Approach to equilibrium in a one-dimensional multicomponent gas of Maxwellian particles

Otto J. Eder and Maximilian Posch
Austrian Research Center Seibersdorf, A-2444 Seibersdorf, Austria
(Received 21 April 1986)

The system of coupled linearized Boltzmann equations for a multicomponent gas mixture of particles interacting via a Maxwellian-type potential is solved for the spatially homogeneous case. The αth component of the gas mixture is described by its concentration c_α, mass m_α, and the initial distribution of velocities $h_\alpha^0(v)$; the collisions with particles of species β are characterized by the interaction parameter $\sigma_{\alpha\beta}^0$. The eigenvalue spectrum of the linearized collision operator for arbitrary concentrations, masses, and interaction parameters is studied and the time-dependent velocity distribution function for each component is derived. As examples the binary and ternary systems are discussed briefly. The time-dependent velocity distribution function for a binary mixture is calculated for several mass ratios showing the development of two branches within the first few collisions. Furthermore the mass dependence of Boltzmann's H function is studied in detail. Finally we discuss the time dependence of the mean velocity and mean-square velocity for each species in a ternary mixture. While in a binary mixture these quantities vary monotonically in time, there are mass and concentration ratios in ternary systems, where one of the species—starting with less than its equilibrium share of energy—can acquire more energy than its equilibrium value for a limited period of time.

I. INTRODUCTION

We consider a spatially homogeneous, one-dimensional ν-component gas mixture consisting of quasi-Maxwellian point particles characterized by their concentrations c_α, masses m_α, initial velocity distributions $h_\alpha^0(v)$ and interaction parameters $\sigma_{\alpha\beta}^0$ $(\alpha,\beta=1,2,\ldots,\nu)$.

The level of our description is the system of collision-coupled linearized Boltzmann equations, where the form of the collision cross section takes care of the quasi-Maxwellian interaction between the particles. The problem is then to find the eigenvalue spectrum of the collision operator and to calculate the time-dependent deviation from the equilibrium velocity distribution function for each component subject to a given initial distribution.

Most investigations have been concerned either with tagged (single) particle motion in systems with equal masses or limiting cases in binary systems, where either the mass and/or the concentration of a tagged particle is considered to be much larger or much smaller than the corresponding quantity of the bath particles. The cases, where the interaction between the tagged particles can be neglected, lead to the linear transport equations, encountered, e.g., in the neutron-moderation process. The simple interactions between the particles considered are generally of the repulsive type, $V_{\alpha\beta}(r)=\sigma_{\alpha\beta}r^{-n}$, with the cases of hard-core $(n=\infty)$, Maxwellian $(n=4)$, and Coulomb $(n=1)$ interaction of special interest. Exact theoretical results, numerical simulations, and calculations from master equations help to understand this fundamental problem of classical statistical mechanics.

The case of one-dimensional single-particle motion of hard rods with equal masses was studied in great detail by several authors.[1–10] Far less work has been done for one-dimensional systems containing different masses.[11–14] For extremely rare and heavy particles[15–19] ($c_1\approx0$, $m_1\gg m_2$—Rayleigh piston problem) and rare but light particles[20,21] ($c_1\approx0$, $m_1\ll m_2$—Lorentz gas) the problem has been solved. In the former case $(m_1\gg m_2)$ the Boltzmann equation can be transformed into a Fokker-Planck equation with time-dependent coefficients for $m_1/m_2\to\infty$ or solved by the Ω-expansion method for large but finite mass ratios m_1/m_2. In the latter case $(m_1\ll m_2)$ the Boltzmann equation can be solved due to special properties of the scattering kernel. In either case it is the mass ratio which makes the problem amenable to treatment and the actual form of the interaction does not play a central role.

In general the transport equation is nonlinear and one is concerned with collision-correlated motion in low-density systems. One hopes—considering small deviations from equilibrium only—that the transport equation can be linearized and still produce physically meaningful results. The model we are going to treat in Sec. II is the one-dimensional spatially homogeneous multicomponent mixture. Furthermore we assume a simple quasi-Maxwellian interaction, which allows an analytical solution of the linearized Boltzmann equations for this system. In Sec. III some examples are presented: For a binary mixture we show the time dependence of the velocity distribution functions of the two species and how momentum and energy is exchanged between the constituents of the mixture in the dynamical process to attain the equilibrium distribution. For small times we compare the short-time expansion with the exact solution to elucidate the effect of the first collisions in the development of the two branches of the distribution function. Furthermore Boltzmann's H function is computed and the dependence on mass ratio, concentration, and initial conditions for short times is discussed. For a ternary mixture we show how momentum and energy relaxation exhibits a new behavior (nonmonotonic approach to equilibrium), a phenomenon which can occur in the presence of more than two species.

II. THE ONE-DIMENSIONAL ν-COMPONENT MAXWELL GAS

The system of Boltzmann equations for ν components reads in one dimension[22]

$$\frac{\partial}{\partial t}h_\alpha(v_{10},t) = \sum_\beta \int dv_{20}\,|v_{20}-v_{10}|\,\sigma_{\alpha\beta}[h_\alpha(v_{11},t)h_\beta(v_{21},t) - h_\alpha(v_{10},t)h_\beta(v_{20},t)] \tag{1a}$$

with the initial conditions

$$h_\alpha(v,0)=h_\alpha^0(v)\ , \tag{1b}$$

where v_{11} and v_{21}—the post-collisional velocities—are given by

$$v_{11}=\frac{2m_\beta v_{20}+(m_\alpha-m_\beta)v_{10}}{m_\alpha+m_\beta}\ ,\qquad v_{21}=\frac{2m_\alpha v_{10}+(m_\beta-m_\alpha)v_{20}}{m_\alpha+m_\beta} \tag{1c}$$

and the velocity distribution function h_α is normalized to the number density of species α, $\int h_\alpha(v,t)dv=n_\alpha$ (here and throughout the paper the integration is extended over the whole real axis). Note that in the sum on the right-hand side of Eq. (1a) the term for $\beta=\alpha$ vanishes, since in one dimension a collision between like particles merely exchanges velocities and therefore does not change the distribution.

In analogy to the three-dimensional case we *assume* the collision cross section to be inversely proportional to the relative velocity, i.e.,

$$|v_{20}-v_{10}|\,\sigma_{\alpha\beta}=\sigma_{\alpha\beta}^0\ , \tag{2}$$

where $\sigma_{\alpha\beta}^0=\sigma_{\beta\alpha}^0$ depends on the masses m_α and m_β only. In one dimension the post-collisional velocities are uniquely determined by momentum and energy conservation [see Eq. (1c)], whereas in three dimensions they are related via the collision cross section $\sigma_{\alpha\beta}$. In three dimensions the dependence of $\sigma_{\alpha\beta}$ on the relative velocity $|v_{20}-v_{10}|$ for a purely repulsive r^{-n}-interaction potential is given by[22] $|v_{20}-v_{10}|^{-4/n}$, which leads to a velocity independent expression for $|v_{20}-v_{10}|\sigma_{\alpha\beta}$ for $n=4$—the Maxwell potential. This justifies one to call a particle interaction in one dimension quasi-Maxwellian, if it obeys Eq. (2).

After scaling the time by $\tau=nt$, where $n=\sum_\alpha n_\alpha$, and also the distribution function , $(1/n)h_\alpha\to h_\alpha$, the system (1a) reads

$$\frac{\partial}{\partial\tau}h_\alpha(v_{10},\tau)=\sum_\beta\sigma_{\alpha\beta}^0\int dv_{20}[h_\alpha(v_{11},\tau)h_\beta(v_{21},\tau) - h_\alpha(v_{10},\tau)h_\beta(v_{20},\tau)] \tag{3}$$

with the normalization $\int h_\alpha(v,\tau)dv=c_\alpha$ and $c_\alpha=n_\alpha/n$, $\sum_\alpha c_\alpha=1$.

