Equilibrium distribution functions
of a homogeneous multicomponent gas mixture;
inequality of partial temperatures

Yurii M. Loskutov
Physics Faculty, Moscow State University, Moscow 119899 Russia

Abstract

It is shown that the partial temperatures of a homogeneous multicomponent gas mixture in the thermodynamical equilibrium cannot be equal to each other. New general solutions for equilibrium distribution functions of the multicomponent mixture are found. Parameters (including partial temperatures) involved in these solutions are determined by means of physical conditions which follow from a notion of the stable thermodynamical equilibrium. The found relations of the partial temperatures to the mean mixture temperature are dependent on the molecular weights and concentrations of the components. Some possible consequences of the developed approach are discussed.
1 General remarks

There is a considerable body of work on the study of the distribution functions and kinetic equations (see, e.g., [1]–[12] – this list is quite incomplete). However up to the present a certain question is overlooked. As shown below, this question is of fundamental importance because it qualitatively changes traditional view on the thermodynamical equilibrium state.

Imagine that we observe collisions of molecules in a mixture of free gases (i.e. gases that are subject to no external field) in the state of thermodynamical equilibrium. Then the first thing we should notice is that for every time interval $\Delta t_0$, which equals the mean free time, the number of collisions of particles with velocities $\mathbf{v}_1 \cdot \mathbf{v}_2 < 0$ (I-type collisions) will exceed the number of collisions of particles with velocities $\mathbf{v}_1 \cdot \mathbf{v}_2 > 0$ (II-type collisions). This is a direct consequence of the well-known inequality of probabilities of I-type and II-type collisions. If the mixture consists of two components then the above considerations can be applied to collisions of similar (i.e., of equal masses) molecules as well as to collisions of different ones. Therefore the case of equal mean kinetic energies of molecules of ”light” and ”heavy” components cannot correspond to the thermodynamical equilibrium state (in equilibrium $U = \text{const}$ where $U$ is the internal energy). Indeed, it is well known from classical mechanics that in I-type collisions of particles with equal kinetic energies light particles gain energy while heavy ones lose it. In the case of II-type collisions the picture is the opposite. So, as the probabilities of I-type collisions exceed the probabilities of II-type ones, the equality of mean kinetic energies of light and heavy molecules cannot be maintained: the light component will increase its energy to some extent while the heavy component energy will decrease respectively. The energy transfer from the heavy particles to the light ones will stop when the mean energy of molecules of the ”light” component exceeds at a certain value the mean energy of the ”heavy” component. Now in every time interval $\Delta t_0$ the mean collision-induced change $\overline{\Delta T}_\alpha$ of kinetic energy of molecules of the two

$^1$In principle, this statement holds not only for binary collisions.
components (α = 1 and α = 2) becomes zero. Obviously it is this state which should be called equilibrium.

Notice that if the mean energy change is determined with respect to a time interval \( dt \) smoothed over many collisions we wouldn’t be able to follow the process of energy redistribution at a ”discrete” level of individual collisions. In other words, the condition \( \overline{dT_\alpha}/dt = 0 \) generally would not allow to estimate the ratio of the mean kinetic energies of molecules of one and the other kind at the equilibrium state. This means that the condition \( \overline{dT_\alpha}/dt = 0 \) corresponds in general to a whole set of solutions for distribution functions (see Section 2 below). Unlike this, the condition \( \Delta T_\alpha = 0 \) would imply the state of thermodynamical equilibrium with no energy redistribution between the components, so this condition corresponds to well-defined distribution functions (see Section 2 below). It is these functions that lead to an inequality of mean kinetic energies \( T_\alpha \) of different kind molecules at the equilibrium state.

This conclusion means that the representation of binary distribution function as a product of the one-particle (Maxwell-type) functions would contradict the necessary condition of absence of energy redistribution between the components at the equilibrium state. To show this, consider the BBGKI-type equations restricted to the case of binary collisions:

\[
\frac{df_i}{dt} + (v_i \cdot \nabla_i)f_i = \sum_k n_k \int \frac{\partial \Phi_{ik}(|r_k - r_i|)}{\partial r_i} \frac{\partial F_{ik}}{\partial p_i} d^3 x_k d^3 p_k,
\]

\[
\frac{\partial F_{ik}}{\partial t} + (v_i \cdot \nabla_i)F_{ik} + (v_k \cdot \nabla_k)F_{ik} - \frac{\partial \Phi_{ik}(|r_k - r_i|)}{\partial r_i} \frac{\partial F_{ik}}{\partial p_i} - \frac{\partial \Phi_{ik}(|r_k - r_i|)}{\partial r_k} \frac{\partial F_{ik}}{\partial p_k} = 0,
\]

where all the notations are standard. In view of the conditions imposed, the derivative \( \partial F_{ik}/\partial t \) in equations (2) can be ignored. Then after an integration over \( x_k, p_k \) one obtains

\[
\int \frac{\partial \Phi_{ik}}{\partial r_i} \frac{\partial F_{ik}}{\partial p_i} d^3 x_k d^3 p_k = \int (v_k - v_i) \frac{\partial F_{ik}}{\partial r_{ik}} d^3 x_{ik} d^3 p_{ik},
\]

where \( r_{ik} = r_k - r_i \). Applying now the common (see, e.g., [9, 10, 12]) procedure of integration with respect to \( x_{ik} \) and letting\[ ^2 \]

\[
F_{ik}|_{|r_{ik}| \to \infty} \rightarrow F_{ik}(t, p_i, p_k),
\]

\[ ^2 \text{The notation (3) merely symbolises optionality of factorizing binary functions in single ones in transition to collision integrals with the use of unitary operators which } \text{”move aside” } \text{the events at } |r_{ik}| \rightarrow \infty \text{ to the states before and after scattering.} \]
one puts the equations (1) in the form

\[
\frac{\partial f_1}{\partial t} = n_1 \int d^3 \tilde{v}_1 \, d\sigma_{11} \, u_{11} [F'_{11}(v'_1, \tilde{v}'_1, t) - F_{11}(v_1, \tilde{v}_1, t)] + \\
+ n_2 \int d^3 v_2 \, d\sigma_{12} \, u_{12} [F'_{12}(v'_1, v'_2, t) - F_{12}(v_1, v_2, t)],
\]

