RELAXATION OF SPATIALLY UNIFORM DISTRIBUTION FUNCTION IN THE CASE OF NON-UNIFORM ENERGY DISTRIBUTION

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PACS 51.10.+y, 05.20.Dd,
05.20.Gg

Relaxation processes in a model system are studied with the use of a kinetic equation. In a first approximation with respect to the concentration, an expression for the temperature as a function of the time has been derived in the spatially uniform case and for the Maxwell distribution function with a non-uniform energy distribution over the rotational and translational degrees of freedom. The relaxation time is shown to decrease, as the difference between the initial and equilibrium values of average translational kinetic energy diminishes and the equilibrium temperature grows. The time of the average translational (rotational) energy relaxation to the equilibrium value is found to be reciprocal to the square root of the equilibrium temperature and to the particle concentration. For the intrinsic moment of inertia, which is equal to the moment of inertia of a spherical particle with certain effective radius, the relaxation time is minimal. Relaxation times for some parameters of particles in the system concerned are calculated.

1. Introduction

Plenty of theoretical researches dealing with non-equilibrium processes in rarefied systems have been made since L. Boltzmann had written down his kinetic equation for the first time. The calculations of transport coefficients, which are based on a certain model describing the particle interaction in the medium, comprise the main task of kinetic theory. However, this task does not exhaust the role of kinetic theory. Its mathematical apparatus developed for calculating the transfer and relaxation coefficients in the case of rarefied gases allows the limits for the application of non-equilibrium thermodynamics to be established in the case of arbitrary physical media. For instance, the techniques for solving of Boltzmann kinetic equation have been well developed for a weakly rarefied one-atomic gas, when the mean free path is much shorter than the characteristic size of the problem. In particular, these are the Chapman–Enskog [1] and Grad [2] methods, which formed a basis for the substantiation of non-equilibrium thermodynamics in both its classical variant [3] and various generalizations [4–6].

In the last decades, the development of the kinetic theory of molecular gases gave rise to the appearance of an approach based on the generalized Boltzmann kinetic equation [7–9]. In this equation, the conventional Boltzmann integral is modified to describe a system of particles, in which the energy is distributed at collisions of particles not only over the translational degrees of freedom, but also over the rotational ones. In the framework of this approach, the system of gas-dynamic equations, the expressions for the entropy flux, and so forth are written down.

The development of models capable of an adequate and, simultaneously, simpler description of transport processes in a molecular gas at the qualitative level is a challenging task, which has a pure theoretical value and is important for the explanation of features experimentally observed in the course of non-equilibrium processes. In particular, an extremely important role in engineering is played by the processes of heat transfer in a gas and the processes of gas relaxation to the equilibrium state (for example, see work [10]). For instance, while calculating the thermal regimes of flying vehicles, aircraft turbines, rockets, and so on, the efficiency of energy exchange between gas layers and between gas molecules and a solid surface is dealt with. In the general case, the mechanism of heat transfer in gases is rather complicated. However, from the microscopic viewpoint, the main problem consists in the description of molecular scattering at collisions of molecules with the surface and with one another at a distance of their mean free path from the surface (see, e.g., work [11]). As the experience shows, the classical description of a system under study is sufficient in many cases for the qualitative analysis. For this purpose, some rather idealized models can be used.

Relaxation processes in gases can be described in terms of the energy exchange at molecular collisions. In particular, in work [12], the symmetry of the mechanical energy of a model system with respect to the action of a projection operator on the two-body state vector was used to determine the physical mechanism of translational and angular momenta exchange at collisions of perfectly rigid rough balls (the classical model for the collision of two perfectly rigid rough balls from the viewpoint of the kinematics of intrinsic angular and translational momenta was proposed by Bryan as early as in 1894 (see, e.g., works [1, 9])). The described method allows a relation between the phases of two model molecules before and after the collision to be found without characterizing the interaction between particles with the use of a potential.

In works [13–16], a system with a fixed number of particles and a model mechanism of exchange of translational and angular momenta between hard rough balls at their collision [12] were considered. On the basis of the dynamics of localized (delta-function-like) distributions of such particles in the phase space, it was demonstrated that the kinetic (macroscopic) equation for this system, when being considered in the Bogolyubov splitting approximation in the nine-dimensional phase space, has the form of the Boltzmann–Enskog equation, which was derived earlier in a more phenomenological style in work [1] and considered in the hydrodynamic approximation in work [9]. The obtained equation was proved to have a solution in the form of the microscopic phase density. Hence, in the case of the approximation of binary collisions, the equation obtained precisely describes the evolution of a dynamical model system.