Before linearizing Eq. (3) we consider the case of equal masses. In this case $v_{11}=v_{20}$ and $v_{21}=v_{10}$ holds and all $\sigma_{\alpha\beta}^0$ are equal and can be absorbed in the time scaling. Carrying out the integration in Eq. (3) yields the following system of differential equations:

$$\frac{\partial}{\partial\tau}h_\alpha=c_\alpha h_\Sigma-h_\alpha,\quad \alpha=1,\ldots,\nu \tag{4}$$

where we have defined

$$h_\Sigma(v,\tau):=\sum_\beta h_\beta(v,\tau)\ . \tag{5}$$

Taking the sum of the ν equations (4), we get

$$\frac{\partial}{\partial\tau}h_\Sigma=0 \tag{6}$$

which means that the sum of the distribution functions does not change in time

$$h_\Sigma(v,\tau)\equiv h_\Sigma(v)=\sum_\beta h_\beta^0(v)\ . \tag{7}$$

Now the system (4) decouples and can be solved easily for every component yielding

$$h_\alpha(v,\tau)=c_\alpha h_\Sigma(v)+[h_\alpha^0(v)-c_\alpha h_\Sigma(v)]e^{-\tau}\ . \tag{8}$$

Equation (8) shows that the h_α *do* change in time, but do not approach a Maxwell-Boltzmann equilibrium distribution but the sum of the initial distributions multiplied with a concentration, indicating a redistribution of velocities between particles of different species.

In the case of arbitrary masses we linearize the system (3) in the usual way by setting

$$h_\alpha(v,\tau)=f_\alpha(v)[1+\Phi_\alpha(v,\tau)]\ , \tag{9a}$$

where f_α denotes the Maxwell-Boltzmann equilibrium distribution

$$f_\alpha(v)=\frac{c_\alpha}{\sqrt{\pi}v_{T_\alpha}}e^{-v^2/v_{T_\alpha}^2},\quad v_{T_\alpha}^2=\frac{2kT}{m_\alpha} \tag{9b}$$

and the function Φ_α has to fulfill the following normalization condition:

$$\int f_\alpha(v)\Phi_\alpha(v,\tau)dv=0\ . \tag{10a}$$

Furthermore we *require* that

$$\lim_{\tau\to\infty}\Phi_\alpha(v,\tau)=0 \tag{10b}$$

which is commonly assumed, but does not hold in the case of equal masses (see above).

Inserting Eq. (9) into Eq. (3) and neglecting higher-order terms in Φ_α yields the following system of linearized Boltzmann equations for the deviation from the equilibrium:

$$\frac{\partial}{\partial \tau}\Phi_\alpha(v_{10},\tau)=\sum_\beta \int dN_{\alpha\beta}[\Phi_\alpha(v_{11},\tau)+\Phi_\beta(v_{21},\tau) -\Phi_\alpha(v_{10},\tau)-\Phi_\beta(v_{20},\tau)] , \tag{11a}$$

where

$$dN_{\alpha\beta}=\sigma_{\alpha\beta}\,|\,v_{20}-v_{10}\,|\,f_\beta(v_{20})dv_{20} \tag{11b}$$

is the average number of collisions per unit time between a particle of species α with initial velocity v_{10} and particles of species β with velocity v_{20}.

The system (11a) has to be solved subject to the initial conditions

$$\Phi_\alpha(v,0)=\Phi_\alpha^0(v):=h_\alpha^0(v)/f_\alpha(v)-1 . \tag{12}$$

The system (11a) can be written in the canonical form of an integro-differential equation, if we introduce the following transition probabilities (integral kernels) (Ref. 23)

$$\int \Psi_\alpha(v_{11})dN_{\alpha\beta}=:\int \omega_{\alpha\beta}^{(s)}(v_{10}\to v_{11})\Psi_\alpha(v_{11})dv_{11} , \tag{13a}$$

$$\int \Psi_\beta(v_{21})dN_{\alpha\beta}=:\int \omega_{\alpha\beta}^{(d)}(v_{10}\to v_{21})\Psi_\beta(v_{21})dv_{21} , \tag{13b}$$

$$\int \Psi_\beta(v_{20})dN_{\alpha\beta}=:\int \omega_{\alpha\beta}^{(r)}(v_{10}\to v_{20})\Psi_\beta(v_{20})dv_{20} , \tag{13c}$$

and the collision frequency

$$P_\alpha=\sum_\gamma P_{\alpha\gamma}=\sum_\gamma \int dN_{\alpha\gamma} , \tag{14}$$

where Ψ_α and Ψ_β are arbitrary functions of the velocity. Note that the variables v_{11} and v_{21} on the left-hand sides of Eqs. (13a) and (13b) are functions of v_{10} and v_{20} [see Eq. (1c)], whereas on the right-hand side they are integration variables.

The system (11a) now reads

$$\frac{\partial}{\partial \tau}\Phi_\alpha(v,\tau)=\sum_\beta \int W_{\alpha\beta}(v\to v')\Phi_\beta(v',\tau)dv' , \tag{15a}$$

where

$$W_{\alpha\beta}(v\to v')=\delta_{\alpha\beta}[S_\alpha(v\to v')-P_\alpha\delta(v-v')] +C_{\alpha\beta}(v\to v') , \tag{15b}$$

with

$$S_\alpha(v\to v')=\sum_\gamma \omega_{\alpha\gamma}^{(s)}(v\to v') \tag{15c}$$

and

$$C_{\alpha\beta}(v\to v')=\omega_{\alpha\beta}^{(d)}(v\to v')-\omega_{\alpha\beta}^{(r)}(v\to v') . \tag{15d}$$

This can be written in a more compact form by introducing vector and matrix notation. Defining $\Phi=(\Phi_1,\Phi_2,\ldots,\Phi_\nu)^T$ and $W(\cdots)=\int dv'\,W_{\alpha\beta}(v\to v')(\cdots)$, we have

$$\frac{\partial}{\partial \tau}\Phi=W\Phi . \tag{16}$$

Next we want to show, that W is a negative semidefinite operator, following arguments used in three dimensions. Defining a scalar product by

$$(\Phi,\Psi)=\sum_\alpha \int f_\alpha(v)\Phi_\alpha(v)\Psi_\alpha(v)dv , \tag{17}$$

we get, starting from Eq. (11a)

$$(\Phi,W\Psi)=\sum_{\alpha,\beta}\sigma_{\alpha\beta}^0\int\int f_\alpha(v_{10})f_\beta(v_{20})[\Psi_\alpha(v_{11})+\Psi_\beta(v_{21})-\Psi_\alpha(v_{10})-\Psi_\beta(v_{20})]\Phi_\alpha(v_{10})dv_{20}\,dv_{10} . \tag{18a}$$

In two steps: (i) interchanging α with β and v_{10} with v_{20} in Eq. (18a), and (ii) performing a variable transformation (v_{10},v_{20}) to (v_{11},v_{21}) according to Eq. (1c), we get

$$(\Phi,W\Psi)=-\tfrac{1}{4}\sum_{\alpha,\beta}\sigma_{\alpha\beta}^0\int\int f_\alpha(v_{10})f_\beta(v_{20})[\Phi_\alpha(v_{11})+\Phi_\beta(v_{21})-\Phi_\alpha(v_{10})-\Phi_\beta(v_{20})] \times[\Psi_\alpha(v_{11})+\Psi_\beta(v_{21})-\Psi_\alpha(v_{10})-\Psi_\beta(v_{20})]dv_{20}\,dv_{10} . \tag{18b}$$

Putting $\Psi=\Phi$ in Eq. (18b) shows that

$$(\Phi,W\Phi)\le 0 \tag{19}$$

and the equal sign holds only if $\Phi_\alpha(v)$ is a linear combination of 1, $m_\alpha v$, and $m_\alpha v^2$.

