_{ri} = \varepsilon_{ri} - \varepsilon_{ri+1}$, $\Delta\varepsilon_{aj} = \varepsilon_{aj+1} - \varepsilon_{aj}$. In such a way the parameters σ_0, n^*, σ_{ri}, $\Delta\varepsilon_{ri}$, m^*, σ_{aj}, $\Delta\varepsilon_{aj}$ define the multistep potential of interaction completely. For MSPI the region Ω of binary interactions consists of $\lim_{\Delta r^{(k)} \to +0}[\sigma_k - \Delta r^{(k)}, \sigma_k + \Delta r^{(k)}]$, $\{k = 0, \ldots, N^*\}$, where $\Delta r^{(0)} \to +0$ due to the singular nature of the potential under consideration. This potential has the finite range of action $\max\{\sigma_k\} = \sigma_{N^*} > 0$. In geometrical interpretation, for interaction area one has a set of concentric spheres of radii σ_k, $k = 0, \ldots, N^*$ and the MSPI has then the following typical dimensions: $\Delta r_0^* = \max\{\Delta r^{(k)}\} \to +0$, $\{k = 0, \ldots, N^*\}$, $\Delta\sigma = \min\{\sigma_k - \sigma_{k-1}\} > 0$, $\{k = 1, \ldots, N^*\}$, $\Delta\sigma_{\max} = \max\{\sigma_k\} = \sigma_{a_{m^*}}$, $\{k = 0, \ldots, N^*\}$, and the folloving typical times (corresponding to those dimensions): $\tau_0^* = \Delta r_0^*/|\vec{g}_0| \to +0$ is the interaction time on each of the walls separately; $\Delta\tau = \Delta\sigma/|\vec{g}_0|$ is the time of motion between the two nearest neighboring walls; $\tau_{\text{total}} = \sigma_{\max}/|\vec{g}_0|$ is the time of motion of the whole system of walls in MSPI for some pair of particles, where $\vec{g}_0$ is an average relative velocity (of two particles). As far as interaction in areas between the walls (horizontal steps) is absent, one may introduce some

average time of a free motion in a system τ_{f}, which depends on the MSPI geometry and the particle density. And because of $\tau_0^* \to +0$, $\Delta\tau > 0$, we see that the time τ_{f} can be scaled to an arbitrary small value by virtue of a geometrical changing of the potential shape and increasing the particle density. The following inequality then holds: $\tau_0^* \ll \tau_{\mathrm{f}} \ll \Delta\tau \leqslant \tau_{\mathrm{total}} \leqslant \tau_{\mathrm{m}}$ (condition of a time hierarhy). Similar inequality between different time scales exists in the Boltzmann kinetic theory: $\tau_{\mathrm{c}} \ll \tau_{\mathrm{f}} \ll \tau_{\mathrm{m}}$, where τ_{c} is the interaction (collision) time, τ_{m} is the the characteristic scale of time for hydrodynamic (macroscopic) variables.

The well known operator of a pair interaction between two particles in the Boltzmann theory contains a limit $\tau \to -\infty$ which physically means consideration of an interaction dynamics during the time $|\tau|$ far more longer than interaction time τ_{c}, i.e. $|\tau|/\tau_{\mathrm{c}} \to \infty$. In such a way, the parameter τ_0 appearing in the general structure for the collision operator derived within the frame of non-equilibrium statistical operator method [5,8–10]

$$I_{\mathrm{coll}}(x_1;t) = \int \mathrm{d}x_2\, L(1,2) \lim_{\frac{\tau}{\tau_0}\to-\infty} \mathrm{e}^{iL_2\tau} g_2(\vec{r}_1,\vec{r}_2;t) f_1(x_1;t+\tau) f_1(x_2;t+\tau) \tag{2}$$