(4)

\[
\frac{\partial f_2}{\partial t} = n_2 \int d^3 \tilde{v}_2 \, d\sigma_{22} \, u_{22} [F'_{22}(v'_2, \tilde{v}'_2, t) - F_{22}(v_2, \tilde{v}_2, t)] + \\
+ n_1 \int d^3 v_1 \, d\sigma_{21} \, u_{21} [F'_{21}(v'_2, v'_1, t) - F_{21}(v_2, v_1, t)].
\]

Here \( u_{11} \equiv |v_1 - \tilde{v}_1|, \ u_{22} \equiv |v_2 - \tilde{v}_2|, \ u_{12} = u_{21} \equiv |v_2 - v_1|, \) \( d\sigma_{ik} \) are the differential scattering cross-sections of \((i, k)\) molecules, and the primed symbols correspond to the state after scattering; besides that, a transition from integrals over momentum space to integrals over a space of velocities was made for later convenience.

In carrying out the limit (3) a hypothesis of correlation moderation principle is usually used, that is the limiting function \( F_{ik} \) is reduced to a product of the one-particle functions

\[
F_{ik}(t, p_i, p_k) = f_i(t, p_i) f_k(t, p_k).
\]

(3a)

Thus the system (4) becomes closed with respect to single functions, its solutions in the case of thermodynamical equilibrium being Maxwell distributions

\[
f_i = A_i \exp(-m_i v_i^2 / 2\theta)
\]

(5)

with one parameter \( \theta \) which determines the temperature of the mixture.

In the equations (4) there appear probabilities \( dw_{ik} = n_k u_{ik} d\sigma_{ik} \) of collision and scattering of particles per unit time. If one replaces these probabilities by probabilities of single collision between particles with velocities \( v_i, v_k \) per unit volume

\[
dw_{ik} \equiv n_{ik} dw_{ik} / n_k \sigma_{ik} \int u_{ik} \, d\Omega = \\
= \frac{3n_{ik} d\sigma_{ik}}{2\pi \sigma_{ik}} \frac{v_i v_k |v_k - v_i|}{|v_k + v_i|^3 - |v_k - v_i|^3}
\]

(6)

following from the expression for \( dw_{ik} \) \((n_{ik} \) being a number of such collisions per unit volume), then the corresponding collision integrals in (4) will give the changes of one-particle functions under single collisions per unit volume. Replacement of \( dw_{ik} \) by \( dw_{ik} \)
in (4) together with substitution of $\Delta f_i$ instead of $\partial f_i/\partial t$ will have no effect on the distribution functions in the thermodynamical equilibrium state. As for conditions of absence of energy redistribution between the components, they will acquire the form

$$
\Delta T_1 = \int d^3v_1\,d^3\tilde{v}_1\,dw_{11}\,F_{11}\Delta T_1 + \int d^3v_1\,d^3v_2\,dw_{12}\,F_{12}\Delta T_1 = 0. \tag{7}
$$

The increment $\Delta T_1 \equiv T'_1 - T_1$ caused by a collision of molecules with masses $m_1$ and $m_2$ is determined by

$$
T'_1 - T_1 = \mu(\mathbf{u} \cdot \mathbf{v}) - \mu(\mathbf{u}' \cdot \mathbf{v}), \tag{8}
$$

where $\mu \equiv m_1m_2/m$, $m \equiv m_1 + m_2$, $\mathbf{u} \equiv \mathbf{v}_2 - \mathbf{v}_1$, $\mathbf{u}' \equiv \mathbf{v}'_2 - \mathbf{v}'_1$, $\mathbf{v} \equiv (m_1\mathbf{v}_1 + m_2\mathbf{v}_2)/m$.

Substituting in (7) the expressions (8) and (3a) with account for (5) it is easy to see that the first integral in (7) vanishes while the second, which is connected with collisions of molecules of different masses, remains nonzero. This means that the solutions of the form (3a) based on correlation moderation principle do not satisfy the condition of absence of energy redistribution between light and heavy components. Therefore solutions (3a) with the only parameter $\theta$ should be replaced by more general solutions depending not only on the energy but also on other integrals of motion, that is solutions with a large number of parameters.

As such, a possibility of introducing of various integrals of motion into solutions of the kinetic equations doesn’t contradict anything and is very natural because a Liouville equation for the distribution function of a system of $N$ particles can in principle include $6N$ integrals of motion. Still the question remains how does this agree with the Gibbs distribution which is deduced from rather general considerations? It should be noted here that the Gibbs canonical distribution is obtained under the assumption (guaranteed for systems of a very large number of particles) that boundaries contribute only an ignorable part of interaction energy of neighbouring regions. It will be shown in the following sections that the general solution for equilibrium distribution functions involves terms much smaller than the boundary ones inevitably arising in the tradi-

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3To find the mean collision-induced change $\Delta T_\alpha$, we should take the difference $\Delta T_\alpha = T'_\alpha - T_\alpha$ multiply it by the probability of collision and scattering $dw_{ik}$ and after this to sum over all finite states and average (by means of $F_2$) over all initial states. The second condition $\Delta T_2 = 0$ will be a consequence of the first one in the case of a two-component mixture.
tional derivation of the Gibbs distribution. If one ignores them the general solution will transform into the Gibbs distribution with all the corresponding implications. On the contrary, if one takes them into account in transition to the single and binary distribution functions, these small terms will give a contribution comparable with that of the energy integral.