Since we would like to expand Φ in a complete set of orthogonal functions, we investigate the kernels $W_{\alpha\beta}$ in more detail. The transition probabilities defined in Eqs. (13a)–(13c) can be calculated using Eq. (1c):

$$\omega_{\alpha\beta}^{(s)}(v_{10}\to v_{11})=\sigma_{\alpha\beta}^0\frac{m_\alpha+m_\beta}{2m_\beta}f_\beta\left[\frac{m_\alpha+m_\beta}{2m_\beta}v_{11}-\frac{m_\alpha-m_\beta}{2m_\beta}v_{10}\right] , \tag{20a}$$

$$\omega_{\alpha\beta}^{(d)}(v_{10}\to v_{21})=\sigma_{\alpha\beta}^0\frac{m_\alpha+m_\beta}{|\,m_\alpha-m_\beta\,|}f_\beta\left[\frac{m_\alpha+m_\beta}{m_\alpha-m_\beta}v_{21}-\frac{2m_\alpha}{m_\alpha-m_\beta}v_{10}\right] , \tag{20b}$$

$$\omega_{\alpha\beta}^{(r)}(v_{10}\to v_{20})=\sigma_{\alpha\beta}^0 f_\beta(v_{20}) . \tag{20c}$$

The kernels $\omega_{\alpha\beta}^{(s)}$ and $\omega_{\alpha\beta}^{(d)}$ are of the same functional form and this type of function is related to the Hermite polynomials $H_n(x)$ via Mehler's formula[24]

$$\frac{1}{(1-z^2)^{1/2}}\exp\left[-\left[\frac{x-yz}{(1-z^2)^{1/2}}\right]^2\right]=e^{-x^2}\sum_{n=0}^{\infty}\frac{z^n}{2^n n!}H_n(x)H_n(y),\quad |z|<1\ . \tag{21}$$

Putting

$$z=(m_\alpha-m_\beta)/(m_\alpha+m_\beta)$$

and

$$z=2(m_\alpha m_\beta)^{1/2}/(m_\alpha+m_\beta)\ ,$$

respectively, we arrive at the following expansions for the transition probabilities:

$$\omega_{\alpha\beta}^{(s)}(v_{10}\to v_{11})=\sigma_{\alpha\beta}^0\frac{c_\beta}{\sqrt{\pi}v_{T_\alpha}}e^{-v_{11}^2/v_{T_\alpha}^2}\sum_{n=0}^{\infty}\frac{1}{2^n n!}\left[\frac{m_\alpha-m_\beta}{m_\alpha+m_\beta}\right]^n H_n(v_{11}/v_{T_\alpha})H_n(v_{10}/v_{T_\alpha})\ , \tag{22a}$$

$$\omega_{\alpha\beta}^{(d)}(v_{10}\to v_{21})=\sigma_{\alpha\beta}^0\frac{c_\beta}{\sqrt{\pi}v_{T_\beta}}e^{-v_{21}^2/v_{T_\beta}^2}\sum_{n=0}^{\infty}\frac{1}{2^n n!}\left[\frac{2(m_\alpha m_\beta)^{1/2}}{m_\alpha+m_\beta}\right]^n H_n(v_{21}/v_{T_\beta})H_n(v_{10}/v_{T_\alpha})\ . \tag{22b}$$

This representation enables us to calculate the action of $W_{\alpha\beta}$ [see Eq. (15b)] on a Hermite polynomial

$$\int W_{\alpha\beta}(v\to v')H_m(v'/v_{T_\beta})dv'=\left\{\delta_{\alpha\beta}\sum_\gamma\sigma_{\alpha\gamma}^0c_\gamma\left[\left[\frac{m_\alpha-m_\gamma}{m_\alpha+m_\gamma}\right]^m-1\right]+\sigma_{\alpha\beta}^0c_\beta\left[\left[\frac{2(m_\alpha m_\beta)^{1/2}}{m_\alpha+m_\beta}\right]^m-\delta_{m0}\right]\right\}H_m(v/v_{T_\alpha})\ , \tag{23}$$

where we have used the orthogonality relation of the Hermite polynomials

$$\int e^{-x^2}H_m(x)H_n(x)dx=\sqrt{\pi}2^m m!\delta_{mn}\ . \tag{24}$$

Equation (23) suggests the expansion of the functions $\Phi_\alpha(v,\tau)$ in a series of Hermite polynomials with time-dependent coefficients, i.e.,

$$\Phi_\alpha(x,\tau)=\sum_{n=0}^{\infty}a_n^{(\alpha)}(\tau)H_n(x)\ . \tag{25}$$

Here we have introduced scaled functions according to

$$\Phi_\alpha(v,\tau)\to\Phi_\alpha(v/v_{T_\alpha},\tau)=\Phi_\alpha(x,\tau)\ ;$$

and in the same way we scale f_α, h_α, etc. Inserting Eq. (25) into Eq. (16a) multiplying with $e^{-x^2}H_m(x)$, and integrating, yields the following systems of differential equations for the time functions:

$$\frac{\partial}{\partial\tau}a_m=W_m a_m\ , \tag{26}$$

where $a_m=(a_m^{(1)},a_m^{(2)},\ldots,a_m^{(\nu)})^T$ and W_m is a $\nu\times\nu$ matrix, the elements of which are zero for $m=0$, and for $m\geq1$ we have [see Eq. (23)]

$$w_{\alpha\beta}^{(m)}=\sigma_{\alpha\beta}^0c_\beta\left[\frac{2(m_\alpha m_\beta)^{1/2}}{m_\alpha+m_\beta}\right]^m\quad\text{for }\alpha\neq\beta\ , \tag{27a}$$

$$w_{\alpha\alpha}^{(m)}=\sum_{\gamma(\neq\alpha)}\sigma_{\alpha\gamma}^0c_\gamma\left[\left[\frac{m_\alpha-m_\gamma}{m_\alpha+m_\gamma}\right]^m-1\right]\ . \tag{27b}$$

For $m=0$ we have

$$\frac{\partial}{\partial\tau}a_0^{(\alpha)}=0 \tag{28}$$

which is an expression for particle conservation for each species. Because of the requirement $\lim_{\tau\to\infty}\Phi_\alpha(x,\tau)=0$ we get

$$a_0^{(\alpha)}(\tau)\equiv0\ . \tag{29}$$

For $m\geq1$ we make the ansatz

$$a_m(\tau)=a_m^0e^{\lambda^{(m)}\tau} \tag{30}$$

which leaves us with the eigenvalue problem

$$W_m a_m^0=\lambda^{(m)}a_m^0\ . \tag{31}$$

Next we want to investigate the eigenvectors and eigenvalues of W_m. Since the matrix $C^{1/2}W_mC^{-1/2}$, where $C=\text{diag}(c_1,c_2,\ldots,c_\nu)$, is symmetric, there exist real eigenvalues $\lambda_1^{(m)},\lambda_2^{(m)},\ldots,\lambda_\nu^{(m)}$ and ν orthonormal eigenvectors forming an orthogonal matrix Q_m ($Q_m^{-1}=Q_m^T$) so that

$$Q_m^TC^{1/2}W_mC^{-1/2}Q_m=\text{diag}(\lambda_1^{(m)},\lambda_2^{(m)},\ldots,\lambda_\nu^{(m)})=:\Lambda_m\ . \tag{32}$$

Defining $P_m:=C^{-1/2}Q_m$, we find $P_m^{-1}W_mP_m=\Lambda_m$ and for P_m^{-1} we obtain

$$P_m^{-1}=P_m^TC \tag{33a}$$

or

$$P_m^TCP_m=I\ . \tag{33b}$$

This means, that the eigenvectors $p_\alpha^{(m)}$ of W_m fulfill the following condition:

$$p_\alpha^{(m)T} C p_\beta^{(m)} = \delta_{\alpha\beta} , \tag{33c}$$

or—denoting the components of $p_\alpha^{(m)}$ by $p_{\gamma,\alpha}^{(m)}$—

$$\sum_\gamma c_\gamma p_{\gamma,\alpha}^{(m)} p_{\gamma,\beta}^{(m)} = \delta_{\alpha\beta} , \tag{33d}$$

but we also have because of $P_m P_m^T = C^{-1}$

$$\sum_\gamma p_{\alpha,\gamma}^{(m)} p_{\beta,\gamma}^{(m)} = \frac{1}{c_\alpha} \delta_{\alpha\beta} . \tag{33e}$$

Thus we have shown that the matrix W_m can be diagonalized and possesses ν linear-independent eigenvectors $(p_1^{(m)}, p_2^{(m)}, \dots, p_\nu^{(m)}) = P_m$, which fulfill Eqs. (33a)–(33e).