may be identified with τ_0^*, and $\Delta r_0 \equiv \Delta r_0^* = \tau_0|\vec{g}_0|$. In equation (2) we use notations as usual: $x = \{\vec{r},\vec{p}\}$ is a set of phase space variables, g_2 is a binary correlation function, $f_1(x;t)$ is one-particle distribution function, and $L_2 = L_2^{(0)} + L(1,2)$, where $L_2^{(0)}$ and $L(1,2)$ are two-particle Liouville operators [8–10] of the free motion and interaction, respectively. Taking into account that f_1 is continuous in arbitrary point of space and g_2 is continuous over $\vec{r}_{12}$ out of the region Ω, and the evidence of the limit $\tau \to -0$, we understand that the collision integral for MSPI is split into several parts. Physically this means that during the time interval of order of free motion τ_{f}, two particles can interact only at one of the walls of the MSPI. Interaction of the same pair of particles during this time interval in several subregions Ω is impossible. Moreover, if one considers a separate pair of particles, it appears that in space of velocities their interaction at one of the walls does not depend on interaction at the rest ones. It is caused by the fact that during the time of motion between neighboring walls, the pair of particles interacts many times with the medium and velocity correlations weaken. So, during some interaction of the pair of particles at a potential wall, this pair does not "remember" its velocities after the previous "meeting". The great part of configurational correlations conserves and is taken into account by the factor g_2. However, the property of additivity for collision integral is broken, if the condition of a time hierarhy is not fulfilled. In this case one should consider complex interference phenomena.

We see that all parts of the collision integral will have the same structure. In order to obtain analytical expressions for them, it is necessary to consider the action of two-particle operator of evolution $\lim_{\tau\to-0} \mathrm{e}^{iL_2\tau}$ at the external $r_{12} = \sigma_k + \Delta r_0$ and internal $r_{12} = \sigma_k - \Delta r_0$ surfaces of the sphere of radius σ_k. Going similarly to the derivation of the kinetic equation of the RET theory [1,2,11] and taking into account the system of attractive and repulsive walls, one obtains the following kinetic equation:

$$\left(\frac{\partial}{\partial t} + \vec{v}_1 \frac{\partial}{\partial \vec{r}_1}\right) f_1(x_1;t) = \int \mathrm{d}x_2\, \hat{T} g_2^{\mathrm{q}} f_1(x_1;t) f_1(x_2;t), \tag{3}$$

where $g_2^{\mathrm{q}} \equiv g_2^{\mathrm{q}}\Big(\vec{r}_1,\vec{r}_2|n(t),\beta(t)\Big)$ is defined in the usual way from the maximum of the entropy functional and in its turn is the functional of local values of density $n(\vec{r}_1;t)$ and inverse temperature $\beta(\vec{r}_1;t) = 1/(k_{\mathrm{B}}T)$, k_{B} is the Boltzmann constant and T is the local temperature. In (3) $\hat{T}$ is an operator which describes interaction of two particles in presence of MSPI:

$$\hat{T} = \hat{T}_{\mathrm{hs}} + \sum_{i=1}^{n^*} \hat{T}_{ri} + \sum_{j=1}^{m^*} \hat{T}_{aj}, \quad \hat{T}_{\mathrm{hs}} = \sigma_0^2 \int \mathrm{d}\hat{\sigma}\, \hat{\sigma}\vec{g}\, \theta(\hat{\sigma}\vec{g}) \left\{\delta\left(\vec{r}_1 - \vec{r}_2 + \hat{\sigma}\sigma_0^+\right) B_a(\hat{\sigma}) - \delta\left(\vec{r}_1 - \vec{r}_2 - \hat{\sigma}\sigma_0^+\right)\right\}. \tag{4}$$

