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# Approach to Equilibrium of a Boltzmann-Equation Solution

Robert M. Ziff
*Department of Mechanical Engineering, State University of New York, Stony Brook, New York 11794*

and

Sofia D. Merajver
*Department of Chemistry, Polytechnic Institute of New York, Brooklyn, New York 11201*

and

G. Stell
*Departments of Mechanical Engineering and Chemistry, State University of New York, Stony Brook, New York 11794*
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The generalized $H$ theorem, $(-d/dt)^n H \geq 0$, is verified for $n \leq 30$ for the Bobylev-Krook-Wu solution of the Boltzmann equation, and for $d$-dimensional generalizations of that solution, $1 \leq d \leq 6$.

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According to the $H$ theorem of Boltzmann, the approach to equilibrium for any solution $f(v,t)$ of the Boltzmann equation (BE) is accompanied by a monotonic decrease in the value of the $H$ function, which is defined by

$$H(t) \equiv \int f(v,t) \ln f(v,t)\, d\vec{v}. \tag{1}$$

Thus $dH/dt \leq 0$, equality holding for equilibrium. A possible extension of the $H$ theorem, first discussed by McKean[1] and Harris,[2] states that *all* derivatives of $H(t)$ approach their equilibrium value of zero monotonically, or equivalently that the successive derivatives of $H$ alternate in sign:

$$(-1)^n d^n H/dt^n \geq 0, \quad n = 1, 2, 3, \ldots . \tag{2}$$

If this very strong result were proven to be true, it would imply that the approach to equilibrium for the nonlinear BE is "infinitely smooth," with no oscillations or change in sign in any derivative. As McKean has conjectured, this "super $H$ theorem" might also serve the purpose of distinguishing the $H$ function defined in (1) from a large class of functions that also lead, monotonically, to the correct value of the entropy when equilibrium is attained and thus would make (1) the unique definition of an off-equilibrium "entropy" functional.

The validity of the alternating derivative property has been examined in many situations. Harris,[2-6] Simons,[7,8] Shear,[9] McElwain and Pritchard,[10] Yao,[11] and Rouse and Simons[12,13] have verified (1) for various restricted kinetic models, both linear and nonlinear, in some cases for all $n$, while in other cases for just a few values of $n$. The validity of (2) for the *linearized* BE, which is valid close to equilibrium, has been proven for all $n$[4,7,8] On the other hand, for a solution of the Bhatnagar-Gross-Krook (BGK) equation for Maxwell molecules, Simons[14] has found that (2) fails for $n = 11$. We also note that, in a discrete model, Maass[15] has found a counterexample to the conjecture that (2) implies $H$ uniquely. A related question that has been examined is whether, in near-equilibrium transport processes, the thermodynamic entropy satisfies an alternating derivative property analogous to Eq. (2). Simons[16-18] has shown that for many physical processes, such as heat conduction, the entropy is convex ($\ddot{S} \geq 0$). However, for the actual, spatially homogeneous BE, neither a general proof of (2), nor a counterexample, has been found. Indeed, the only models where (2) has been shown to hold for all $n$ are very simplified caricatures of the BE.

In this Letter we consider the verification of (2) for an exact solution to the BE. Of course, while a counterexample to (2) would disprove it, a particular solution that is shown to satisfy (2) only lends support to the conjecture. On the other hand, the investigation of the $H$ function of any exact solution of the BE is of considerable interest in itself, illuminating the way in which the gas described by the BE relaxes into equilibrium from the particular initial state that corresponds to that solution. We consider the exact solution of the BE, for a system of Maxwell molecules, found by Bobylev[19] and by Krook and Wu[20] (BKW). Rouse and Simons[13] have shown that (2) is satisfied for this solution, for $n = 2$ only. We derive a general expression for the $n$th derivative of $H$ for the BKW solution that allows (2) to be tested for all $n$, although to determine the sign of the derivatives, numerical calculations are required. More generally, we consider a $d$-dimensional generalization of the BKW solution,[21-23] which includes, when $d = 2$, an exact solution of the Tjon-Wu model.[24]

The $d$-dimensional generalization of the three-dimensional BKW solution is given by[21-23]

$$f(v, t) = \frac{\exp(-v^2/2\alpha)}{(2\pi\alpha)^{d/2}}\left[\frac{2\alpha - d + d\alpha}{2\alpha} + \frac{v^2}{2}\left(\frac{1-\alpha}{\alpha^2}\right)\right], \tag{3}$$

where $\alpha \equiv 1 - e^{-t}$. The time, $t$, has been scaled by a constant, $\lambda$, which depends upon the angular dependence of the differential scattering cross section (which is assumed to be inversely proportional to the relative velocity). The requirement that $f$ be positive implies that $t \geq \ln[(d+2)/2]$.