Here, we note that the dynamics of a localized distribution of such particles interacting by a certain rule [12] in the phase space allows the corresponding evolution equation to be constructed (see work [15]), the structure of which is similar to that of the Liouville equation. The equation obtained can be used to construct a hierarchical chain of Bogolyubov equations, similarly to what was done, e.g., for the distribution functions dependent on the position and the spatial orientation of long molecules in liquid crystals (see work [17]).

In this work, we prove that, for the model system concerned [12], the kinetic equation for the averaged angular momentum (or rotational momentum) has an analytical solution in the spatially uniform case with a Maxwell-like distribution function, when the energy is distributed non-uniformly over the degrees of freedom. The obtained solution is used calculate the relaxation time to the state of thermodynamic equilibrium.

The Maxwell-like distribution as a tool to describe the behavior of a system near its equilibrium state was first proposed by L.D. Landau in work [18] while considering the problem of temperature equalization in a two-component plasma. Under definite conditions (see works [18, 19]), this method allows the relaxation in the two-component plasma to be described rather successfully. However, as can be demonstrated on the basis of the Chapman–Enskog approach generalized in work [19] and used there for the consideration of a two-component plasma, “the traditional idea about a universal role of the Maxwell distribution in the description of quasi-equilibrium states is not confirmed” (cited from work [19]). Moreover, as was revealed in work [20], if the Chapman–Enskog method (see work [1]) is used, the time-independent quasiequilibrium states of a two-temperature plasma, generally speaking, are not “pure” Maxwell ones. It is worth noting here that the exact analytical solution, which is obtained in our work, proves that the initial excitation given in the form of a Maxwell-like distribution function with different translational and rotational “temperatures” and with the preservation of this form in time can guarantee that the system will return into a state with identical energy distributions over the degrees of freedom. However, the issue concerning the preservation of this Maxwell-like form in time for the considered case of the collision integral (see works [13, 15]) requires further researches. A probable much smaller order of magnitude for quasiequilibrium corrections in the problem dealt with in work [19] testifies in favor of the model distribution adopted here even in the case considered in work [21], when there exists an energy (particle) source with low enough intensity. More general relaxation properties (such as, e.g., a periodic energy transfer between rotational and translational degrees of freedom) can probably be obtained within the method developed in work [19]. We should also note that the examined Maxwell shape of the initial distribution with different translational and rotational “temperatures” can be physically substantiated owing to the possibility of a “superquick” excitation of the rotational motion of molecules by an electromagnetic pulse (for instance, a strong enough pulse in the far infra-red region can be used during the collision time interval, when a dipole moment of non-polar molecules arises) and to a relatively small number of “excited” molecules in comparison with the molecules that “still” remain in the local equilibrium state (it is generally adopted and is observed in rotational and vibrational molecular spectra).

The presented theoretical study of the “relaxation” kinetics of a model system can be applied, for example, to the description of a sufficiently rarefied system of nonpolar molecules. The results obtained are actual for the modern branch of researches, where the rarefied systems of rather heavy molecules and nanoparticles are studied (e.g., see work [22]). The regularities observed in the course of non-equilibrium processes, which run in such systems, differ substantially from those that take place in an ordinary one-atomic gas [8, 10].

2. Relaxation of a Distribution Function of the Maxwell Type

Consider a closed, spatially uniform system near its equilibrium state. Let us study the dependence of the average energy of translational molecule motion on the time in the case where the initial average energies of translational and rotational motions are different (see work [16]). For this purpose, let us obtain the time derivative of the average translational energy,

$$\frac{d}{dt}\langle P^2\rangle = \frac{d}{dt}\int f(\boldsymbol{X},t)P^2 d\boldsymbol{X} =$$

$$= \int P^2 \frac{d}{dt} f(\boldsymbol{X},t)d\boldsymbol{X} = \int I_B(\boldsymbol{X},t)P^2 d\boldsymbol{X}, \qquad (1)$$

where $f(\boldsymbol{X},t)$ is the distribution function, I_B is the collision integral, $\frac{d}{dt}f(\boldsymbol{X},t) = I_B(\boldsymbol{X},t)$ in the case of a spatially uniform system, and $\boldsymbol{X} = \left(\frac{\boldsymbol{p}}{\sqrt{m}}, \frac{\boldsymbol{M}}{\sqrt{J}}\right) = (\boldsymbol{P}, \boldsymbol{M})$. Here, $\boldsymbol{p}$ and $\boldsymbol{M}$ are the phase translational momentum and the intrinsic phase rotational momentum, respectively. For the closed system,

$$\frac{d}{dt}\left(\langle \boldsymbol{P}^2\rangle + \langle \boldsymbol{M}^2\rangle\right) = 0. \qquad (2)$$