The last expression is nothing but the operator of hard spheres interaction [12], $\hat{\sigma}$ is the unit vector directed from the second particle to the first one, $\vec{g} = \vec{v}_2 - \vec{v}_1$ is the relative velocity. $B_a(\hat{\sigma})$ is the velocities shift operator as in the classical mechanics of elastic collisions. $\hat{T}_{ri}$ and $\hat{T}_{aj}$ are interaction operators at the ith repulsive and at the jth attractive walls [5,6], respectively. In the absence of attractive and repulsive walls ($\Delta\varepsilon_{ri} = 0$, $i = 1,\ldots,n^*$, $\Delta\varepsilon_{aj} = 0$, $j = 1,\ldots,m^*$) kinetic equation (3) transfers to that one of the RET theory [1,2]. In the presence of only one finite attractive wall ($\Delta\varepsilon_{ri} = 0$, $i = 1,\ldots,n^*$, $\Delta\varepsilon_{aj} = 0$, $j = 2,\ldots,m^*$, $\Delta\varepsilon_{a1} \neq 0$) one obtains the kinetic equation of the RDRS theory [13]. Moreover, it can be shown, that in the third special case when the set of walls is merged with some smooth potential ϕ_t and $\Delta\sigma_{ri} = \sigma_{ri} - \sigma_{ri-1} \to 0$, $i = 1,\ldots,n^*-1$, $\Delta\varepsilon_{ri} \to 0$, $n^* \to \infty$; $\Delta\sigma_{aj} = \sigma_{aj+1} - \sigma_{aj} \to 0$, $j = 1,\ldots,m^*-1$, $\Delta\varepsilon_{aj} \to 0$, $m^* \to \infty$; and $-\Delta\varepsilon_{ri}/\Delta\sigma_{ri} \to \phi_t'(\sigma_{ri})$, $\Delta\varepsilon_{aj}\,\Delta\sigma_{aj} \to \phi_t'(\sigma_{aj})$, the kinetic equation (3) transfers to one of the KMFT theory [4].

The normal solution to the kinetic equation (3), and its analytical properties were studied by us in [6]. Here we present the results of numerical computation for transport coefficients. As far as we are working with the MSPI, this problem is not so trivial. If we have any information about real (smooth) potential of interaction, we should deal with a large number of definition parameters. However, when interaction potential is known,

the number of independent master parameters is greatly reduced. The first question appearing then is how to represent an initial smooth interaction potential by a multistep one. Let us consider one possible way of definition in which all distances between walls of the same kind are equal, i.e.: $\Delta\sigma_{ri} = \text{const}$, $i = 1,\ldots,n^*$, $\Delta\sigma_{aj} = \text{const}$, $j = 1,\ldots,m^*$. Then, to define the model interaction potential one needs to set the position of the hard sphere wall σ_0, the position of the most removed attractive wall $\sigma_{\max}$ ($\sigma_{\max} = \sigma_{a_{m^*}}$), the number of short lengths dividing repulsive area $[\sigma_0, \sigma_{\text{mean}}]$ n_p, and the number of short lengths dividing attractive area $[\sigma_{\text{mean}}, \sigma_{\max}]$ m_p, where σ_{mean} is the minimum position of a real interaction potential. Now MSPI is built. Numbers of repulsive n^* and attractive m^* walls are uniquely determined via numbers of dividing lengths n_p and m_p. In this representation of a real interaction potential by MSPI, one realizes original entwining of model potential around real one.

The second question is the problem of optimal dividing, i.e. how to define the parameters σ_0, $\sigma_{\max}$, n_p, m_p so that fair results are obtained already in the first approximation. We tried to solve this problem numerically. Numerical computations of transport coefficients were carried out for Argon with the Lennard-Jones potential

$$\phi_{\text{real}} \simeq \phi_{\text{LJ}} = 4\varepsilon_{\text{LJ}} \left[\left(\frac{\sigma_{\text{LJ}}}{r} \right)^{12} - \left(\frac{\sigma_{\text{LJ}}}{r} \right)^{6} \right], \tag{5}$$

where $\sigma_{\text{LJ}} = 3.405$ Å, $\varepsilon_{\text{LJ}}/k_{\text{B}} = 119.8$ K.

The starting point in numerical analysis of transport coefficients of our theory are expressions for transport coefficients of bulk and shear viscosities with additional equation for binary equilibrium correlation function g_2^{eq} of a system with potential in a form of multistep function. In our calculation we used for g_2^{eq} the following approximation: $g_2^{\text{eq}}(r) = g_2^{(0)}(r)\exp\{-\beta\varphi(r)\}$, where $g_2^{(0)}(r)$ is the binary equilibrium correlation function of hard spheres of diameter σ_0. Its analytical expression is well known [14].