Thus the above considerations imply that in general the equilibrium distribution functions should depend on several integrals of motion, which involve several free parameters. These parameters are determined by the following physical conditions:

1. The one-particle equilibrium distribution functions of molecules of some kind derived from different binary or many-particle distribution functions should be identical.

2. In order for the state of thermodynamical equilibrium to be stable one should require that the energy density be minimal in this state.

3. One should require that the average changes of kinetic energy of molecules per unit volume caused by one-particle collisions be equal to zero to guarantee an absence of energy redistribution between the components.

It will be shown below that these conditions lead to uniquely determined expressions for equilibrium distribution functions.

2 General solutions of kinetic equations for distribution functions of a homogeneous two-component mixture of free gases in thermodynamical equilibrium

Let the system consist of a homogeneous mixture of $N_1$ molecules with mass $m_1$ and $N_2$ molecules with mass $m_2$. Then, as is well known, the equations (1), (2) will be

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4Strictly speaking, they are neglected in deriving the Gibbs distribution as well, because the densities introduced there are searched for as functions of a energy integral, other integrals of motion (e.g., momentum) being ignored.

5In the problem in question this condition is equivalent to that of minimality of free energy, as the state of thermodynamical equilibrium with constant number of particles and constant entropy $S$ and temperature $\theta$, characterizing the whole of gas mixture, is considered.
satisfied at the state of thermodynamical equilibrium by arbitrary functions of two variables (separated by semicolon)

\[ F_{ik} = F_{ik} \left( \mu_{ik} \left( \frac{p_1}{m_1} - \frac{p_2}{m_2} \right)^2 ; \left( \frac{p_1}{m_1} + \frac{p_2}{m_2} \right) \right). \]  

(9)

In order for one-particle distribution functions obtained from the binary ones to have the form of Maxwell-type distributions the two-parameter solutions (9) should be an exponential of quadratic combinations of momenta. Thus, the general solution \( F_{12} \) should have the form

\[ F_{12} = A_{12} \exp \left\{ -C_1 \mu_{12} \left( \frac{p_1}{m_1} - \frac{p_2}{m_2} \right)^2 - C_2 \left( \frac{p_1}{m_1} + \frac{p_2}{m_2} \right)^2 \right\}, \]

where \( p_1 \) and \( p_2 \) denote momenta of particles with masses \( m_1 \) and \( m_2 \), respectively. In what follows it will be more convenient to introduce two parameters \( \theta_{12} \) and \( \lambda \) instead of two constants of integration \( C_1 \) and \( C_2 \), so that

\[ C_1 \equiv (1 - \lambda) / 2\theta_{12}, \quad C_2 \equiv (1 + \lambda) / 2m\theta_{12}. \]

Dealing with \( F_{11} \) and \( F_{22} \) in a similar way, we obtain

\[ F_{11} = A_{11} \exp \left\{ -\frac{1}{2(1 + \lambda_0)} \frac{1}{\theta_1 m_1} \left[ \left( \frac{p_1}{m_1} \right)^2 + \left( \frac{p_2}{m_2} \right)^2 + \frac{\lambda_0}{1 - \lambda_0} \left( \frac{p_1}{m_1} + \frac{p_2}{m_2} \right)^2 \right] \right\}, \]

\[ F_{22} = A_{22} \exp \left\{ -\frac{1}{2(1 + \lambda_0)} \frac{1}{\theta_2 m_2} \left[ \left( \frac{p_1}{m_1} \right)^2 + \left( \frac{p_2}{m_2} \right)^2 + \frac{\lambda_0}{1 - \lambda_0} \left( \frac{p_1}{m_1} + \frac{p_2}{m_2} \right)^2 \right] \right\}, \]

\[ F_{12} = A_{12} \exp \left\{ -\frac{1 - \lambda}{2\theta_1 \theta_2 m_1 m_2} \left[ \frac{m_1}{m} \left( \frac{p_1}{m_1} \right)^2 + \frac{m_2}{m} \left( \frac{p_2}{m_2} \right)^2 + \frac{2\lambda}{1 - \lambda} \left( \frac{p_1}{m_1} + \frac{p_2}{m_2} \right)^2 \right] \right\}. \]

(10)

Here the superscripts (1), (2) of the momenta \( p_i \) refer to the molecular species \((m_1, m_2)\), \( \lambda = \lambda(\varepsilon) \), \( \varepsilon \equiv (m_2 - m_1)/(m_2 + m_1) \), and \( \lambda_0 \equiv \lambda(0) \). The parameter \( \lambda \) describes the degree of correlation of particle momenta in equilibrium. It is easy to see that the conditions \( dT_\alpha / dt = 0 \) corresponding to (7) under substitution of \( dw_{ik} \) instead of \( dw_{ik} \) are satisfied by a family of equilibrium solutions (10) with arbitrary \( \lambda_0 \) and \( \lambda \), as was stated in Section 1. If one assumes \( \lambda = \lambda_0 = 0 \) in (10), functions \( F_{ik} \) will factorize and partial temperatures \( \theta_1 \) and \( \theta_2 \) will become equal to each other by virtue of the

\[ \varepsilon \text{In [13] the solutions for distribution functions of similar molecules are taken with the parameter } \lambda_0 = 0. \text{ Such solutions satisfy the system of equations (1), (2) as well. It would be more consistent, however, to consider } \lambda_0 \text{ as the limit of } \lambda(\varepsilon) \text{ as } \varepsilon \to 0, \text{ where } \varepsilon \equiv (m_2 - m_1)/m. \]
condition 1 of Section 1. This is in contradiction to the condition 3 of Section 1. Hence particular solutions with \( \lambda(\varepsilon) = 0 \) cannot correspond to thermodynamical equilibrium, i.e. more general solutions with \( \lambda(\varepsilon) \neq 0 \) should be taken as equilibrium ones.