Therefore,

$$\frac{d}{dt}\langle \boldsymbol{P}^2\rangle = -\frac{d}{dt}\langle \boldsymbol{M}^2\rangle. \qquad (3)$$

Then, by substituting the expression for $I_B(\boldsymbol{X},t)$ in the form introduced in work [15] into Eq. (1), we obtain

$$\frac{d}{dt}\langle P^2\rangle = -\frac{a^2}{\sqrt{m}}n\times$$

$$\times\int\Bigg(\int\limits_{(\boldsymbol{P}'-\boldsymbol{P})\boldsymbol{\sigma}\geq 0}(\boldsymbol{P}'-\boldsymbol{P})\boldsymbol{\sigma}\left\{\hat{b}(\boldsymbol{\sigma})-1\right\}\times$$

$$\times f(\boldsymbol{X}',t)f(\boldsymbol{X},t)d\boldsymbol{\sigma}d\boldsymbol{X}'\Bigg)\boldsymbol{M}^2 d\boldsymbol{X}, \qquad (4)$$

where n is the concentration. The action of the operator $\hat{b}(\boldsymbol{\sigma})$ is governed by the mechanism of scattering of two perfectly rough hard balls at their collision [12],

$$\hat{b}(\boldsymbol{\sigma})\cdot f(t,\boldsymbol{X})f(t,\boldsymbol{X}') = f(t,\boldsymbol{X}^*)f(t,\boldsymbol{X}'^*),$$

where the phases before and after the collision are connected according to the rule

$$\begin{aligned}
&\boldsymbol{P}^* = \frac{1}{1+\varkappa}\Big[\varkappa\boldsymbol{P} + \boldsymbol{P}' + \sqrt{\varkappa}[\Big(\boldsymbol{M}+\boldsymbol{M}'\Big)\times\boldsymbol{\sigma}]-\\
&-\varkappa\boldsymbol{\sigma}\{(\boldsymbol{P}-\boldsymbol{P}')\boldsymbol{\sigma}\}\Big],\\
&\boldsymbol{M}^* = \frac{1}{1+\varkappa}\Big[\boldsymbol{M} - \varkappa\boldsymbol{M}' + \sqrt{\varkappa}[\boldsymbol{\sigma}\times\Big(\boldsymbol{P}-\boldsymbol{P}'\Big)]+\\
&+\varkappa\boldsymbol{\sigma}\{(\boldsymbol{M}+\boldsymbol{M}')\boldsymbol{\sigma}\}\Big],\\
&\boldsymbol{P}'^* = \frac{1}{1+\varkappa}\Big[\varkappa\boldsymbol{P}' + \boldsymbol{P} - \sqrt{\varkappa}[\Big(\boldsymbol{M}+\boldsymbol{M}'\Big)\times\boldsymbol{\sigma}]+\\
&+\varkappa\boldsymbol{\sigma}\{(\boldsymbol{P}-\boldsymbol{P}')\boldsymbol{\sigma}\}\Big],\\
&\boldsymbol{M}'^* = \frac{1}{1+\varkappa}\Big[\boldsymbol{M}' - \varkappa\boldsymbol{M} + \sqrt{\varkappa}[\boldsymbol{\sigma}\times\Big(\boldsymbol{P}-\boldsymbol{P}'\Big)]+\\
&+\varkappa\boldsymbol{\sigma}\{(\boldsymbol{M}+\boldsymbol{M}')\boldsymbol{\sigma}\}\Big].
\end{aligned} \qquad (5)$$

Here, the unit vector is directed from the center of the ball with the phase $\boldsymbol{X}$ toward the center of the ball with the phase $\boldsymbol{X}'$, and $d\boldsymbol{\sigma}$ is an infinitesimally small element of the solid angle.