TABLE I. Parameters for different theories and calculations for transport coefficient η. Bottom part contains square displacement of results of SET (RET), MET (BH), DRS (RDRS) theories and our theory denoted by GDRS (i.e. generalized DRS) from MD simulation. The GDRS result is the closest to MD simulation. The same parameters were used for calculation of other transport coefficients.

SET (RET)	SIGMZ0=1.047			
MET (BH)	$\sigma_0(T) = \sigma_{\text{LJ}}\,[1.068 + 0.3837\,(k_{\text{B}}T/\varepsilon_{\text{LJ}})]\,/\,[1.000 + 0.4293\,(k_{\text{B}}T/\varepsilon_{\text{LJ}})]$			
DRS (RDRS)	SIGMZ0=0.891, SIGMZM=1.342, EZDRS=0.929			
GDRS	SIGMZ0=0.940, SIGMZM=1.960, n_p=3, m_p=9, n^*=2, m^*=6			
MD	SET (RET)	MET (BH)	DRS (RDRS)	GDRS
0.0	0.01250	0.00794	0.000217	0.000206

First, one calculates the transport coefficients along the gas-liquid saturation curve. There were 5 points of calculation ($\rho_i = mn_i$, T_i, $i = 1,\ldots,5$) along the curve of saturation for which such a transport coefficient as the shear viscosity η is known from the MD simulation [4]. MSPI parameters n_p, m_p, SIGMZ0=$\sigma_0/\sigma_{\text{LJ}}$, SIGMZM=$\sigma_{\max}/\sigma_0$ were defined from the minimum of square displacement of the theory from corresponding MD results. Parameters of the DRS (RDRS) theory were defined in much the same way: SIGMZ0=$\sigma_0/\sigma_{\text{LJ}}$, SIGMZM=$\sigma/\sigma_0$, EDRS=$\varepsilon/\varepsilon_{\text{LJ}}$, as well as for SET (RET) theory: SIGMZ0=$\sigma_0/\sigma_{\text{LJ}}$. Table I shows the results. Calculation of transport coefficients by different theories, their comparison with experimental data and MD simulations are presented in Fig. 2. It is clear to see that GDRS results practically coincide with the experimental data in a wide range of densities and temperatures.

