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# Dynamics of discrete models of binary mixtures in two dimensions: Exact solution

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The binary mixture of interacting disparate particles (heavy and light) in two dimensions has been modeled with the help of discrete-velocity Boltzmann-Broadwell models. These have been solved analytically for all integer and half-integer values of coupling constants. Depending on initial conditions the one-particle distribution functions and the entropy of light particles may exhibit a nonmonotonic behavior, as a function of time.

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The understanding of dynamical phenomena in fluids has been greatly increased through an efficient use of discretized kinetic equations. The set of continuous position and velocity variables $(\mathbf{r}_i, \mathbf{v}_i)$, where $i=1,\ldots,N$ (number of particles in the system), is being replaced by either half-discrete (only $\mathbf{v}_i$ discretized) or fully discrete (both $\mathbf{r}_i$ and $\mathbf{v}_i$) variables. The resulting formulations lend themselves to an analytical treatment [1] or permit rapid simulations [2] for a large number of physical and physicochemical problems. In fact the statistical mechanics of such discretized systems has firm fundaments [3] and the growing number of applications [4,5] is accompanied by new theoretical findings [6].

In this work we have attempted to introduce different kinds of particles with different collision rules in order to split the system into several (in our case two) interacting parts. The subsystems would themselves correspond to true particles and the background, respectively.

Such a splitting is not unique as the particles may differ by the values of parameters as the mass, the charge, etc. It is, however, a tradition in statistical mechanics [7] to treat first the mixtures of particles of unequal masses. We follow it here with two additional requirements: while staying within the framework of discrete models, we want both subsystems to be truly interacting and in addition soluble, at least for certain values of coupling constants and initial conditions. (Note that we have recently treated a similar situation, but with one subsystem without interactions [8].) These last conditions are by no means easy to satisfy. In the following we shall present an example of a mixture of particles with unequal masses which satisfies the above requirement. We do not claim that the system is very realistic. The advantage of it is to give the exact solution, which can be thoroughly studied and which will be presented in the following.

We propose and study here a statistical model of binary mixture of very different particles, heavy ($H$) and light ($L$) ones. Our purpose is to establish equations for one-particle distribution functions $f(\mathbf{r}_i, \mathbf{v}_i)$ for coupled $H$ and $L$ particles and to provide their solution in the case of given collision rules. In fact, the binary-mixture problem is not new [7], but to date only various partial solutions are available [9,10]. In the following we will present the solutions of space-homogeneous transport equations and derive expressions for the entropy.

We are interested here in a two-dimensional system of particles which can move only in four mutually perpendicular directions with the same speed $|\mathbf{v}|=1$. If for the moment we assume that there are no interactions between the particles, such a four-velocity model can be achieved through collisions between particles and a set of fixed, randomly distributed squares with diagonals pointing in the direction of motion. Such a "wind-tree" model has been introduced a long time ago [11] by Ehrenfest and Ehrenfest and is exactly soluble. A very readable exposition of this model in Ref. [12] prompted us to generalize it to a more complicated situation of a binary mixture of interacting particles. Let $\psi_i(t)$ and $\varphi_i(t)$ $(i=1,\ldots,4)$ be one-particle distribution functions of heavy and light particles, respectively, which are normalized $[\sum_{i=1}^{4}\psi_i(t)=1$ and $\sum_{i=1}^{4}\varphi_i(t)=1]$. For both $H$ and $L$ particles separately we allow head-on collisions which conserve the momentum and flip the outgoing particles velocity. In addition there exists a coupling between $H$ and $L$ particles—indeed a very asymmetric one: whereas the $H$ particles are totally unaffected by the collisions with $L$ particles, only the head-on collisions between $H$ and $L$ particles change the state of $L$ particles, as illustrated in Fig. 1. This model is a generalization of the Lorentz gas [13]: the scattering centers for $L$ particles are $H$ particles. The latter display their own dynamics governed by their collisions. We suppose also that the system is spatially uniform. (The nonuniform situation does not allow in general an analytical solution [14].) The set of eight coupled kinetic equations now reads