Let $f(t,\boldsymbol{X})$ look like

$$f(\boldsymbol{X},t) = \frac{1}{(T_1T_2)^{3/2}\pi^3}e^{-\frac{\boldsymbol{P}^2}{T_1}-\frac{\boldsymbol{M}^2}{T_2}}, \qquad (6)$$

where, for convenience, the doubled Boltzmann constant is equal to 1 (or the temperature is reckoned in corresponding units). According to the first equation,

$$\frac{3}{2}T_1(t) = \langle \boldsymbol{P}^2\rangle, \frac{3}{2}T_2(t) = \langle \boldsymbol{M}^2\rangle,$$

which corresponds to three translational and three rotational degrees of freedom. Note that the quantities T_1 and T_2 stand for the average translational and rotational, respectively, components of the total mechanical energy of the system. Strictly speaking, they cannot be considered as thermodynamic parameters. Then, for the temperature (in the sense given above) that corresponds to translational degrees of freedom, we obtain the equation

$$\frac{3}{2}\frac{d}{dt}T_1(t) = -\frac{a^2}{\sqrt{m}}\left(\frac{1}{(T_1T_2)^{3/2}\pi^3}\right)^2 n\int \boldsymbol{M}^2\times$$

$$\times\Bigg(\int\limits_{(\boldsymbol{P}'-\boldsymbol{P})\boldsymbol{\sigma}\geq 0}(\boldsymbol{P}^{'}-\boldsymbol{P})\boldsymbol{\sigma}\Bigg\{e^{-\frac{\boldsymbol{P}^{*2}+\boldsymbol{P}^{'*2}}{T_1}}e^{-\frac{\boldsymbol{M}^{*2}+\boldsymbol{M}^{'*2}}{T_2}}-$$

$$-e^{-\frac{\boldsymbol{P}^{2}+\boldsymbol{P}^{'2}}{T_1}}e^{-\frac{\boldsymbol{M}^{2}+\boldsymbol{M}^{'2}}{T_2}}\Bigg\}d\boldsymbol{\sigma}d\boldsymbol{P}^{'}d\boldsymbol{M}^{'}\Bigg)d\boldsymbol{P}d\boldsymbol{M}. \tag{7}$$

Let us change the order of integration and make the variable transformations

$$\frac{3}{2}\frac{d}{dt}T_1(t)=-\frac{a^2}{\sqrt{m}}\left(\frac{1}{(T_1T_2)^{3/2}\pi^3}\right)^2 n\times$$

$$\times\int\Bigg(\int\limits_{(\boldsymbol{P}'-\boldsymbol{P})\boldsymbol{\sigma}\geq 0}(\boldsymbol{P}^{'}-\boldsymbol{P})\boldsymbol{\sigma}\left\{\boldsymbol{M}^{*2}(-\boldsymbol{\sigma})-\boldsymbol{M}^2\right\}\times$$

$$\times e^{-\frac{\boldsymbol{P}^{2}+\boldsymbol{P}^{'2}}{T_1(t)}}e^{-\frac{\boldsymbol{M}^{2}+\boldsymbol{M}^{'2}}{T_2(t)}}d\boldsymbol{P}^{'}d\boldsymbol{M}^{'}d\boldsymbol{P}d\boldsymbol{M}\Bigg)d\boldsymbol{\sigma}, \tag{8}$$

where $\boldsymbol{M}^{*2}(-\boldsymbol{\sigma})$ is expressed by means of relations that describe the model system of rigid rough balls in the case of the specular reflection (5) of the two-particle phase at collisions; here, the notation $(-\boldsymbol{\sigma})$ means only the functional dependence on the unit vector direction.

Let us calculate the integral on the right-hand side of the expression

$$\mathfrak{I}=\int\Bigg(\int\limits_{(\boldsymbol{P}'-\boldsymbol{P})\boldsymbol{\sigma}\geq 0}(\boldsymbol{P}^{'}-\boldsymbol{P})\boldsymbol{\sigma}\left\{\boldsymbol{M}^{*2}(-\boldsymbol{\sigma})-\boldsymbol{M}^2\right\}\times$$

$$\times e^{-\frac{\boldsymbol{P}^{2}+\boldsymbol{P}^{'2}}{T_1}}e^{-\frac{\boldsymbol{M}^{2}+\boldsymbol{M}^{'2}}{T_2}}d\boldsymbol{P}^{'}d\boldsymbol{M}^{'}d\boldsymbol{P}d\boldsymbol{M}\Bigg)d\boldsymbol{\sigma}=$$

$$=\int\Bigg(\int\limits_{(\boldsymbol{P}'-\boldsymbol{P})\boldsymbol{\sigma}\geq 0}(\boldsymbol{P}^{'}-\boldsymbol{P})\boldsymbol{\sigma}\,e^{-\frac{\boldsymbol{P}^{2}+\boldsymbol{P}^{'2}}{T_1}}e^{-\frac{\boldsymbol{M}^{2}+\boldsymbol{M}^{'2}}{T_2}}\times$$

$$\times\left\{\frac{1}{(1+\varkappa)^2}\Big\{\boldsymbol{M}-\varkappa\boldsymbol{M}^{'}+\sqrt{\varkappa}[-\boldsymbol{\sigma},\boldsymbol{P}-\boldsymbol{P}^{'}]+\right.$$

$$\left.+\varkappa\boldsymbol{\sigma}\left(\boldsymbol{\sigma}(\boldsymbol{M}+\boldsymbol{M}^{'})\right)\Big\}^2-\boldsymbol{M}^2\right\}d\boldsymbol{P}^{'}d\boldsymbol{M}^{'}d\boldsymbol{P}d\boldsymbol{M}\Bigg)d\boldsymbol{\sigma}. \tag{9}$$