Transformed to the variable $x = v^2/2$, (1) becomes

$$H = \frac{(2\pi)^{d/2}}{\Gamma(d/2)} \int_0^\infty x^{d/2-1} f \ln f \, dx, \tag{4}$$

where the fact that the surface area of a sphere in $d$ dimensions equals $2\pi^{d/2}/\Gamma(d/2)$ has been used. Inserting the $f$ of (3) into (4) we get an explicit expression for $H$, but because of the logarithm, the integral cannot be performed in closed form. A substantial simplification occurs upon differentiating $H$ with respect to $t$, rearranging terms, and integrating by parts. We find

$$\frac{dH}{dt} = -\frac{1}{\Gamma(d/2)(e^t - 1)^2} \int_0^\infty \frac{x^{1+d/2} e^{-x}\, dx}{(x+y)^2}, \tag{5}$$

where $y \equiv e^t - 1 - d/2$. The requirement that $t \geq \ln[(d+2)/2]$ implies simply $y \geq 0$. This integral can be expressed as the hypergeometric function $U$, defined by[25]

$$\Gamma(a) U(a, b, z) \equiv \int_0^\infty e^{-zt} t^{a-1} (1+t)^{b-a-1}\, dt. \tag{6}$$

Applying Kummer's transform,[25]

$$U(a, b, z) = z^{1-b} U(1 + a - b, 2 - b, z), \tag{7}$$

we find an alternative expression for (5):

$$\begin{aligned}\frac{dH}{dt} &= -\frac{d(d+2)}{4(e^t - 1)^2} \int_0^\infty \frac{x e^{-yx}\, dx}{(1+x)^{2+d/2}} \\ &= -\frac{d(d+2)}{4(e^t - 1)^2} u_{1,d}(y),\end{aligned} \tag{8}$$

where we define

$$u_{n,d}(y) \equiv \int_0^\infty \frac{x^n e^{-yx}\, dx}{(1+x)^{2+d/2}}, \tag{9}$$

which is more convenient than $U$. Now because $(e^t - 1)^{-1}$ has the alternating-derivative property, and because products of functions with this property also have this property, it is sufficient to prove that $h$, defined by

$$\frac{dh}{dt} \equiv u_{1,d}(y) \tag{10}$$

satisfies

$$(-1)^n \frac{d^n h}{dt^n} \leq 0, \quad n = 1, 2, 3, \ldots. \tag{11}$$

Differentiating (10), one finds that

$$\frac{d^2 h}{dt^2} = -e^t u_{2,d}(y) \leq 0, \tag{12}$$

$$\frac{d^3 h}{dt^3} = -e^t u_{2,d}(y) + e^{2t} u_{3,d}(y), \tag{13}$$

$$\vdots$$

$$\frac{d^n h}{dt^n} = \sum_{i=1}^{n-1} (-1)^i e^{it} a_{i,n} u_{i+1,d}(y), \tag{14}$$

where the positive $a_{i,n}$ satisfy

$$a_{i,n} = i a_{i,n-1} + a_{i-1,n-1} \tag{15}$$

with $a_{1,n} = 1$, $a_{n,n} = 0$ ($n = 2, 3, 4, \ldots$). Although the second derivative, (12), is clearly negative, the sign of the higher derivatives is not obvious. We shall find their sign by numerically evaluating the terms of (14).

For each value of $t$ or $y$, we must calculate the $u_{i+1,d}$. First $u_{0,d}$ is calculated; it is related to the incomplete $\Gamma$ function or (for even $d$) the exponential integral:

$$u_{0,d}(y) = e^y y^{1+d/2}\Gamma(-1-d/2, y) = e^y E_{2+d/2}, \tag{16}$$

which can be evaluated by series expansions for small $y$ and by a continued-fraction series for large $y$.[26] Then the $u_{n,d}$ follow by

$$y u_{n+1,d}(y) = n u_{n-1,d}(y) + (n - y - 1 - d/2) u_{n,d}(y) \tag{17}$$

which results from (9). When $n = 0$, the term $n u_{n-1,d}$ should be taken as 1. After calculating the $a_{i,n}$ by the recursion relation (15), the expression for the derivatives of $h$, (14), may be evaluated.