The solutions (10) also arise from a many-particle distribution function \( F \) satisfying the stationarity condition on every interval \( \Delta t_0 \). It has the form

\[
F = A \exp \left\{ -\frac{1}{2 (1 + \lambda_0) \theta_1 m_1} \left[ \sum_{i_1=1}^{N_1^{(11)}} P_{i_1}^{(1)} \frac{\lambda_0 P_{i_1}^{2}}{1 - (N_1^{(11)} - 1) \lambda_0} \right] - \frac{1}{2 (1 + \lambda_0) \theta_2 m_2} \left[ \sum_{i_2=1}^{N_2^{(22)}} P_{i_2}^{(2)} \frac{\lambda_0 P_{i_2}^{2}}{1 - (N_2^{(22)} - 1) \lambda_0} \right] - \frac{1 - \lambda}{2 \theta_{12} m} \left[ \frac{m}{m_1} \sum_{i_3=1}^{N_1^{(12)}} P_{i_3}^{(1)} + \frac{m}{m_2} \sum_{i_3=1}^{N_2^{(12)}} P_{i_3}^{(2)} + \frac{2 \lambda P_{i_3}^{(12)}}{1 - (N_1^{(12)} + N_2^{(12)} - 1) \lambda + \left( N_1^{(12)} - N_2^{(12)} \right) \varepsilon \lambda} \right] \right\},
\]

(11)

where

\[
P_{\alpha}^{(11)} = \sum_{i_1=1}^{N_1^{(11)}} P_{i_1}, \quad P_{\alpha}^{(22)} = \sum_{i_2=1}^{N_2^{(22)}} P_{i_2}, \quad P_{\alpha}^{(12)} = \sum_{i_3=1}^{N_1^{(12)}} P_{i_3} + \sum_{i_3=1}^{N_2^{(12)}} P_{i_3},
\]

indices \( i_1, i_2, \) and \( i_3 \) label the molecules corresponding to collisions \((m_1, m_1), (m_2, m_2), \) and \((m_1, m_2)\), while \( N_1^{(11)} \), \( N_2^{(22)} \) and \( N_1^{(12)}, N_2^{(12)} \) are the numbers of molecules of the two kinds in the associated groups, the relations \( N_1^{(11)} + N_1^{(12)} = N_1, \ N_2^{(22)} + N_2^{(12)} = N_2 \) being satisfied.

In the case of a large number of molecules the terms in (11) with \( N_{\alpha}^{(\alpha\beta)} \) in the denominator will be small compared to the others, since, due to the chaotic nature of molecular motion, the momenta \( P_{\alpha}^{(\alpha\beta)} \) cannot exceed the momenta \( P_\alpha \) by a significant amount. If one neglects these terms then by virtue of relations

\[
\frac{1}{(1 + \lambda_0) \theta_1} = \frac{1 - \lambda}{\theta_{12}} = \frac{1}{(1 + \lambda_0) \theta_2} = \frac{1}{\theta_0},
\]

following from the indistinguishability of molecules of the same kind, one obtains the Gibbs distribution with the unique temperature \( \theta_0 \) and all corresponding implications.

\[\text{7The reference frame is chosen so that the mean momentum of molecules of the mixture is equal to zero.}\]
for binary and single distribution functions. Unlike this, if one takes these terms into account when deriving single and binary distribution functions then their final contribution will turn out to be comparable with that of other terms. Indeed, it can be easily verified that each integration over one of the momenta $(\alpha) p$ is equivalent to decreasing of the corresponding $N_{\alpha}^{(\alpha,\beta)}$ in (11) by unit. Therefore the solutions (10) correspond to the solutions (11) with $N_{1}^{(11)} = 2$, $N_{2}^{(22)} = 2$, and $N_{1}^{(12)} = N_{2}^{(12)} = 1$, the other $N_{\alpha}^{(\alpha,\beta)}$ being equal to zero.

We can find solution (10) by another way. Let us introduce a new value $\tilde{H} \equiv \log F_{12}$ and find its mean change (but not the change of the mean) in a unit of time which takes place by collision and scattering. To make this it is necessary to take the difference in $\tilde{H}$ before and after collision (i.e. $\tilde{H}' - \tilde{H}$) multiply this difference by the probability of collision and scattering in a unit time (i.e. by $n_{12} u_{12} d\sigma_{12}$) and after this to integrate over all finite states and average over initial (i.e. by means of $F_{12}$ before scattering) states. Then

$$\frac{d\tilde{H}}{dt} = n_{12} \int (\log F_{12}' - \log F_{12}) F_{12} d\sigma_{12} d^3 p_1 d^3 p_2 d^3 x_1 d^3 x_2 =$$

$$= -\frac{n_{12}}{2} \int (F_{12}' - F_{12}) \log \frac{F_{12}'}{F_{12}} d\sigma_{12} d^3 p_1 d^3 p_2 d^3 x_1 d^3 x_2 .$$

From this expression one can easily find that

$$\frac{d\tilde{H}}{dt} \leq 0 .$$

The equality is achieved if $\log F_{12}' = \log F_{12}$. Thus, $\log F_{2}$ is the additive integrals of the motion of two bodies that is described by (10).