Here, the bracketed comma, $[\ldots,\ldots]$, denotes the vector product. After changing to a new Cartesian coordinate system $(\boldsymbol{\xi},\boldsymbol{\eta},\boldsymbol{\sigma})$, in which the axis OZ is parallel to $\boldsymbol{\sigma}$, the integral $\mathfrak{I}$ reads

$$\frac{1}{(1+\varkappa)^2}\int\Bigg(\int\limits_{(\boldsymbol{P}'-\boldsymbol{P})\boldsymbol{\sigma}\geq 0}d\boldsymbol{P}^{'}d\boldsymbol{M}^{'}d\boldsymbol{P}d\boldsymbol{M}\,\left(P_\sigma^{'}-P_\sigma\right)\times$$

$$\times e^{-\frac{P_\sigma^2+P_\xi^2+P_\eta^2+P_\sigma^{'2}+P_\xi^{'2}+P_\eta^{'2}}{T_1}}e^{-\frac{M_\sigma^2+M_\xi^2+M_\eta^2+M_\sigma^{'2}+M_\xi^{'2}+M_\eta^{'2}}{T_2}}\times$$

$$\times\Big\{-(\varkappa^2+2\varkappa)(M_\xi^2+M_\eta^2)+\varkappa^2(M_\xi^{'2}+M_\eta^{'2})-$$

$$-2\varkappa(M_\xi^{'}M_\xi+M_\eta^{'}M_\eta)+2\sqrt{\varkappa}(M_\eta-kM_\eta^{'})(P_\xi-P_\xi^{'})+$$

$$+2\sqrt{\varkappa}(kM_\xi^{'}-M_\xi)(P_\eta-P_\eta^{'})+\varkappa(P_\xi-P_\xi^{'})^2+$$

$$+\varkappa(P_\eta-P_\eta^{'})^2\Big\}\Bigg)d\boldsymbol{\sigma}, \tag{10}$$

where the differential $d\boldsymbol{P}=dP_\sigma dP_\xi dP_\eta$, and so on. Since the exponent power is an even function, and the integration is carried out over the whole phase space, the integrals of terms in the braces with odd powers of the integration variables equal zero. In addition, the integrals of similar terms in the braces with opposite signs mutually compensate each other. Then the latter formula can be rewritten in the form

$$\mathfrak{I}=\frac{1}{(1+\varkappa)^2}\int\Bigg(\int\limits_{(\boldsymbol{P}'-\boldsymbol{P})\boldsymbol{\sigma}\geq 0}(P_\sigma^{'}-P_\sigma)\times$$

$$\times e^{-\frac{P_\sigma^2+P_\xi^2+P_\eta^2+P_\sigma^{'2}+P_\xi^{'2}+P_\eta^{'2}}{T_1}}e^{-\frac{M_\sigma^2+M_\xi^2+M_\eta^2+M_\sigma^{'2}+M_\xi^{'2}+M_\eta^{'2}}{T_2}}\times$$

$$\times\Big\{-2\varkappa(M_\xi^2+M_\eta^2)-2\varkappa(M_\xi^{'}M_\xi+M_\eta^{'}M_\eta)+$$

$$+\varkappa(P_\xi-P_\xi^{'})^2+\varkappa(P_\eta-P_\eta^{'})^2\Big\}d\boldsymbol{P}^{'}d\boldsymbol{M}^{'}d\boldsymbol{P}d\boldsymbol{M}\Bigg)d\boldsymbol{\sigma}. \tag{11}$$

Let us introduce new variables $(\widetilde{\boldsymbol{P}},\widetilde{\boldsymbol{M}})=\left(\dfrac{\boldsymbol{P}}{\sqrt{T_1}},\dfrac{\boldsymbol{M}}{\sqrt{T_2}}\right)$. Then, with regard for the equality of the integration variables P_ξ, P_η and $P_\xi^{'}$, $P_\eta^{'}$ (it becomes evident if one removes the parenthesis), the integral $\mathfrak{I}$ looks, in terms of new notations, as

$$\mathfrak{I}=-\frac{2\varkappa}{(1+\varkappa)^2}T_1^{7/2}T_2^3\int\Bigg(\int\limits_{\widetilde{P}_\sigma^{'}-\widetilde{P}_\sigma\geq 0}(\widetilde{P}_\sigma^{'}-\widetilde{P}_\sigma)\times$$