Since the integral operator W is negative semidefinite, the matrices W_m are as well, meaning that all eigenvalues are negative or zero. Since $W_0 \equiv 0$ we have ν zero eigenvalues corresponding to particle conservation for each of the ν species. For $m = 1$ we find

$$\sum_\beta \sqrt{m_\beta} w_{\alpha\beta}^{(1)} = 0 \tag{34}$$

which shows that W_1 has an eigenvalue $\lambda_1^{(1)} = 0$ corresponding to the conservation by total momentum. The respective normalized eigenvector [cf. Eq. (33e)] is given by

$$p_1^{(1)} = \left[\sum_\gamma c_\gamma m_\gamma \right]^{-1/2} (\sqrt{m_1}, \sqrt{m_2}, \dots, \sqrt{m_\nu})^T \tag{35a}$$

which has

$$\sum_\gamma c_\gamma \sqrt{m_\gamma} p_{\gamma,\alpha}^{(1)} = 0 \text{ for } \alpha \geq 2 \tag{35b}$$

as a consequence for the other eigenvectors of W_1. For $m = 2$ we deduce from

$$\sum_\beta w_{\alpha\beta}^{(2)} = 0 \tag{36}$$

that $\lambda_1^{(2)} = 0$—corresponding to energy conservation—and

$$p_1^{(2)} = (1, 1, \dots, 1)^T , \tag{37a}$$

which means for the components of the other eigenvectors of W_2

$$\sum_\gamma c_\gamma p_{\gamma,\alpha}^{(2)} = 0 \text{ for } \alpha \geq 2 . \tag{37b}$$

In the Appendix we show that there are no other zero eigenvalues of the matrices W_m.

Since we have shown the existence of ν linear-independent eigenvectors, the time function is given by [cf. Eq. (30)]

$$a_m(\tau) = \sum_\gamma s_\gamma^{(m)} p_\gamma^{(m)} e^{\lambda_\gamma^{(m)} \tau}, \quad m \geq 1 \tag{38}$$

and the coefficients $s_\gamma^{(m)}$ have to be determined from the initial conditions. Defining "Fourier coefficients" ($n \geq 1$)

$$t_\alpha^{(n)} := \frac{1}{\sqrt{\pi} 2^n n!} \int e^{-u^2} \Phi_\alpha(u,0) H_n(u) du = \frac{1}{c_\alpha} \frac{1}{2^n n!} \int h_\alpha^0(u) H_n(u) du , \tag{39}$$

we get from Eqs. (25) and (38) for $\tau = 0$

$$t^{(n)} = P_n s^{(n)} , \tag{40}$$

where we have introduced the vectors $s^{(n)} = (s_1^{(n)}, s_2^{(n)}, \dots, s_\nu^{(n)})^T$ and $t^{(n)} = (t_1^{(n)}, t_2^{(n)}, \dots, t_\nu^{(n)})^T$. With the aid of Eq. (33a) we get for the coefficients $s_\gamma^{(n)}$

$$s^{(n)} = P_n^T C t^{(n)} \text{ or } s_\gamma^{(n)} = \sum_\beta p_{\beta,\gamma}^{(n)} c_\beta t_\beta^{(n)} . \tag{41}$$

Collecting the terms we finally arrive at the following solution for the deviations from the equilibrium in a ν component Maxwell gas mixture in one dimension

$$\Phi_\alpha(x,\tau) = \sum_{n=1}^{\infty} \frac{1}{2^n n!} \left[\sum_\gamma M_{\alpha,\gamma}^{(n)} e^{\lambda_\gamma^{(n)} \tau} \right] H_n(x) , \tag{42a}$$

with

$$M_{\alpha,\gamma}^{(n)} = p_{\alpha,\gamma}^{(n)} \sum_\beta p_{\beta,\gamma}^{(n)} \int h_\beta^0(u) H_n(u) du . \tag{42b}$$

Since we require $\lim_{\tau \to \infty} \Phi_\alpha(x,\tau) = 0$, the coefficients of the exponential with zero eigenvalue, $M_{\alpha,1}^{(1)}$ and $M_{\alpha,1}^{(2)}$, have to vanish. For $M_{\alpha,1}^{(1)}$ this is equivalent to [$H_1(x) = 2x$, $p_{\beta,1}^{(1)} = \sqrt{m_\beta}$ from Eq. (35a)]

$$\sum_\beta m_\beta \int u h_\beta^0(u) du = 0 , \tag{43}$$

and this is just the total momentum, since we assumed the center of mass at rest [cf. Eq. (11b)]; and every set of initial conditions $h_1^0, h_2^0, \dots, h_\nu^0$ has to fulfill Eq. (43).

In the case of $M_{\alpha,1}^{(2)} = 0$ this is equivalent to [$H_2(x) = 4x^2 - 2$, $p_{\beta,1}^{(2)} = 1$ from Eq. (37a)]

$$\sum_\beta m_\beta \int u^2 h_\beta^0(u) du = kT \tag{44}$$

which is the total energy. But also total momentum and total energy of the system have to be constant for all times τ; this requires that

$$\sum_\alpha m_\alpha \int u f_\alpha(u) [1 + \Phi_\alpha(u,\tau)] du = 0 \text{ for all } \tau . \tag{45}$$

Inserting Φ_α from Eqs. (42a) and (42b), this is equivalent to

$$\sum_\alpha c_\alpha \sqrt{m_\alpha} M_{\alpha,\gamma}^{(1)} = 0 \text{ for } \gamma \geq 2 \tag{46a}$$

or

$$\sum_\alpha c_\alpha \sqrt{m_\alpha} p_{\alpha,\gamma}^{(1)} \sum_\beta \sqrt{m_\beta} p_{\beta,\gamma}^{(1)} \int u h_\beta^0(u) du = 0 \text{ for } \gamma \geq 2 , \tag{46b}$$

and this is true because of Eq. (35b). In the same way one can show, using Eq. (37b), that the total energy is constant over time.

III. EXAMPLES

A. The velocity distribution in a binary mixture

In this section we will study as a first example the case of a binary mixture ($\nu=2$) in more detail. We introduce the mass ratio $\mu:=m_2/m_1$, and assume, without loss of generality, $\mu\geq 1$. We then get for the eigenvalues ($m\geq 1$; the only interaction parameter σ_{12}^0 has been absorbed in the time scaling)

$$\lambda_m^{\pm}=\begin{cases}-\frac{1}{2}(1-b^m)\pm\frac{1}{2}[(c_1-c_2)^2(1-b^m)^2+4c_1c_2\mu^m d^{2m}]^{1/2}, & m \text{ even}\\ -\frac{1}{2}[1+b^m(c_1-c_2)]\pm\frac{1}{2}[(b^m+c_1-c_2)^2+4c_1c_2\mu^m d^{2m}]^{1/2}, & m \text{ odd},\end{cases} \tag{47a}$$

with

$$b=\frac{1-\mu}{1+\mu},\quad d=\frac{2}{1+\mu}. \tag{47b}$$

The eigenvalue spectrum of a binary mixture for the special case $c_1=c_2=\frac{1}{2}$ as a function of μ has been recently studied by Dickman.[25] According to the previous section we have $\lambda_1^+=\lambda_2^+=0$.