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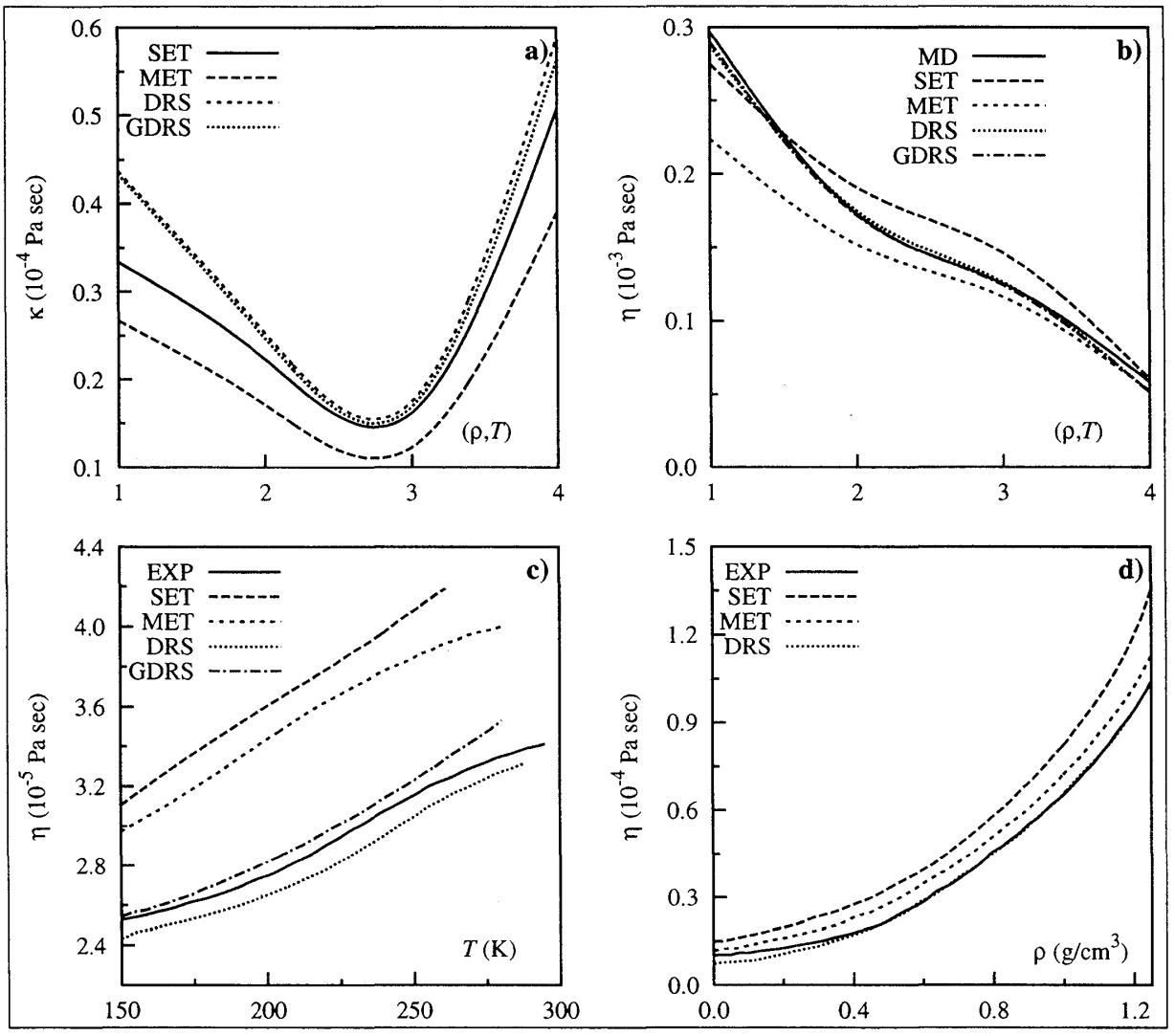

FIG. 2. Transport coefficients for Argon. a) bulk viscosity κ along the liquid-vapour curve. x-axis is in units of ρ(g/cm^3), namely: 1.4327, 1.4180, 1.1621 and 0.8017 for 1, 2, 3 and 4, respectively. b) shear viscosity η. x-axis is in units of (ρ(g/cm^3),T(K)), namely: $\rho_1 = 1.43$, $T_1 = 83.9$, $\rho_2 = 1.28$, $T_2 = 104.5$, $\rho_3 = 1.16$, $T_3 = 119.56$ and $\rho_4 = 0.802$, $T_4 = 147.1$. c) $\eta = \eta(T)$ at $\rho = \rho_{cr}$; d) $\eta = \eta(\rho)$ at $T = 139.7$ K. Experimental data plotted in c) and d) are taken from [15].

マルチステップ型ポテンシャル法による稠密な気体と流体の運動論的方程式

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我々が最近提唱したマルチステップ型ポテンシャル系の運動論的方程式の解析を行う。このポテンシャルは、硬い球面部分、引力壁、及び、斥力壁で構成されている。このようなモデルは、今までにあった多数の稠密な気体と流体に関する半経験論的な理論を統一したものである。マルチステップ型ポテンシャルのある特徴的なパラメータに対して得られた結果を用いると、標準的なチャップマン・エンスコッグ法による従来の運動論的方程式を再構成することができる。過去にアルゴンについて実験と分子動力学的計算シミュレーションが行われている。そこでは、密度や温度をパラメータとしたときの様々な輸送係数が求められている。我々の理論は、この結果を最もよく再現している。