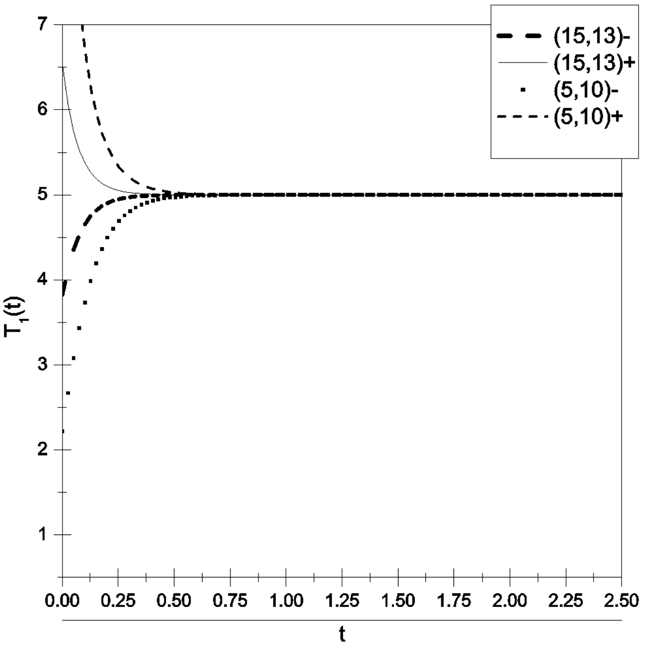

Fig. 1. Time dependences of the average translational energy. Different signs correspond to different relations: $T_1 < T$ (+) and $T_1 > T$ (−). The numbers in the parentheses denote the parameters $(c, T_1^{1/2}\nu)$ in relative units

$$\times\, e^{-(\widetilde{P}^2+\widetilde{P}'^2+\widetilde{M}^2+\widetilde{M}'^2)}\Big\{T_2(\widetilde{M}_\xi^2+\widetilde{M}_\eta^2)-$$

$$-T_1(\widetilde{P}_\xi^2+\widetilde{P}_\eta^2)\Big\}d\widetilde{\boldsymbol{P}'}\,d\widetilde{\boldsymbol{M}'}\,d\widetilde{\boldsymbol{P}}d\widetilde{\boldsymbol{M}}\Big)d\boldsymbol{\sigma}=$$

$$=-\frac{2\varkappa}{(1+\varkappa)^2}\,T_1^{7/2}\,T_2^3\,\{T_2-T_1\}\cdot\widetilde{\Im}, \tag{12}$$

where

$$\widetilde{\Im}=2\int\Big(\int\limits_{\widetilde{P}'_\sigma-\widetilde{P}_\sigma\geq 0}(\widetilde{P}'_\sigma-\widetilde{P}_\sigma)e^{-(\widetilde{P}^2+\widetilde{P}'^2+\widetilde{M}^2+\widetilde{M}'^2)}\times$$

$$\times\widetilde{P}_\xi^2\,d\widetilde{\boldsymbol{P}'}\,d\widetilde{\boldsymbol{M}'}\,d\widetilde{\boldsymbol{P}}d\widetilde{\boldsymbol{M}}\Big)d\boldsymbol{\sigma}. \tag{13}$$

From the relation $3T = \frac{3}{2}(T_1+T_2) = \text{const}$, it follows that $T_2 = 2T - T_1$, and the evolution equation for the temperature reads

$$\frac{3}{2}\frac{d}{dt}T_1 = 2\frac{a^2}{\sqrt{m}}\,n\,\frac{1}{\pi^6}\,\frac{2\varkappa}{(1+\varkappa)^2}\,T_1^{1/2}\,(T-T_1)\cdot\widetilde{\Im}. \tag{14}$$

After the separation of variables, the obtained equation can be solved in quadratures,

$$\int\limits_{T_1(0)}^{T_1(t)}\frac{dT_1}{T_1^{1/2}\,(T-T_1)} = \int\limits_0^t \nu dt, \tag{15}$$

where

$$\nu = \frac{4}{3}\frac{a^2}{\sqrt{m}}\,n\,\frac{1}{\pi^6}\,\frac{2\varkappa}{(1+\varkappa)^2}\cdot\widetilde{\Im}. \tag{16}$$