As initial conditions we select shifted normal distributions with mean-square deviation smaller than the equilibrium value, i.e.,

$$h_\alpha^0(v)=\frac{c_\alpha}{\sqrt{\pi\gamma_\alpha}v_{T_\alpha}}e^{-(v-v_\alpha^0)^2/(\gamma_\alpha v_{T_\alpha}^2)},\quad \gamma_\alpha\leq 1,\quad \alpha=1,2. \tag{48}$$

This class of functions also includes the special initial condition of a δ function for $\gamma_\alpha\to 0$. To be able to compare numerical results we scale all velocities with the *same* factor, i.e., we put $x:=v/v_{T_1}$ as well as $x_\alpha^0:=v_\alpha^0/v_{T_1}$, $\alpha=1,2$. We then get for total momentum and energy, respectively,

$$c_1x_1^0+\mu c_2x_2^0=0 \tag{49a}$$

and

$$c_1(x_1^{02}+\tfrac{1}{2}\gamma_1)+c_2(\mu x_2^{02}+\tfrac{1}{2}\gamma_2)=\tfrac{1}{2}. \tag{49b}$$

In the case of a binary mixture momentum and energy conservation uniquely determine (up to the sign) the scaled initial mean velocities. For the "Fourier-coefficients" [see Eq. (39)] we get[24]

$$\frac{c_\alpha}{\sqrt{\pi\gamma_\alpha}v_{T_\alpha}}\int e^{-(u-v_\alpha^0)^2/(\gamma_\alpha v_{T_\alpha}^2)}H_n(u/v_{T_\alpha})du =c_\alpha[(1-\gamma_\alpha)^n]^{1/2}H_n((v_\alpha^0/v_{T_\alpha})/\sqrt{1-\gamma_\alpha}). \tag{50}$$

This enables us to write down the deviations from the equilibrium distribution function explicitly

$$\Phi_1(x,\tau)=\sum_{n=1}^{\infty}\frac{1}{2^n n!}(M_{n,1}^+e^{\lambda_n^+\tau}+M_{n,1}^-e^{\lambda_n^-\tau})H_n(x), \tag{51a}$$

$$\Phi_2(x,\tau)=\sum_{n=1}^{\infty}\frac{1}{2^n n!}(M_{n,2}^+e^{\lambda_n^+\tau}+M_{n,2}^-e^{\lambda_n^-\tau})H_n(\sqrt{\mu}x), \tag{51b}$$

with

$$M_{n,1}^{\pm}=\mp\frac{\lambda_n^{\mp}+c_2(1-b^n)}{\lambda_n^+-\lambda_n^-}[(1-\gamma_1)^n]^{1/2}H_n(x_1^0/\sqrt{1-\gamma_1}) \pm\frac{c_2(\mu^n)^{1/2}d^n}{\lambda_n^+-\lambda_n^-}[(1-\gamma_2)^n]^{1/2}H_n(\sqrt{\mu}x_2^0/\sqrt{1-\gamma_2}), \tag{52a}$$

$$M_{n,2}^{\pm}=\pm\frac{c_1(\mu^n)^{1/2}d^n}{\lambda_n^+-\lambda_n^-}[(1-\gamma_1)^n]^{1/2}H_n(x_1^0/\sqrt{1-\gamma_1}) \pm\frac{\lambda_n^{\pm}+c_2(1-b^n)}{\lambda_n^+-\lambda_n^-}[(1-\gamma_2)^n]^{1/2}H_n(\sqrt{\mu}x_2^0/\sqrt{1-\gamma_2}). \tag{52b}$$

In order to see the dramatic effects in the time development of

$$h_\alpha(x,\tau)=f_\alpha(x)[1+\Phi_\alpha(x,\tau)]$$

we display two cases; one where the mass ratio is of order 1 ($\mu=1.5$) and the other where the mass ratio is large ($\mu=15$). For the sake of simplicity we select equal concentrations ($c_1=c_2=0.5$). In the first example ($\mu=1.5$) both velocity distribution functions show a qualitatively similar behavior, hence it suffices to look at one of them. Figures 1(a) and 1(b) show the results calculated from Eq. (51a) for the lighter component, viewed from the short and the long-time side. Starting with an initial distribution of the form of a displaced Gaussian centered at a negative initial velocity at x_1^0 with a mean-square deviation of a fraction $\gamma_1=0.1$ of the equilibrium value [see Eq. (48)], one can see in Fig. 1(a) how within the first few collisions the initial distribution decays and at the same time a new branch of the distribution arises. This new branch looks similar in shape as compared to the initial distribution, but is centered now at a positive velocity. This shift of part of the distribution is caused by momentum and energy transfer in collisions of unlike particles. As time proceeds both branches of the distribution build up the Maxwell-Boltzmann equilibrium distribution centered at mean velocity zero. The initial behavior can be understood looking at the short-time expansion of the distribution function given by

$$h_1(x,\Delta\tau)=(1-\Delta\tau c_2)h_1^0(x)+\Delta\tau\frac{c_1c_2}{\sqrt{\pi}}\left\{\frac{1}{\sigma_{11}}\exp\left[-\left[\frac{(x-bx_1^0)^2}{\sigma_{11}^2}\right]\right]+\frac{1}{\sigma_{22}}\exp\left[-\left[\frac{(x-\mu\,dx_2^0)^2}{\sigma_{22}^2}\right]\right]\right\}-\Delta\tau c_2 f_1(x)+O((\Delta\tau)^2)\,, \tag{53a}$$

$$h_2(x,\Delta\tau)=(1-\Delta\tau c_1)h_2^0(x)+\Delta\tau\frac{c_1c_2}{\sqrt{\pi}}\left\{\frac{1}{\sigma_{12}}\exp\left[-\left[\frac{\mu(x+bx_2^0)^2}{\sigma_{12}^2}\right]\right]+\frac{1}{\sigma_{21}}\exp\left[-\left[\frac{\mu(x-dx_1^0)^2}{\sigma_{21}^2}\right]\right]\right\}-\Delta\tau c_1 f_2(x)+O((\Delta\tau)^2) \tag{53b}$$

where

$$\sigma_{1\alpha}^2=b^2\gamma_\alpha+\mu d^2,\quad \alpha=1,2\,, \tag{53c}$$

$$\sigma_{2\alpha}^2=\mu d^2\gamma_\alpha+b^2,\quad \alpha=1,2 \tag{53d}$$

and shown in Fig. 2 for $\mu=1.5$.

In the second example ($\mu=15$) the light component shows qualitatively the same behavior as the distribution discussed above. The heavy component does not show the development of two branches, since both the shift of the initial velocity from zero and the velocity shift in the first collisions are small (Fig. 3).

Since for $\mu=1$ the velocity distribution function has a special behavior [see Eq. (8)] and does not approach a Maxwell-Boltzmann equilibrium distribution in one dimension, we show it in Fig. 4 for $c_1=c_2=0.5$.

Expressions for the time-dependent mean velocity and mean-square velocity for each species can be easily calculated

$$\langle x\rangle_1(\tau)=c_1x_1^0e^{\lambda_1^-\tau}\,, \tag{54a}$$

$$\langle x\rangle_2(\tau)=c_2x_2^0e^{\lambda_1^-\tau}\,, \tag{54b}$$

with

$$\lambda_1^-=-1-b(c_1-c_2)\,, \tag{54c}$$

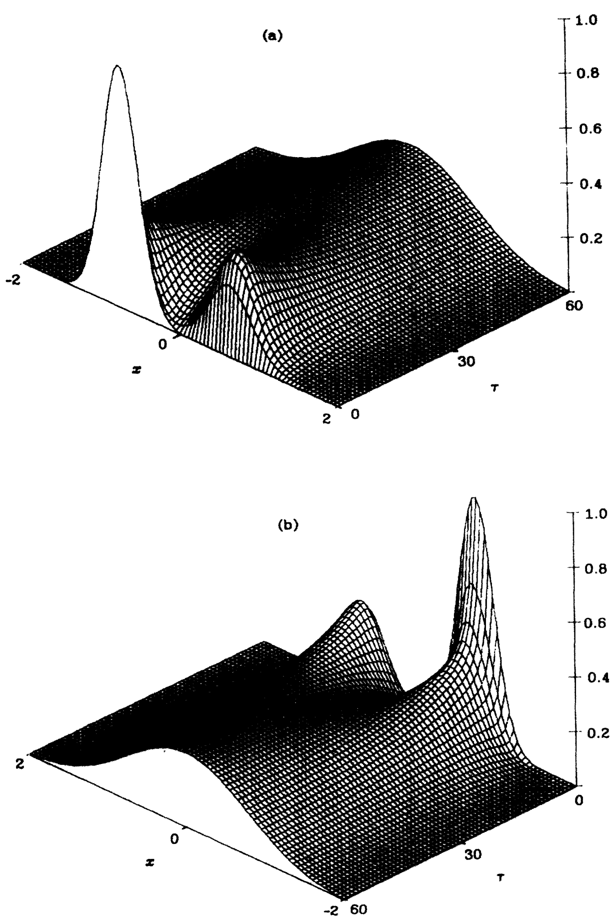

FIG. 1. (a) The distribution of the light component $h_1(x,\tau)$ of the binary equimolar mixture and mass ratio $\mu=1.5$ viewed from the short-time side, where the fast increase of the second branch can be seen. Note, that this increase is much faster than the following approach to equilibrium. (b) The same distribution function $h_1(x,\tau)$ as in (a) viewed from the long-time side. Here the fast decrease of the initial distribution, together with the rather slow decrease to thermal equilibrium, can be seen.