In accordance with the condition 1 of Section 1, imposing a requirement of the identity of one-particle distribution functions derived from $F_{ii}$ and $F_{ik}$, that is demanding that

$$f_1 = \int F_{11} d^3 \tilde{P}_2 = \int F_{12} d^3 \tilde{P}_1 = A_1 \exp \left\{ - \frac{(1) p_1}{2 m_1 \theta_1} \right\} ,$$

$$f_2 = \int F_{22} d^3 \tilde{P}_2 = \int F_{12} d^3 \tilde{P}_1 = A_2 \exp \left\{ - \frac{(2) p_1}{2 m_2 \theta_2} \right\} ,$$

one obtains the relations between the parameters:

$$\theta_1 = \frac{\theta_{12} + \varepsilon \lambda}{1 - \varepsilon \lambda}, \quad \theta_2 = \frac{\theta_{12} - \varepsilon \lambda}{1 - \varepsilon \lambda}. \quad (12)$$

8These relations could also be obtained from (11) if one lets $N_{1}^{(11)} = 1$ or $N_{1}^{(12)} = 1$ and $N_{2}^{(22)} = 1$ or $N_{2}^{(12)} = 1$, the other $N_{\alpha}^{(\alpha,\beta)}$ being equal to zero.
To establish a relation between the temperatures $\theta_1$, $\theta_2$, and $\theta_{12}$ and the mean temperature of the mixture $\theta$ we make use the condition of minimality of the energy density $E$ of the system in thermodynamical equilibrium formulated at the end of Section 1: $\partial E(\lambda)/\partial \lambda = 0$, where $E(\lambda) = n_1 \theta_1 + n_2 \theta_2$, $\theta_1$ and $\theta_2$ being determined by (12). This implies

$$\theta_{12} = C \frac{1 - \lambda^2}{n + (n_1 - n_2) \varepsilon \lambda},$$

where $n = n_1 + n_2$. The constant $C = n_1 \theta_1 + n_2 \theta_2$, which equals to the mean kinetic energy density of the mixture, may be set also as $n\theta$. Thus one finds

$$\theta_{12} = \frac{(1 - \lambda^2) n\theta}{n + (n_1 - n_2) \varepsilon \lambda},$$

(13)

$$\theta_1 = \frac{(1 + \varepsilon \lambda) n\theta}{n + (n_1 - n_2) \varepsilon \lambda}, \quad \theta_2 = \frac{(1 - \varepsilon \lambda) n\theta}{n + (n_1 - n_2) \varepsilon \lambda}.$$

We can obtain expressions (13) from (12) if we require that the mean temperature of the mixture ($\theta$) will be determined by the formula $\theta = (n_1/n)\theta_1 + (n_2/n)\theta_2$ that with the physical point of view is quite clear.

A remarkable thing here is the dependence of partial equilibrium temperatures $\theta_1$ and $\theta_2$ on molecular weights and concentrations of the components. If due to some reasons the molecular mixture splits into a set of subsystems with an substantial domination of molecules of some sort in each of them (with $n_2 \gg n_1$ in some subsystems and $n_1 \gg n_2$ in others) then the partial temperatures $\theta_1$ and $\theta_2$ of subsystems will practically become equal — see (13). This effect is due to the fact that collisions of molecules of different types which account for inequality of $\theta_1$ and $\theta_2$ will occur only in the vicinity of boundaries of subsystems. In view of the above the heat transfer from a cold body to a hot one becomes impossible.

Finally, we establish a relation between $\lambda$ and $\varepsilon$ making use of the third condition formulated at the end of Section 1, namely that of absence of the energy redistribution between molecules of the mixture under collisions in thermodynamical equilibrium. Taking into account in (7) that the integral containing $F_{11}$ is identically zero, one obtains the equation

$$\int d^3v_1 d^3v_2 (T'_1 - T_1) F_{12} dw_{12} = 0,$$

(7a)
where $T'_1 - T_1$ is defined in (8). After integration over scattering angles and one of the velocities it can be cast into the form

$$
\int_{-\infty}^{\infty} dx \frac{x^2|1+x|^3}{|1+x|^3 - |1-x|^3} \int_0^{1} dy \frac{y^2 x^2 - 1 + \varepsilon y^2 (1+x)^2}{(x^2 - 2bxy^2 + a^2)^4} = 0, \quad (14)
$$

where

$$a^2 \equiv (1 - \varepsilon)(1 - \varepsilon \lambda)/(1 + \varepsilon)(1 + \varepsilon \lambda), \quad b \equiv \lambda(1 - \varepsilon)/(1 + \varepsilon \lambda).$$

Integration in (14) can be carried out only with respect to one variable. Thus the dependence of $\lambda$ on $\varepsilon$ is to be evaluated by numerical methods. The corresponding algorithm turns out to be simpler if both integrations are left in (14). The numerical values of $\lambda$ corresponding to different values of $\varepsilon$ are represented in Table 1 (1.000e-03 means $1.000 \cdot 10^{-3}$ and so forth). Figure 1 shows the dependence graphically. As indicated there, the value of $\lambda$ is positive for all $\varepsilon$ and tends to zero as $\varepsilon \to 1$ which is clear from qualitative considerations: as $\varepsilon \to 1$ the probabilities of I-type and II-type collisions tend to be equal together with $\theta_1$ and $\theta_2$. Shown in figure 2 is the dependence of $\varepsilon \lambda$ on $\varepsilon$ corresponding to the ratio of partial equilibrium temperatures $\theta_1$ and $\theta_2$. It demonstrates that the maximal difference of temperatures of light ($\theta_1$) and heavy ($\theta_2$) components is achieved at molecular weight ratio $m_2/m_1 \simeq 4.26$ and amounts to 15.5% of $\theta_2$. Far from this point the difference $\theta_1 - \theta_2$ smoothly decreases and tends to zero as $\varepsilon \to 0$ and $\varepsilon \to 1$.