By integrating equality (15), we obtain

$$\ln\left(\left|\frac{\sqrt{T}+\sqrt{T_1(t)}}{\sqrt{T}-\sqrt{T_1(t)}}\right|\cdot\left|\frac{\sqrt{T}-\sqrt{T_1(0)}}{\sqrt{T}+\sqrt{T_1(0)}}\right|\right) = \sqrt{T}\,\nu\,t. \tag{17}$$

Whence, the ultimate expressions for the average translational energy are

$$T_1(t) = T\frac{\left(c-e^{-\sqrt{T}\,\nu\,t}\right)^2}{\left(c+e^{-\sqrt{T}\,\nu\,t}\right)^2},\quad \text{for}\quad T_1(0) < T; \tag{18}$$

$$T_1(t) = T\frac{\left(c+e^{-\sqrt{T}\,\nu\,t}\right)^2}{\left(c-e^{-\sqrt{T}\,\nu\,t}\right)^2},\quad \text{for}\quad T_1(0) > T, \tag{19}$$

where

$$c = \left|\frac{\sqrt{T}+\sqrt{T_1(0)}}{\sqrt{T}-\sqrt{T_1(0)}}\right|. \tag{20}$$

To visualize the result obtained and to make its analysis simpler, let us illustrate the time dependence of the temperature for various c- and $\sqrt{T}\nu$-values (see Fig. 1). The figure allows us to draw conclusion that the relaxation time for the average translational energy T_1 to its equilibrium value *NEGT* decreases as the quantities c and $\sqrt{T}\nu$ grow. Accordingly, the relaxation time increases with the simultaneous reduction of ν and c.

2.1. Relaxation Time

Let us consider the expression for the time dependence of the average translational energy and examine the kinetic parameter of this process, the relaxation time. According to the condition $T \cong T_1$, we have the approximate equality

$$\ln\left|\frac{\sqrt{T}-\sqrt{T_1(0)}}{\sqrt{T}-\sqrt{T_1(t)}}\right| \cong \sqrt{T}\,\nu\,t. \tag{21}$$

The relaxation time $\tau = \dfrac{1}{\sqrt{T}\,\nu}$ can be determined from the condition $\left|\dfrac{\sqrt{T}-\sqrt{T_1(0)}}{\sqrt{T}-\sqrt{T_1(t)}}\right| = e$, which gives rise to the result

$$\tau = \frac{3\pi^6\sqrt{m}(1+\varkappa)^2}{8\widetilde{\Im}\sqrt{T}\,a^2\,n\,\varkappa} \tag{22}$$

or

$$\tau = \frac{3\pi^6(ma^2+4J)^2}{32\widetilde{\Im}\sqrt{T}\,\sqrt{m}a^4\,n\,J}, \tag{23}$$

where J is the intrinsic momentum of inertia of the molecule.

In Fig. 2, the dependence of the relaxation time on the parameter $\varkappa$ is depicted. The minimum value of τ is attained at $\varkappa = 1$ or, equivalently, $J = \dfrac{ma^2}{4}$. In other words, we have a single extremum of the function $\tau(J)$ for the intrinsic momentum of inertia that is equal to the momentum of inertia of a spherical particle. In addition, the relaxation time is reciprocal to the square root of the equilibrium temperature and to the particle concentration.

Let us take into account that the approximate value for the mean free path of particles equals $L = \dfrac{1}{\pi n a^2}$, and the average velocity of thermal motion is $\vartheta = \sqrt{\dfrac{3RT}{\mu}}$. Then, using the integral value $\widetilde{\Im} = 2\sqrt{2}\pi^{13/2}$, expression (22) looks like

$$\tau = \frac{3\sqrt{\pi}}{32}\frac{L}{\vartheta}\frac{(1+\varkappa)^2}{\varkappa}. \tag{24}$$

In Table 1, the relaxation times for some parameters of particles of the system are quoted. For the given temperature and concentration, the ratio between the relaxation times in a system of balls, $\tau_\bullet$, and a system of spheres, $\tau_\circ$, approximately equals 1.23. A system of heavy spherical particles with a molar mass of 0.72 kg/mol can correspond to a system of fullerene molecules C_{60}. While calculating the relaxation time, we supposed the mean free path to be approximately equal to 10^{-5}–10^{-4} m, which corresponds to the change in the concentration by an order of magnitude, provided the given diameter of particles (about 10^{-8} m).