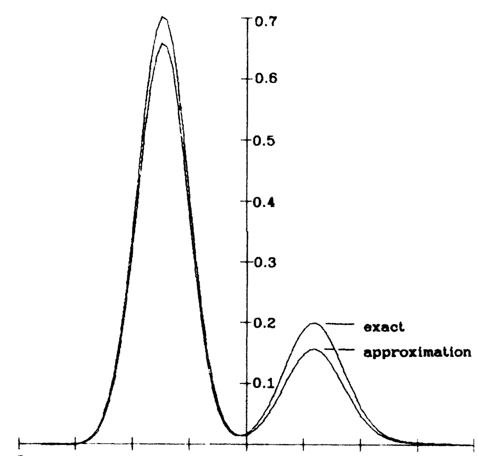

FIG. 2. For $\tau=0.5$, $c_1=c_2$, and $\mu=1.5$ the exact solution for $h_1(x,\tau)$ [see Eq. (51a)] is compared with the solution of the difference equation [Eq. (53a)]. The mean velocity of the second branch is determined by momentum and energy conservation in the first collision.

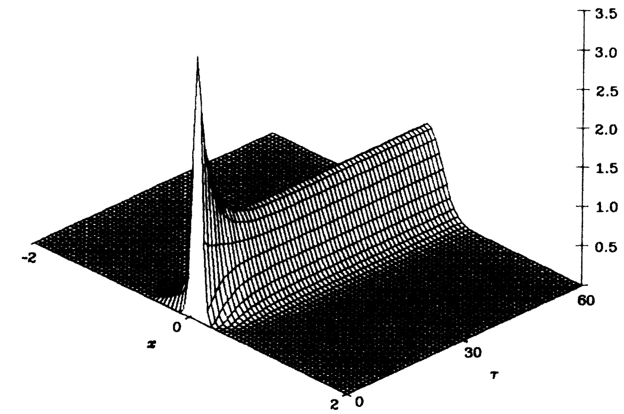

FIG. 3. The distribution function $h_2(x,\tau)$ of the heavy component of an equimolar mixture for $\mu=15$.

and

$$\langle x^2\rangle_1(\tau)=c_1\left[x_1^{02}+\frac{\gamma_1}{2}-\frac{1}{2}\right]e^{\lambda_2^-\tau}+\frac{c_1}{2}\,, \tag{55a}$$

$$\langle x^2\rangle_2(\tau)=c_2\left[x_2^{02}+\frac{\gamma_2}{2\mu}-\frac{1}{2\mu}\right]e^{\lambda_2^-\tau}+\frac{c_2}{2\mu}\,, \tag{55b}$$

with

$$\lambda_2^-=-1+b^2\,. \tag{55c}$$

In the former case the relevant eigenvalue λ_1^- is mass independent for equimolar mixtures, while in the latter case the eigenvalue λ_2^- is independent of concentration for all mass ratios. Equations (54) and (55) show that these quantities approach their equilibrium values monotonically.

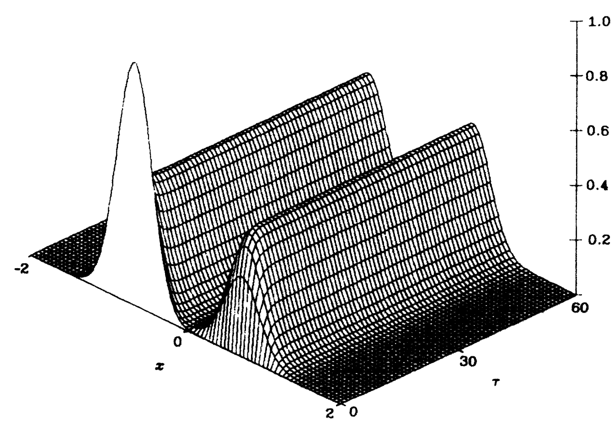

FIG. 4. The distribution of particles "1" of a binary mixture with $\mu=1$ and $c_1=c_2$, where the initial distributions are at $\pm v^0$, respectively. From Eq. (7) it is known that the sum of the initial distributions does not change with time and does therefore not approach a Maxwell-Boltzmann distribution. The redistribution of velocities between the two components can be seen from the changes in the distribution of the particles "1" [cf. Eq. (8)].

B. Boltzmann's H function

Since we have solved the linearized Boltzmann equation for a multicomponent mixture of Maxwellian particles, we can use this result to calculate Boltzmann's H function. The example we discuss is again for a binary mixture with mass ratios $\mu\geq 1.5$. For numerical reasons smaller mass ratios and δ-function-like initial conditions cannot be treated in a straightforward manner. Using the same initial conditions as above we can calculate

$$H(\tau)=\sum_{\alpha}\int h_\alpha(x,\tau)\ln h_\alpha(x,\tau)dx\,. \tag{56}$$

In Fig. 5 we plotted the difference $H(\tau)-H_{\rm eq}$ for a set of μ values. In this expression $H_{\rm eq}$ and the initial value $H(0)$ for a binary system are given by

$$H_{\rm eq}=\lim_{\tau\to\infty}H(\tau)$$
$$=c_1\ln c_1+c_2\ln\sqrt{\mu}c_2-\tfrac{1}{2}(1+\ln\pi)\,, \tag{57a}$$

$$H(0)=c_1\ln\frac{c_1}{\sqrt{\gamma_1}}+c_2\ln\frac{\sqrt{\mu}c_2}{\sqrt{\gamma_2}}-\tfrac{1}{2}(1+\ln\pi)\,. \tag{57b}$$

The time derivative of $H(\tau)$ for $\tau=0$ can be calculated analytically and is given by

$$\dot H(0)=\frac{2x_1^0}{\gamma_1}\langle\dot x\rangle_1(0)-\frac{1}{\gamma_1}\langle\dot x^2\rangle_1(0)+\frac{2\mu x_2^0}{\gamma_2}\langle\dot x\rangle_2(0)-\frac{\mu}{\gamma_2}\langle\dot x^2\rangle_2(0)\,. \tag{58}$$

It is most interesting to note that the initial slope of $H(\tau)$ for equimolar systems and $\gamma_1=\gamma_2=:\gamma$ does not depend on the mass ratio

$$\dot H(0)=1-\frac{1}{\gamma}\,. \tag{59}$$

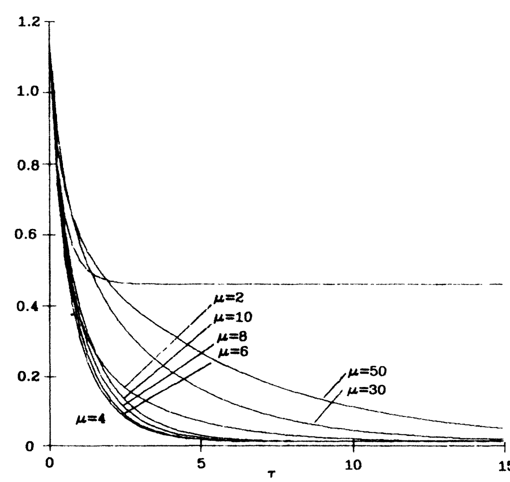

FIG. 5. The approach to thermal equilibrium of an equimolar mixture as described by $H(\tau)-H_{\rm eq}$ for $c_1=c_2$. Both $H(0)-H_{\rm eq}$ and $\dot H(0)$ are independent of the mass ratio μ. Note the interesting dependence on the mass ratio, and especially, that for $\mu=1$ the system does not approach the same limit.