### 3 General solutions for equilibrium distribution functions in the case of multicomponent mixture

For a multicomponent mixture which formed by molecules with masses $m_1 \leq m_2 \leq \ldots \leq m_s$, the binary distribution functions in thermodynamical equilibrium expressed in terms of velocities will be in conformity with (10):

$$F_{\alpha\alpha} = (1 - \lambda_0^2)^{-3/2} \frac{m_{\alpha}}{2\pi\theta_{\alpha}} \exp \left\{ -\frac{m_{\alpha}}{2(1 - \lambda_0^2)\theta_{\alpha}} \left[ \frac{\nu_{\alpha}^2}{V_1} + \frac{\nu_{\alpha}^2}{V_2} + 2\lambda_0 \frac{\nu_{\alpha}^2}{V_1} \cdot \nu_{\alpha}^2 \right] \right\},$$

\footnote{The proof of equality of mean kinetic energies of different molecules suggested in [14] cannot be true because it is overlooked there that the change $\Delta T_1$ is not a kinetic value but is determined instead by a dynamical collision process which has a stochastic character not taken into account in [14].}

\footnote{In [13] there was an error in the numerical algorithm found already after the publication. The corrected results were published later [15].}
\[ F_{\alpha\beta} = \frac{[(1 - \lambda^{2}_{\alpha\beta}) m_{\alpha} m_{\beta}]^{3/2}}{(2\pi\theta_{\alpha\beta})^{3}} \exp \left\{ -\frac{m_{\alpha\beta}}{4\theta_{\alpha\beta}} \left[ (1 - \varepsilon_{\alpha\beta})(1 - \varepsilon_{\alpha\beta}\lambda_{\alpha\beta}) \mathbf{V}_{1}^{2} + (1 + \varepsilon_{\alpha\beta})(1 + \varepsilon_{\alpha\beta}\lambda_{\alpha\beta}) \mathbf{V}_{1}^{2} + 2\lambda_{\alpha\beta}(1 - \varepsilon_{\alpha\beta}^{2}) \mathbf{V}_{1} \cdot \mathbf{V}_{2} \right] \right\}, \]  

(15)

Here \( m_{\alpha\beta} \equiv m_{\alpha} + m_{\beta} \), \( \varepsilon_{\alpha\beta} = -\varepsilon_{\beta\alpha} \equiv (m_{\beta} - m_{\alpha})/m_{\alpha\beta} \), and the dependent quantities \( m_{\alpha\beta} \) and \( \varepsilon_{\alpha\beta} \) are related to the independent ones \( m_{1\alpha} \) and \( \varepsilon_{1\alpha} \) as

\[ m_{\alpha\beta} = m_{1\alpha} + \varepsilon_{1\beta} m_{1\beta}, \quad \varepsilon_{\alpha\beta} = (\varepsilon_{1\beta} - \varepsilon_{1\alpha})/(1 - \varepsilon_{1\alpha}\varepsilon_{1\beta}). \]  

(16)

Functions (15) can be obtained from the many-particle distribution function

\[ F = A \exp \left\{ -\frac{1}{2(1 + \lambda_{0})} \sum_{\alpha_{1}}^{s} \frac{1}{m_{\alpha}} \left[ \sum_{i=1}^{N_{\alpha}^{(\alpha\alpha)}} (\alpha_{i})^{2} P_{i}^{\alpha} + \sum_{\beta} \frac{\lambda_{0}P_{(\alpha\alpha)}^{2}}{1 - (N_{\alpha}^{(\alpha\alpha)} - 1) \lambda_{0}} \right] - \sum_{\beta > \alpha = 1}^{s} \frac{1 - \lambda_{\alpha\beta}}{2\theta_{\alpha\beta}m_{\alpha\beta}} \left[ \sum_{i=1}^{N_{\alpha}^{(\alpha\beta)}} (\alpha_{i})^{2} P_{i}^{\alpha} + \frac{\lambda_{\alpha\beta}}{m_{\alpha} m_{\beta}} \sum_{i=1}^{N_{\alpha}^{(\alpha)} N_{\beta}^{(\alpha\beta)}} (\beta_{i})^{2} P_{i}^{\beta} + \frac{2\lambda_{\alpha\beta}P_{(\alpha\beta)}^{2}}{1 - (N_{\alpha}^{(\alpha\beta)} + N_{\beta}^{(\alpha\beta)} - 1) \lambda_{\alpha\beta} + (N_{\alpha}^{(\alpha\beta)} - N_{\beta}^{(\alpha\beta)}) \varepsilon_{\alpha\beta}\lambda_{\alpha\beta}} \right] \right\}, \]  

(17)

where

\[ P_{(\alpha\alpha)}^{\alpha} \equiv \sum_{i=1}^{N_{\alpha}^{(\alpha\alpha)}} P_{i}^{\alpha}, \quad P_{(\alpha\beta)}^{\alpha} \equiv \sum_{i=1}^{N_{\alpha}^{(\alpha\beta)}} P_{i}^{\alpha} + \sum_{i=1}^{N_{\beta}^{(\alpha\beta)}} P_{i}^{\beta}, \]

and \( N_{\alpha}^{(\alpha\beta)} \) is a number of molecules with mass \( m_{\alpha} \) taking part in \( (m_{\alpha}, m_{\beta}) \)-collisions. If in the case of large numbers of molecules of different kinds one ignores in (17) the terms with \( N_{\alpha}^{(\alpha\beta)} \) in denominator then as in Section 2 one obtains the Gibbs distribution with the single temperature common for all components.