T a b l e. Relaxation times

μ, g/mol	L/a	T, K	$\varkappa$	mol. type	τ, s
16	10^3	300	1	sphere	1.70×10^{-8}
16	10^3	300	2.5	ball	2.10×10^{-8}
720	10^3	300	1	sphere	1.15×10^{-7}
720	10^3	300	2.5	ball	1.41×10^{-7}
720	10^4	300	2.5	ball	1.41×10^{-6}
16	10^4	300	10	ball with a heavy core	4.30×10^{-7}
720	10^4	300	10	ball with a heavy core	2.99×10^{-6}

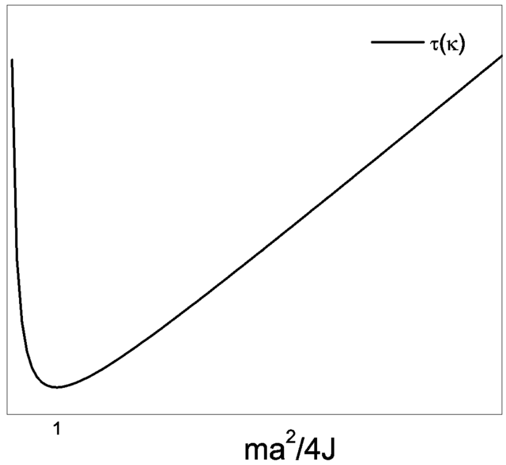

Fig. 2. Dependence of the relaxation time τ on the parameter $\varkappa = \dfrac{ma^2}{4J}$

In the expression for the relaxation time in the system under study, we can factorize a multiplier that characterizes the relaxation time in a one-atomic gas, $\widetilde{\tau}$. Since the relaxation time for a one-atomic gas has an order of the ratio between the mean free path and the average velocity, Eq. (24) can be presented in the form

$$\tau = \frac{3\sqrt{\pi}}{32}\frac{(1+\varkappa)^2}{\varkappa}\widetilde{\tau}. \tag{25}$$

The formula testifies that, provided the same values for the mean free paths and the mean quadratic velocities, the ratio between the relaxation times for the process concerned in the case $\varkappa = 1$ and in the one-atomic gas is approximately equal to 0.66.

3. Conclusions

To summarize, a model system has been studied in the spatially uniform case. In the first approximation with respect to the concentration, an analytical expression for the temperature as a function of time has been obtained in the case of a non-uniform initial energy distribution over the degrees of freedom. The corresponding kinetic equations for the “translational” and “rotational” temperatures (considered as the averaged translational or rotational, respectively, momentum) with the Maxwell-like distribution function and with a non-uniform initial distribution of energy ocer the degrees of freedom are shown to have analytical solutions.

It is found that a reduction of the difference between the initial average translational (rotational) energy and the equilibrium one, as well as the growth of the equilibrium temperature, results in a decrease of the relaxation time. The time of the average translational (rotational) energy relaxation to the equilibrium value is shown to be reciprocal to the square root of the equilibrium temperature and to the particle concentration. For the intrinsic momentum of inertia, which equals the momentum of inertia of a spherical particle with certain effective radius, the relaxation time attains the minimum value.

For the given temperature and concentration, the ratio between the characteristic relaxation times for a system of rough balls, $\tau_\bullet$, and a system of rough spheres, $\tau_\circ$, equals 1.23, i.e. exceeds 1.

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Received 15.03.12.
Translated from Ukrainian by O.I. Voitenko

РЕЛАКСАЦІЯ ПРОСТОРОВО ОДНОРІДНОЇ ФУНКЦІЇ РОЗПОДІЛУ ЗА УМОВИ НЕОДНОРІДНОГО РОЗПОДІЛУ ЕНЕРГІЇ

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Резюме

У роботі досліджено релаксацію модельної системи з використанням кінетичного рівняння. У просторово однорідному випадку, а також максвеллівської функції розподілу з неоднорідним розподілом енергії за ступенями вільності (обертальними і поступальними), у першому наближенні за концентрацією знайдено вираз для температури як функції часу. Показано, що із зменшенням різниці між початковим та рівноважним значеннями середньої поступальної енергії і зростанням рівноважної температури час релаксації зменшується. Знайдено, що час релаксації середньої поступальної (обертальної) енергії до рівноважного значення обернено пропорційний кореню квадратному від рівноважної температури та обернено пропорційний концентрації частинок. Для власного моменту інерції, що дорівнює моменту інерції сферичної частинки із ефективним радіусом, значення часу релаксації набуває мінімального значення. Обчислено значення часу релаксації для окремих параметрів частинок системи.