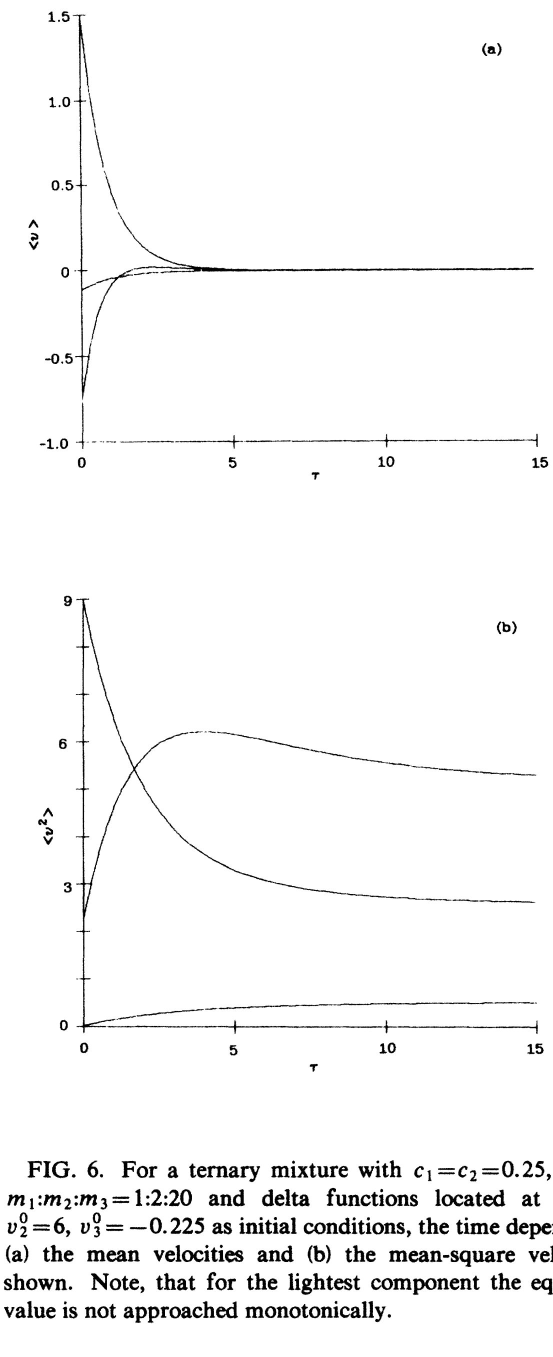

FIG. 6. For a ternary mixture with $c_1=c_2=0.25$, $c_3=0.5$, $m_1{:}m_2{:}m_3=1{:}2{:}20$ and delta functions located at $v_1^0=-3$, $v_2^0=6$, $v_3^0=-0.225$ as initial conditions, the time dependence of (a) the mean velocities and (b) the mean-square velocities is shown. Note, that for the lightest component the equilibrium value is not approached monotonically.

However, the mass ratio determines the approach to equilibrium: As time increases, $H(\tau)-H_{\mathrm{eq}}$ decreases faster and faster as μ increases from $\mu=1$ to $\mu\approx4$ and reverses this behavior as μ tends to infinity. The numerical calculations for the H function show the time scales noted earlier in the discussion of the velocity distribution function quite clearly. After a fast initial decay there is again a much slower approach to the equilibrium value observed.

C. Energy relaxation in a ternary mixture

Finally we want to discuss momentum and energy relaxation of a ternary mixture to equilibrium. In contrast to a binary system, where the mean velocities and the mean-square velocities of the two components approach their respective equilibrium values monotonically, we find a new possibility in a ternary system. Because of the functional dependence of these quantities on time (a sum of two weighted exponentials with different decay rates), they can have an extremum for special mass ratios and concentrations. In Figs. 6(a) and 6(b) we show an example where $m_1{:}m_2{:}m_3=1{:}2{:}20$ and $c_1=c_2=0.25$, $c_3=0.5$. In this case one component (the lightest one) acquires, for a given period of time, more momentum or energy than its equilibrium value.

ACKNOWLEDGMENTS

We are grateful to T. Lackner for stimulating discussions and critically reading the manuscript. One of us (M.P.) would like to acknowledge a grant by the Austrian Research Fund.

APPENDIX

In this Appendix we want to show that the matrices W_m, defined in Eqs. (27a) and (27b) have negative eigenvalues only, except for W_1 and W_2, which have exactly one zero eigenvalue each. To this end we define a scalar product of $x=(x_1,x_2,\ldots,x_\nu)^T$ and $y=(y_1,y_2,\ldots,y_\nu)^T$ by

$$(x,y)=\sum_\alpha c_\alpha x_\alpha y_\alpha \tag{A1}$$

and investigate the quadratic form (x,W_mx) for $x\neq0$

$$(x,W_mx)=\sum_{\alpha,\beta} c_\alpha w_{\alpha\beta}^{(m)}x_\alpha x_\beta =\sum_{\alpha,\beta}\sigma_{\alpha\beta}^0 c_\alpha c_\beta\left\{\left[\frac{2(m_\alpha m_\beta)^{1/2}}{m_\alpha+m_\beta}\right]^m x_\alpha x_\beta+\left[\left[\frac{m_\alpha-m_\beta}{m_\alpha+m_\beta}\right]^m-1\right]x_\alpha^2\right\}. \tag{A2}$$

Interchanging α and β in Eq. (A2) and adding the resulting expression yields

$$(x,W_mx)=-\tfrac{1}{2}\sum_{\alpha,\beta}\sigma_{\alpha\beta}^0 c_\alpha c_\beta\left[\frac{2(m_\alpha m_\beta)^{1/2}}{m_\alpha+m_\beta}\right]^m(x_\alpha-x_\beta)^2 -\sum_{\alpha,\beta}\sigma_{\alpha\beta}^0 c_\alpha c_\beta g_{\alpha\beta}^{(m)}x_\alpha^2\,, \tag{A3}$$

with

$$g_{\alpha\beta}^{(m)}:=1-\left[\frac{m_\alpha-m_\beta}{m_\alpha+m_\beta}\right]^m-\left[\frac{2(m_\alpha m_\beta)^{1/2}}{m_\alpha+m_\beta}\right]^m. \tag{A4}$$

For the coefficients $g_{\alpha\beta}^{(m)}$ the following inequalities can be easily proved

$$0=g_{\alpha\beta}^{(2)}<g_{\alpha\beta}^{(4)}<\cdots<g_{\alpha\beta}^{(2n)}<\cdots \quad \text{for } m_\alpha \neq m_\beta \tag{A5}$$

and

$$g_{\alpha\beta}^{(2n)}<g_{\alpha\beta}^{(2n+1)} \text{ for } n\geq 1, \quad m_\alpha \neq m_\beta \; . \tag{A6}$$

Therefore we have $(x,W_m x)<0$ for $m\geq 3$, which means that W_m, $m\geq 3$, has only negative eigenvalues. For $m=2$ we have $(x,W_2 x)=0$ if and only if $x_\alpha=x_\beta$ for all α and β, i.e., $x_\alpha=$const for all α. This proves that W_2 has exactly one zero eigenvalue with corresponding eigenvector $x=(1,\ldots,1)^T$ [cf. Eq. (37a)].