Integration of (17) over one of the momenta \( P_{i}^{\alpha} \) is equivalent to reducing the corresponding \( N_{\alpha}^{(\alpha\beta)} \) in \( F \) by unit, so (15) corresponds to (17) with \( N_{\alpha}^{(\alpha\alpha)} = 2 \) and \( N_{\alpha}^{(\alpha\beta)} = N_{\beta}^{(\alpha\beta)} = 1 \). The condition of coincidence of one-particle functions obtained from different binary ones gives the equalities

\[ \theta_{\alpha} = \theta_{\alpha\beta} \frac{1 + \varepsilon_{\alpha\beta}\lambda_{\alpha\beta}}{1 - \lambda^{2}_{\alpha\beta}}, \quad \theta_{\beta} = \theta_{\alpha\beta} \frac{1 - \varepsilon_{\alpha\beta}\lambda_{\alpha\beta}}{1 - \lambda^{2}_{\alpha\beta}}. \]

With the aid of these relations the dependent \( \lambda_{\alpha\beta} \) are expressed in terms of the independent ones:

\[ \varepsilon_{\alpha\beta}\lambda_{\alpha\beta} = \frac{\varepsilon_{1\beta}\lambda_{1\beta} - \varepsilon_{1\alpha}\lambda_{1\alpha}}{1 - \varepsilon_{1\alpha}\varepsilon_{1\beta}\lambda_{1\alpha}\lambda_{1\beta}}, \]
\[
\lambda_{\alpha\beta} |_{\alpha \neq \beta} = \lambda_{\beta\alpha} |_{\alpha \neq \beta} = \frac{(\varepsilon_{1\beta} \lambda_{1\beta} - \varepsilon_{1\alpha} \lambda_{1\alpha})(1 - \varepsilon_{1\alpha} \varepsilon_{1\beta})}{(1 - \varepsilon_{1\alpha} \varepsilon_{1\beta} \lambda_{1\alpha} \lambda_{1\beta})(\varepsilon_{1\beta} - \varepsilon_{1\alpha})}.
\]

Making use of condition of minimality of energy density of the mixture we obtain
\[
\theta_{\alpha\beta} = n \theta \frac{(1 - \lambda^2_{\alpha\beta})(1 - \varepsilon_{1\alpha} \varepsilon_{1\beta} \lambda_{1\alpha} \lambda_{1\beta})}{(1 + \varepsilon_{1\alpha} \lambda_{1\alpha})(1 + \varepsilon_{1\beta} \lambda_{1\beta})} \left[ \sum_{\nu=1}^{s} n_{\nu} \frac{1 - \varepsilon_{1\nu} \lambda_{1\nu}}{1 + \varepsilon_{1\nu} \lambda_{1\nu}} \right]^{-1},
\]
\[
\theta_{\alpha} = n \theta \frac{1 - \varepsilon_{1\alpha} \lambda_{1\alpha}}{1 + \varepsilon_{1\alpha} \lambda_{1\alpha}} \left[ \sum_{\beta=1}^{s} n_{\beta} \frac{1 - \varepsilon_{1\beta} \lambda_{1\beta}}{1 + \varepsilon_{1\beta} \lambda_{1\beta}} \right]^{-1},
\]
where \( n = n_1 + n_2 + \ldots + n_s \) and \( \theta \) is the mean temperature of the mixture. Independent parameters \( \lambda_{1\alpha} \) will be determined by the condition of absence of energy redistribution between the components:
\[
\sum_{\beta=1}^{s} n_{\alpha\beta} \frac{(1 - \varepsilon_{1\alpha} \varepsilon_{1\beta} \lambda_{1\alpha} \lambda_{1\beta})[(1 - \varepsilon_{1\beta}^2)(1 - \lambda_{1\beta}^2)]^{5/2}}{(1 + \varepsilon_{1\alpha} \lambda_{1\alpha})(1 + \varepsilon_{1\beta} \lambda_{1\beta})} \int_{-\infty}^{\infty} dx \frac{x^2 |1 + x|^3}{|1 + x|^3 - |1 - x|^3}.
\]
\[
\int_{0}^{1} dy \frac{y^2 [x^2 - 1 + \varepsilon_{\alpha\beta} y^2 (1 + x)^2]}{[(1 + \varepsilon_{\alpha\beta})(1 + \varepsilon_{\alpha\beta} \lambda_{\alpha\beta})x^2 - 2 \lambda_{\alpha\beta}(1 - \varepsilon_{\alpha\beta}^2)xy^2 + (1 - \varepsilon_{\alpha\beta})(1 - \varepsilon_{\alpha\beta} \lambda_{\alpha\beta})]^4} = 0.
\]

Here \( n_{\alpha\beta} \) are given by the number of single binary collisions per unit volume of molecules with masses \( m_{\alpha} \) and \( m_{\beta} \). In solving the system of equations (20) it is necessary to take into account the equations (16), (18) expressing the dependent quantities \( \varepsilon_{\alpha\beta} \) and \( \lambda_{\alpha\beta} \) in terms of the independent ones. It is instructive to note also that the terms in (20) with \( \beta = \alpha \) are identically zero — this is easy to see changing the variable \( x \rightarrow 1/x \).