$$\frac{d\psi_i}{dt}=h(\psi_{i+1}\psi_{i+3}-\psi_{i+2}\psi_i), \tag{1}$$

$$\frac{d\varphi_i}{dt}=g(\varphi_{i+1}\varphi_{i+3}-\varphi_{i+2}\varphi_i)+k(\psi_{i+1}\varphi_{i+3}+\psi_{i+3}\varphi_{i+1}-2\psi_{i+2}\varphi_i), \quad i=1,\ldots,4. \tag{2}$$

The collision rules that lead to Eqs. (1) and (2) are illustrated in Fig. 1. The coupling constants $h$, $g$, and $k$ are simple functions of sizes, masses, and velocities and are assumed to be positive constants here. The form of Eqs.

 

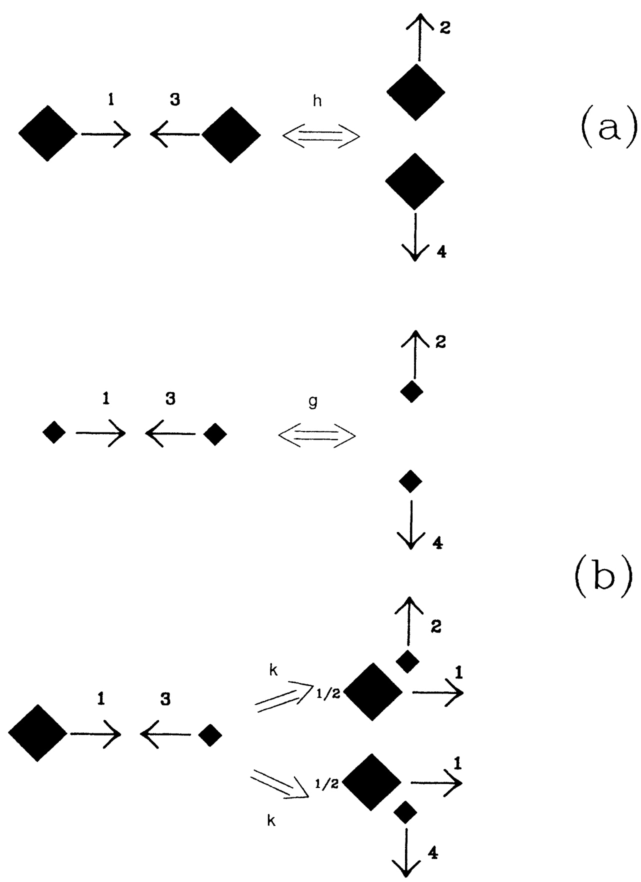


FIG. 1. (a) Schematic representation of collision processes of Eq. (1). (b) Schematic representation of collision processes of Eq. (2). Large and small rhombuses represent heavy and light particles, respectively.

(1) and (2) is recognized as representing two asymmetrically but linearly coupled and spatially uniform Broadwell models [15–18]. The bilinear coupling between $\psi$'s and $\varphi$'s in Eq. (2) is obviously not the most general one. It has the advantage that it allows the analytical solution. The solution of (1) and (2) gives $\psi_i(t)$ and $\varphi_i(t)$ as functions of their initial conditions $\psi_i(0)$ and $\varphi_i(0)$. In the following we describe some analytical solutions obtained for definite initial conditions. The strategy is to solve first the system (1) for $\psi_i(t)$ and then substitute it into (2) in order to solve for $\varphi_i(t)$. If we choose special configurations for heavy particles, namely, $\psi_i(0)=\psi_{i+2}(0)$, then

$$\begin{aligned} \psi_1(t)=\psi_3(t)&=\tfrac{1}{4}(1+de^{-ht}) , \\ \psi_2(t)=\psi_4(t)&=\tfrac{1}{4}(1-de^{-ht}) , \end{aligned} \tag{3}$$

where $2d=\psi_1(0)+\psi_3(0)-\frac{1}{2}$.