For $m=1$ the above argument does not hold, since $g_{\alpha\beta}^{(1)}$ might be negative. However, $(x,W_1 x)$ can be written in the form

$$(x,W_1 x)=-\frac{1}{2}\sum_{\alpha,\beta}\sigma_{\alpha\beta}^0 c_\alpha c_\beta \frac{2m_\alpha m_\beta}{m_\alpha+m_\beta}\left[\frac{x_\alpha}{\sqrt{m_\alpha}}-\frac{x_\beta}{\sqrt{m_\beta}}\right]^2 \tag{A7}$$

which shows that W_1 has negative eigenvalues only, except one zero eigenvalue with corresponding eigenvector $x=(\sqrt{m_1},\sqrt{m_2},\ldots,\sqrt{m_\nu})^T$ [cf. Eq. (35a)].

---

[1]P. Kasperkovitz and J. Reisenberger, Phys. Rev. A **31**, 2639 (1985).

[2]C. Boldrighini, Physica **124A**, 115 (1984).

[3]K. Hiroike, Prog. Theor. Phys. **70**, 988 (1983).

[4]J. Piasecki, J. Stat. Phys. **35**, 635 (1983).

[5]M. R. Hoare, S. Raval, and M. Rahman, Philos. Trans. R. Soc. London, Ser. A **305**, 383 (1982).

[6]A. Gevois, and Y. Pomeau, J. Stat. Phys. **14**, 483 (1976).

[7]O. de Pazzis, Commun. Math. Phys. **22**, 121 (1971).

[8]D. W. Jepsen, J. Math. Phys. **6**, 405 (1965).

[9]J. W. Haus and H. J. Raveche, J. Chem. Phys. **68**, 4969 (1978).

[10]M. Bishop and B. J. Berne, J. Chem. Phys. **60**, 893 (1974).

[11]C. Boldrighini, A. Pelegrinotti, E. Presutti, Ya. G. Sinai, and M. R. Soloveichik, Commun. Math. Phys. **101**, 363 (1985).

[12]J. Marró and J. Masoliver, Phys. Rev. Lett. **54**, 731 (1985); J. Phys. C **18**, 4691 (1985).

[13]J. Masoliver and J. Marro, J. Stat. Phys. **31**, 565 (1983).

[14]Ch. Foidl, P. Kasperkovitz, and O. J. Eder, J. Phys. C (to be published).

[15]Lord Rayleigh, Philos. Mag. **32**, 424 (1891).

[16]N. G. Van Kampen, Can. J. Phys. **39**, 551 (1961).

[17]R. Kubo, K. Matsuo, and K. Kitahara, J. Stat. Phys. **9**, 51 (1973).

[18]O. J. Eder, and T. Lackner, Phys. Rev. A **28**, 952 (1983); **29**, 799 (1984).

[19]O. J. Eder, T. Lackner, and M. Posch, Phys. Rev. A **30**, 1430 (1984).

[20]J. Piasecki and E. Wajnryb, J. Stat. Phys. **21**, 549 (1979).

[21]H. A. Lorentz, Arch. Neerl. **10**, 336 (1905).

[22]J. H. Ferziger and H. G. Kaper, *Mathematical Theory of Transport Processes in Gases* (North-Holland, Amsterdam, 1972).

[23]O. J. Eder, T. Lackner, and M. Posch, J. Chem. Phys. **74**, 5256 (1981).

[24]*Higher Transcendental Functions,* edited by A. Erdelyi (Krieger, Malabar, Florida, 1981), Vol. II.

[25]R. Dickman, J. Stat. Phys. **41**, 607 (1985).

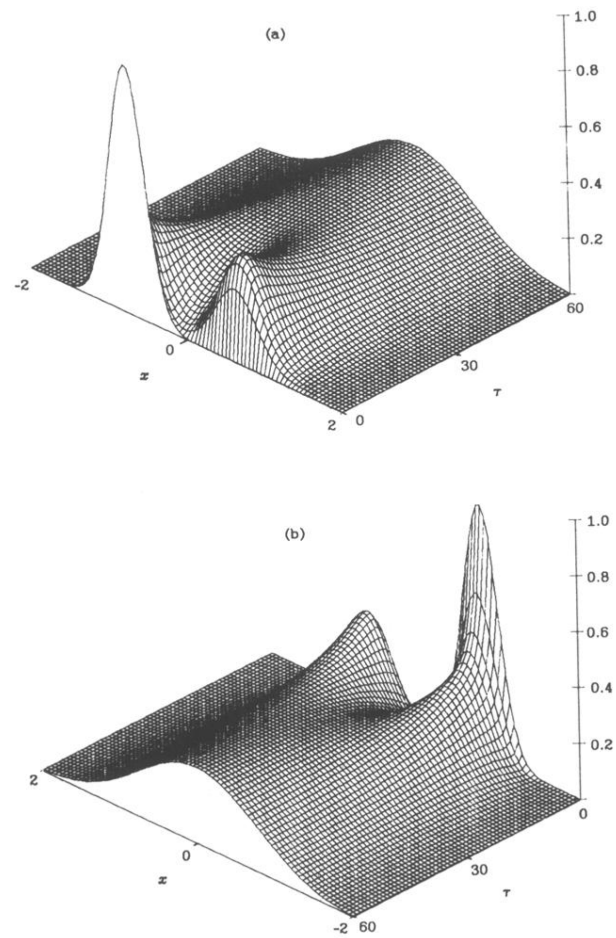

FIG. 1. (a) The distribution of the light component $h_1(x,\tau)$ of the binary equimolar mixture and mass ratio $\mu=1.5$ viewed from the short-time side, where the fast increase of the second branch can be seen. Note, that this increase is much faster than the following approach to equilibrium. (b) The same distribution function $h_1(x,\tau)$ as in (a) viewed from the long-time side. Here the fast decrease of the initial distribution, together with the rather slow decrease to thermal equilibrium, can be seen.

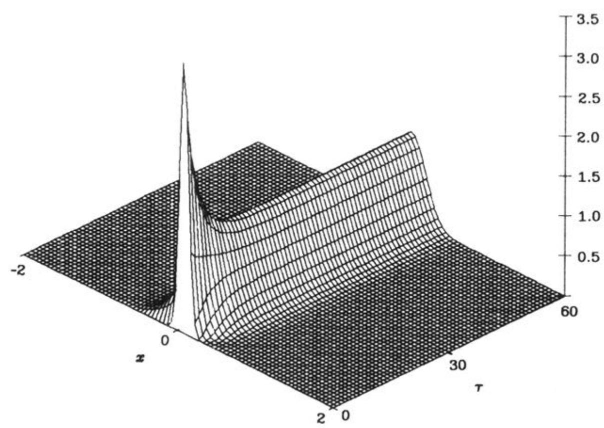

FIG. 3. The distribution function $h_2(x,\tau)$ of the heavy component of an equimolar mixture for $\mu=15$.

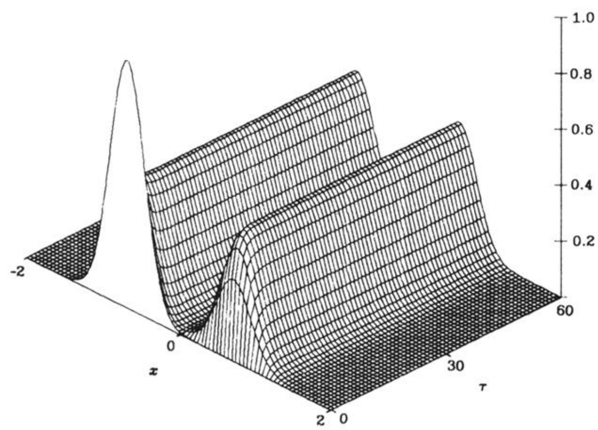

FIG. 4. The distribution of particles "1" of a binary mixture with $\mu=1$ and $c_1=c_2$, where the initial distributions are at $\pm v^0$, respectively. From Eq. (7) it is known that the sum of the initial distributions does not change with time and does therefore not approach a Maxwell-Boltzmann distribution. The redistribution of velocities between the two components can be seen from the changes in the distribution of the particles "1" [cf. Eq. (8)].