The system (20) is too complicated for a general investigation. We are thus led to restrict ourselves to the analysis of the two-component mixture carried out in Section 2 which still gives some information about the main thermodynamical characteristics of the mixture in more general case.

### 4 Conclusion

The general solution for distribution functions of a homogeneous multicomponent mixture of free gases in thermodynamic equilibrium found above predicts different partial temperatures of different components. The ratios of partial temperatures to the mean
temperature of the mixture depend on molecular weights and concentrations of the components — see (13), (19). The effect of inequality of partial temperatures is caused by the inequality of the collision probabilities for particles with velocities $v_1 v_2 < 0$ and $v_1 v_2 > 0$ — see (6). In the case of two-component mixture the maximal difference of partial temperatures occurs at the ratio of molecular weights $m_2/m_1 \simeq 4.26$ and achieves approximately 15.5% of minimal temperature. As the ratio increases or decreases this difference decreases; the character of decrease can be judged from figure 2 taking into account (13). Given a homogeneous mixture of He and Ne atoms with equal concentrations, at the mean temperature of mixture $\theta \sim 300^\circ$K partial temperatures turn out to be $\theta_{He} \sim 321^\circ$K and $\theta_{Ne} \sim 279^\circ$K which may well be verified experimentally.

In the case of multicomponent mixture the parameters $\lambda_{\alpha\beta}$ affecting the values of partial temperatures depend not only on molecular weights but also on concentrations of the components — see (20); the lightest component temperature still exceeds the temperature of other components and the mean temperature — see (19).

The effect of inequality of partial temperatures disappears if the mixture due to some reasons splits into separate regions with domination of specific component in every region — see (19); all temperatures in such an event are practically equal to the mean temperature of the whole system.

If different regions of the large system are filled with molecules of different kinds and separated from each other by small potential barriers (let us call such regions "cells") then under certain conditions an interchange of light molecules not determined by the statistical dispersion of velocities can appear between the "cells". Indeed, as the lightest component temperature exceeds the mean temperature of the "cell", this surplus maybe sufficient for getting over the barrier and penetrating into the other "cell". There these light molecules can enter into reactions with molecules of other kind resulting in particles lighter than the molecules which fill this "cell". Transferring to these particles higher temperature through collisions, this "cell" can push it out back in the first "cell" and so forth. Penetration of foreign admixtures ("viruses") in "cells" will cause redistribution of partial temperatures of its initial components. Heavier admixtures will bring up the mean temperature of molecules originally filling the "cell".
It is not improbable that in the case of multicomponent mixture, selecting molecular weights and concentrations of components it is possible to create a system with the property of enhanced conductivity at not very low temperatures. This issue is based upon solution of the system of equations (20) with simultaneous optimisation of the number of parameters (involving concentrations), so it is a very complicated problem. It is not clear also how stable the system constructed in such a way can be.

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Fig. 1. Graphical dependence $\lambda$ versus $\varepsilon$. 
Fig.2. Graphical dependence of $\varepsilon \lambda$ on $\varepsilon$ indirectly determining the ratio of partial temperatures.
Table 1. Numerical values of parameter $\lambda$ found from equation (14) for different $\varepsilon$.

| $\varepsilon$ | $\lambda$  |
|---------------|-------------|
| 1.00e-03     | 1.780e-01  |
| 1.00e-02     | 1.780e-01  |
| 2.00e-02     | 1.779e-01  |
| 3.00e-02     | 1.778e-01  |
| 4.00e-02     | 1.777e-01  |
| 6.00e-02     | 1.775e-01  |
| 7.00e-02     | 1.774e-01  |
| 8.00e-02     | 1.768e-01  |
| 9.00e-02     | 1.765e-01  |
| 1.00e-01     | 1.763e-01  |
| 1.10e-01     | 1.758e-01  |
| 1.20e-01     | 1.754e-01  |
| 1.30e-01     | 1.750e-01  |
| 1.40e-01     | 1.745e-01  |
| 1.50e-01     | 1.740e-01  |
| 1.60e-01     | 1.735e-01  |
| 1.70e-01     | 1.730e-01  |
| 1.80e-01     | 1.725e-01  |
| 1.90e-01     | 1.715e-01  |
| 2.00e-01     | 1.705e-01  |
| 2.10e-01     | 1.695e-01  |
| 2.20e-01     | 1.685e-01  |
| 2.30e-01     | 1.675e-01  |
| 2.40e-01     | 1.670e-01  |
| 2.50e-01     | 1.665e-01  |
| 2.60e-01     | 1.660e-01  |
| 2.70e-01     | 1.655e-01  |
| 2.80e-01     | 1.645e-01  |
| 2.90e-01     | 1.635e-01  |
| 3.00e-01     | 1.625e-01  |
| 3.10e-01     | 1.615e-01  |
| 3.20e-01     | 1.605e-01  |
| 3.30e-01     | 1.595e-01  |
| 3.40e-01     | 1.585e-01  |
| 3.50e-01     | 1.575e-01  |
| 3.60e-01     | 1.565e-01  |
| 3.70e-01     | 1.555e-01  |
| 3.80e-01     | 1.545e-01  |
| 3.90e-01     | 1.535e-01  |
| 4.00e-01     | 1.525e-01  |
| 4.10e-01     | 1.515e-01  |
| 4.20e-01     | 1.505e-01  |
| 4.30e-01     | 1.495e-01  |
| 4.40e-01     | 1.485e-01  |
| 4.50e-01     | 1.475e-01  |
| 4.60e-01     | 1.465e-01  |
| 4.70e-01     | 1.455e-01  |
| 4.80e-01     | 1.445e-01  |
| 4.90e-01     | 1.435e-01  |
| 5.00e-01     | 1.430e-01  |