Substituting (3) into (2) one can show that (2) can be reduced to a single first-order differential equation for $x(t)=\varphi_1(t)+\varphi_3(t)$:

$$\frac{d}{dt}x=-(g+k)x+\frac{g}{2}[A^2(t)-B^2(t)]+2k\psi_2(t)+\frac{g}{2} \tag{4}$$

with

$$\begin{aligned} \varphi_1(t)&=\tfrac{1}{2}[x(t)+A(t)] , \\ \varphi_2(t)&=\tfrac{1}{2}[1-x(t)+B(t)] , \\ \varphi_3(t)&=\tfrac{1}{2}[x(t)-A(t)] , \\ \varphi_4(t)&=\tfrac{1}{2}[1-x(t)-B(t)] , \end{aligned} \tag{5}$$

where

$$A(t)=C_1\exp\left[-\frac{k}{2}\left[t-\frac{d}{h}e^{-ht}\right]\right] ,$$

$$B(t)=C_2\exp\left[-\frac{k}{2}\left[t+\frac{d}{h}e^{-ht}\right]\right] ,$$

and the constants $C_1$ and $C_2$ are given by $C_1=[\varphi_1(0)-\varphi_3(0)]\exp(-kd/2h)$ and $C_2=[\varphi_2(0)-\varphi_4(0)]\exp(+kd/2h)$. The general solution of Eq. (4) now reads

$$x(t)=e^{-(\gamma+\kappa)t}\left[\frac{\gamma}{\kappa}(d\kappa)^{\gamma}\right]\int\frac{C_1^2e^{-y}-C_2^2e^{y}}{y^{\gamma+1}}dy-\frac{\kappa de^{-t}}{2(\gamma+\kappa-1)}+\frac{1}{2}+C . \tag{6}$$

In Eq. (6) the constant $C$ is as usual determined from the initial conditions on $x(0)$ and we have used reduced constants $g/h=\gamma$, $k/h=\kappa$, and $h=1$, with a variable $y=d\kappa e^{-t}$. The integral in Eq. (6), $I(\gamma)=\int(ae^{-y}-be^{y})y^{-\gamma-1}dy$, can be expressed in terms of known functions for any positive integer or half-integer value of $\gamma$ [19]. Equations (3), (5), and (6) constitute the solution of the problem.

In the following we shall illustrate it by displaying $\varphi_i(t)$, $\psi_i(t)$, and the entropy of the system defined through the $H$ function of Boltzmann $H(t)$, $S(t)=-H(t)=S_H+S_L$, where $(k_B=1)$

$$S(t)=-\sum_{i=1}^{4}[\psi_i(t)\ln\psi_i(t)+\varphi_i(t)\ln\varphi_i(t)]. \tag{7}$$

In the following figures we are presenting the solutions for $\varphi_i(t)$ as a function of initial conditions $\varphi_i(0)$ and the coupling constants $h=\tau_H^{-1}$, $g=\tau_L^{-1}$, and $k=\tau_{HL}^{-1}$, where $\tau_H$ and $\tau_L$ are relaxation times for $H$ and $L$ particles separately and $\tau_{HL}$ is the relaxation time determined by the $H$-$L$ collision processes. The time dependence reflects directly different time scales set by $\tau$'s.

In Fig. 2(a) we plot $\psi_i(t)$ of Eq. (3) and $\varphi_i(t)$ for an asymmetrical choice of initial conditions on $\varphi_i(0)$ with $k=g=h$. All of the $\varphi_i(t)$ display clearly nonmonotonic behavior with time, with a local extremum followed by a slow relaxation towards equilibrium $\varphi_i(\infty)=\frac{1}{4}$. In Fig. 2(b) the partial entropies $S_L(t)$ and $S_H(t)$ are displayed, with a small anomaly in $S_L(t)$ clearly visible.

In Fig. 3 the value of $k$ is fixed to $k=1$ alongside with given initial conditions $\varphi_i(0)$. The $\varphi_i(t)$ are plotted as a function of $g=h$. The overshoots in $\varphi_i(t)$ increase with $g$ decreasing (for $\tau_{HL}<\tau_L$ the overshoots are larger than for $\tau_{HL}>\tau_L$); see Fig. 3(a). The anomalies in $S_L(t)$ behave correspondingly; see Fig. 3(b).

In Fig. 4 the values of $g=h$ are fixed alongside with initial conditions and $\varphi_i(t)$ are studied as a function of $k$. If the $H$-$L$ collision time $\tau_{HL}$ is larger than $\tau_L$ ($g<k$), the extrema of $\varphi_i(t)$ are much wider than in the opposite case, Fig. 4(a). In Fig. 4(b) the corresponding entropies are presented. The positions of local entropy minima do depend on $k$ whereas their depths are $k$ independent.

The origin of such a characteristic nonmonotonic behavior of $L$ particles is the interplay between the dynamics of $L$ and $H$ particles. As seen from Eq. (3) the $H$ particles reach their equilibrium with the relaxation time $\tau_H$, obviously independent of $L$ particles. The relaxation of $L$ particles is strongly perturbed by the $H$ particles in

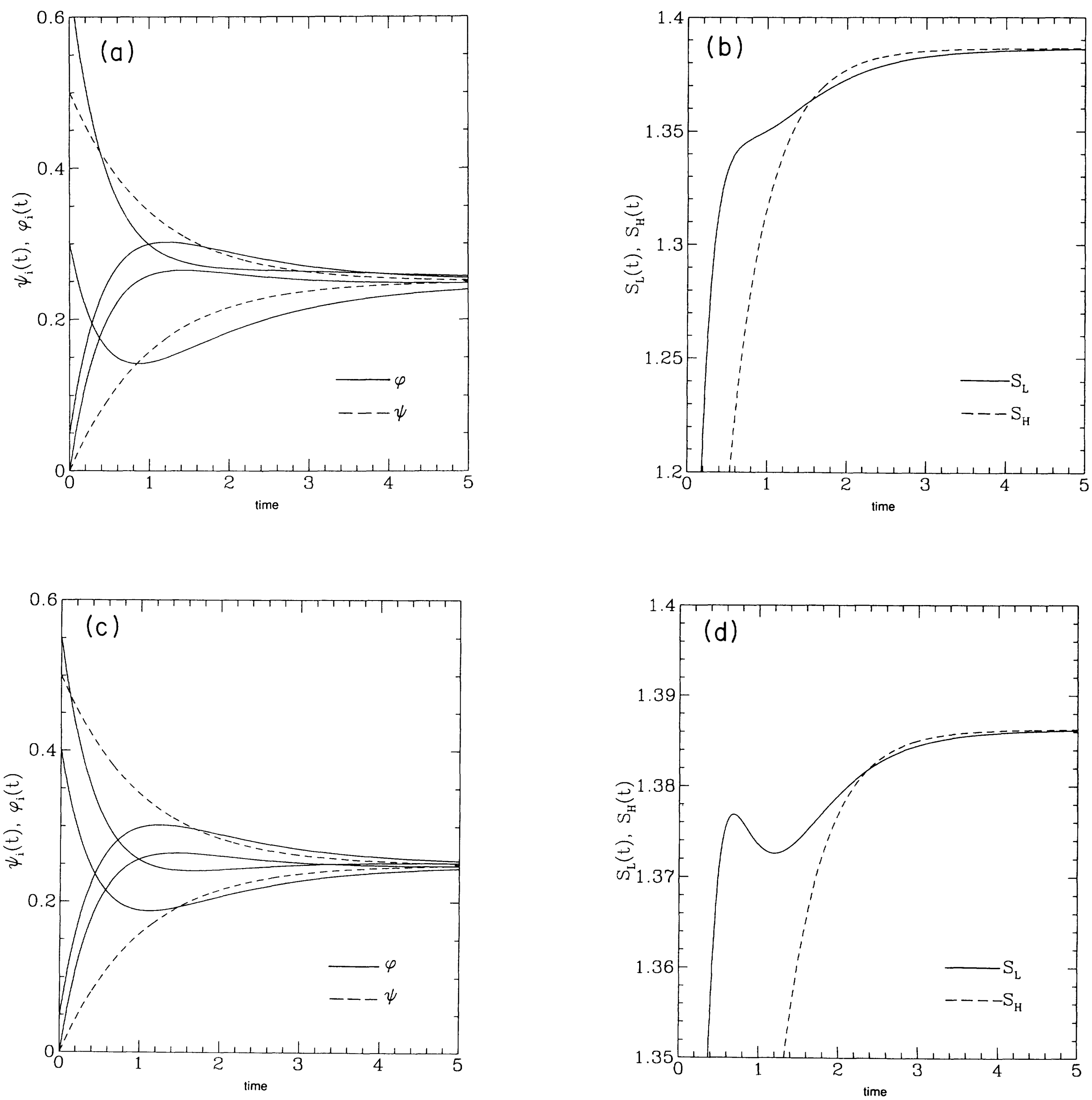


FIG. 2. Dimensionless one-particle distribution functions $\psi_i(t)$ and $\varphi_i(t)$ [Eqs. (4)–(6)] and dimensionless partial entropies $S_H(t)$ and $S_L(t)$ [Eq. (7)] plotted as a function of time for $h=g=k=1$: (a) $\psi_1(t)=\psi_3(t)$ and $\psi_2(t)=\psi_4(t)$ for $\psi_1(0)=\psi_3(0)=\frac{1}{2}$; $\varphi_i(t)$ ($i=1,\ldots,4$) for $\varphi_1(0)=0$, $\varphi_2(0)=0.3$, $\varphi_3(0)=0.05$, and $\varphi_4(0)=0.65$; (b) $S_L(t)$ and $S_H(t)$ for the initial conditions of (a); (c) same as in (a), but for initial conditions $\varphi_1(0)=0$, $\varphi_2(0)=0.4$, $\varphi_3(0)=0.05$, and $\varphi_4(0)=0.55$; and (d) $S_L(t)$ and $S_H(t)$ for the initial conditions of (c).

the $t$ region where $\psi_i(t)$ is far from the equilibrium values $\psi_i(\infty)=\frac{1}{4}$. The measure of this perturbation is the strength of the coupling constants $g$ and $k$, relative to $h$. For $g=0$ and the times for which $\psi_i(t)=\frac{1}{4}$ ($H$ particles practically "thermalized"), the model reduces to the original wind-tree model [11] with a perfect monotonic behavior of $\varphi_i(t)$. For $g\neq0$ and small values of $k$ the overshoots of $\varphi_i(t)$ appear. These anomalies in $\varphi_i(t)$ result as the $L$ particles are first dragged on by the $H$ particles (which are out of equilibrium) before they can relax themselves toward their own equilibrium. The anomalies increase as the coupling $k$ increases. We note that the whole range of coupling constants (with the restriction that $\gamma$ is an integer or a half-integer) can be explored easily. We stress that it is only the partial entropy of the system of light particles which displays an anomaly as a function of time. The total entropy $S(t)$, Eq. (7), is a perfectly increasing function of time and consequently Boltzmann's $H$ theorem [20] is not violated. It is worth mentioning here that the possible existence of a *subsystem* which does not satisfy the $H$ theorem is frequently evoked and amply discussed in the textbooks [20,21].

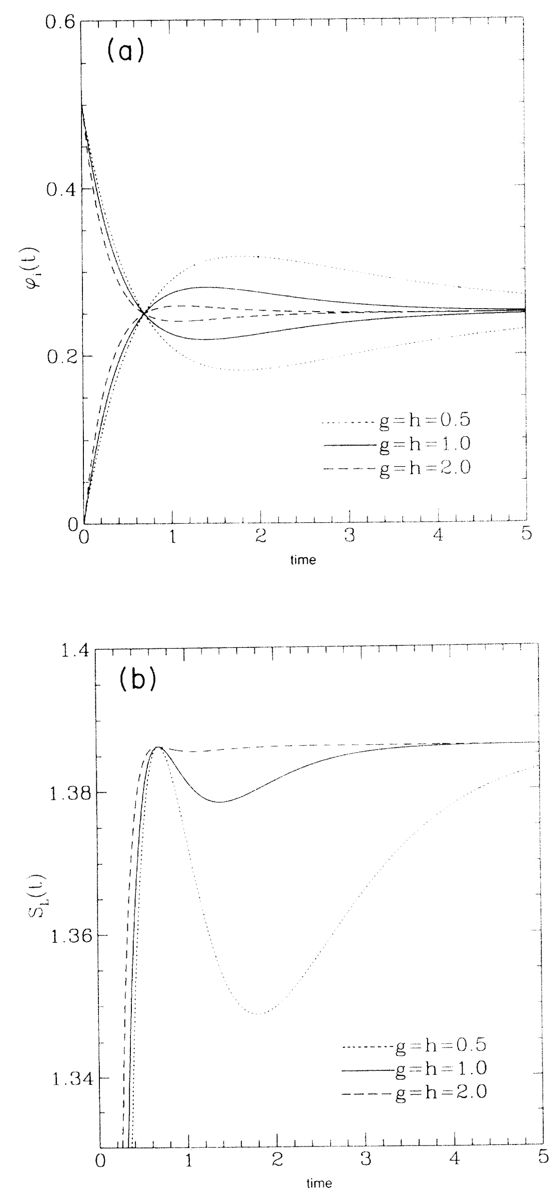


FIG. 3. Dimensionless one-particle distribution functions $\varphi_i(t)$ [Eqs. (4)–(6)] and dimensionless partial entropies $S_H(t)$ and $S_L(t)$ [Eq. (7)] plotted as a function of time for $k=1$, for different values of $g=h$: (a) $\varphi_1(t)=\varphi_3(t)$ and $\varphi_2(t)=\varphi_4(t)$ for $\psi_1(0)=\psi_3(0)=0$, and $\varphi_2(0)=\varphi_4(0)=\frac{1}{2}$ and (b) $S_L(t)$ for the initial conditions of (a).

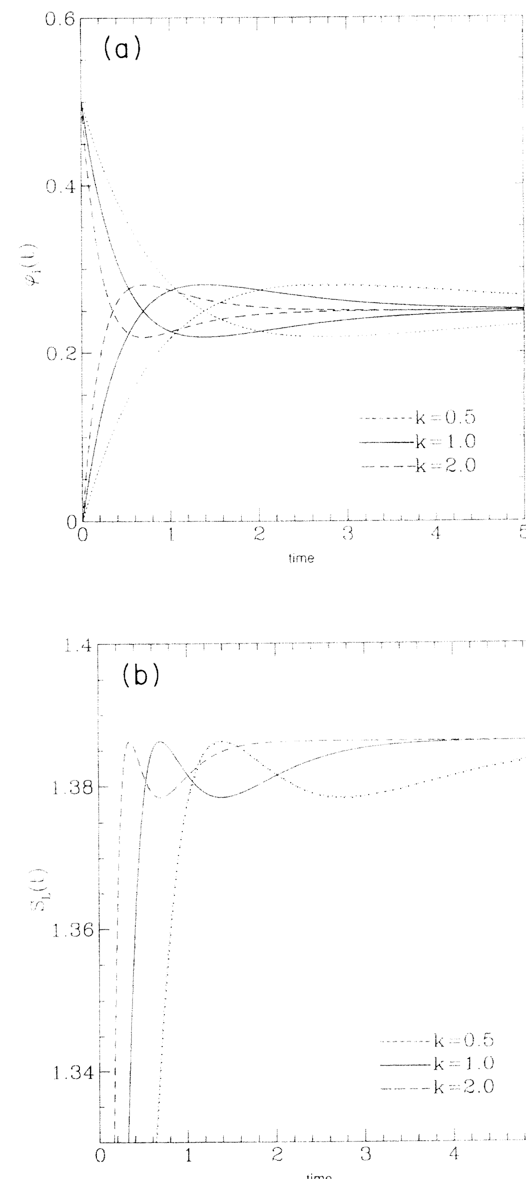


FIG. 4. Dimensionless one-particle distribution functions $\varphi_i(t)$ [Eqs. (4)–(6)] and dimensionless partial entropies $S_H(t)$ and $S_L(t)$ [Eq. (7)] plotted as a function of time for $g=h=1$ for different values of $k$: (a) $\varphi_1(t)=\varphi_3(t)$ and $\varphi_2(t)=\varphi_4(t)$ for $\psi_1(0)=\psi_3(0)=0$ and $\varphi_2(0)=\varphi_4(0)=\frac{1}{2}$ and (b) $S_L(t)$ for the initial conditions of (a).

The essence of this discussion is that the $H$ theorem is supposed to function for a closed isolated system satisfying certain conditions for collision processes. If such a system is broken up in, say, two distinct subsystems which are interacting, then the $H$ theorem has no reason to be satisfied by any of these systems separately. In fact it can be shown on some exceedingly simple models, such as the harmonic oscillator coupled to a heat bath (see [22]), that it is indeed the case. Concerning the truly interacting system we known of no concrete examples where this could be shown analytically. (In our previous work we could observe this phenomenon on a model whose one subsystem was noninteracting [8].) We have achieved it here with the help of an exactly soluble discretized kinetic model of two-dimensional interacting particles.

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[19] We quote here two representative examples of $I(\gamma)$ (for $a,b=$const):

$$I(5)=-\frac{ae^{y}}{4}\left[\frac{1}{y^4}+\frac{1}{3y^3}+\frac{1}{8y^2}+\frac{1}{8y}\right]+\frac{a}{24}\mathrm{Ei}(y)$$
$$-\frac{be^{-y}}{4}\left[-\frac{1}{y^4}+\frac{1}{3y^3}-\frac{1}{8y^2}+\frac{1}{8y}\right]-\frac{b}{24}\mathrm{Ei}(-y)\;,$$
$$I(\tfrac{13}{2})=-2ae^{y}\left[\frac{1}{11}\frac{1}{y^{11/2}}+\frac{2}{99}\frac{1}{y^{9/2}}+\frac{4}{693}\frac{1}{y^{7/2}}+\frac{8}{3465}\frac{1}{y^{5/2}}\right]$$
$$+\left[\frac{16}{10\,395}\frac{1}{y^{3/2}}+\frac{32}{10\,395}\frac{1}{y^{1/2}}\right]$$
$$-2a\frac{32}{10\,395}\sqrt{\pi}i\,\mathrm{erf}(i\sqrt{y}\,)$$
$$-2be^{-y}\left[\frac{1}{11}\frac{1}{y^{11/2}}-\frac{2}{99}\frac{1}{y^{9/2}}+\frac{4}{693}\frac{1}{y^{7/2}}-\frac{8}{3465}\frac{1}{y^{5/2}}\right]$$
$$+\left[\frac{16}{10\,395}\frac{1}{y^{3/2}}-\frac{32}{10\,395}\frac{1}{y^{1/2}}\right]$$
$$-2b\frac{32}{10\,395}\sqrt{\pi}\,\mathrm{erf}(\sqrt{y}\,)\;,$$

where $\mathrm{Ei}(y)$ and $\mathrm{erf}(y)$ are the exponential integral and the error function, respectively. Note that $i\,\mathrm{erf}(i\sqrt{y}\,)$ is for $y>0$ a *real* function related to Dawson's integral [see *Handbook of Mathematical Functions*, edited by M. Abramowitz and I. A. Stegun (Dover, New York, 1971)].
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