We carried out the above procedure, for $d = 1$ to 6, taking a wide range of $y$, and for $n$ up to 30. Because of the cancellations that occur with the alternating terms of (14), we utilized double precision, significant to 33 figures. We find that the McKean conjecture is satisfied for all cases that we considered. For example, the results for $d = 3$ are shown in Fig. 1, where the first twenty derivatives of $h$ are plotted as a function of $t$.

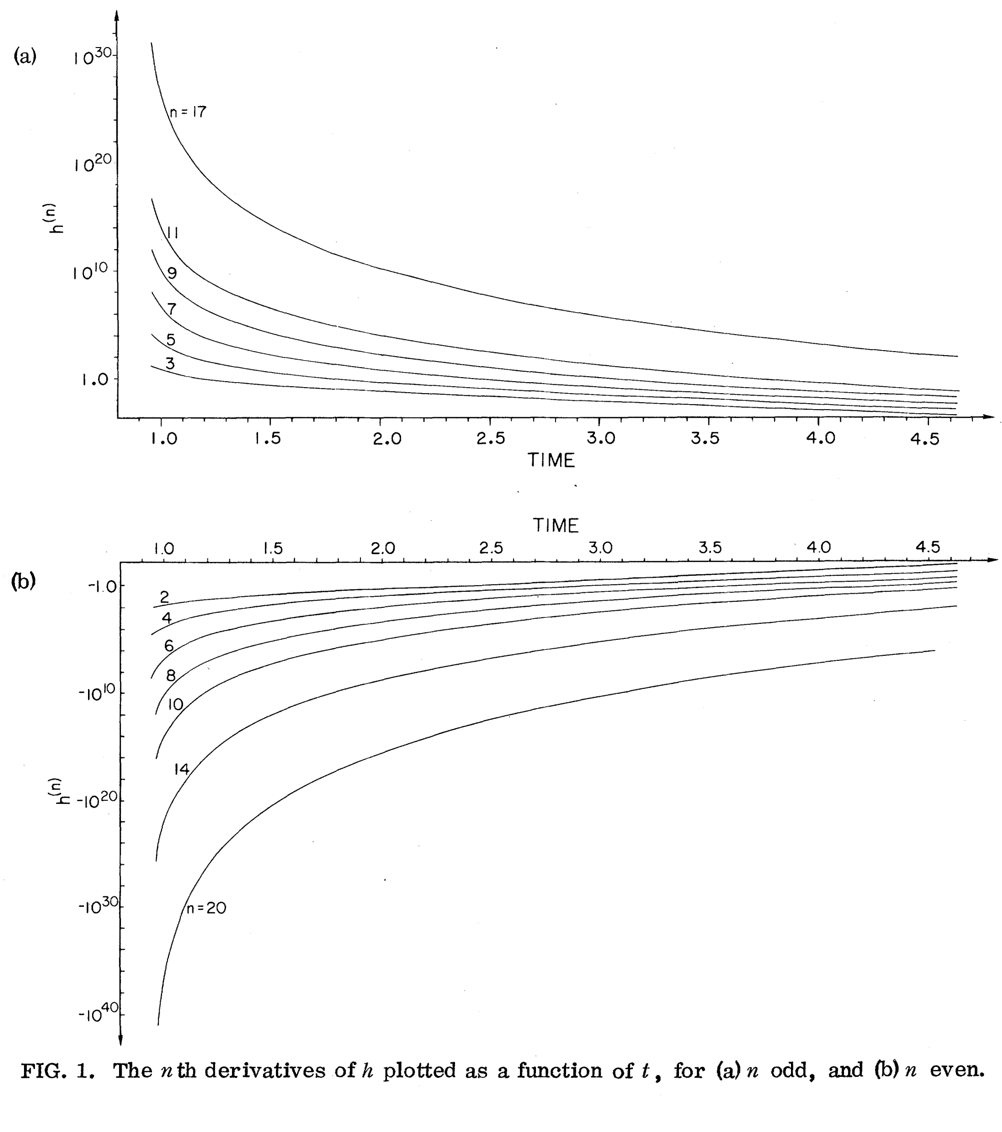


FIG. 1. The $n$th derivatives of $h$ plotted as a function of $t$, for (a) $n$ odd, and (b) $n$ even.

The validity of (2) for large $t$ (or $y$) is already implied by the linearized BE. Our results strongly support the conclusion that (2) holds for all $n$, $d$, and $y \geq 0$.

Note that the approach to equilibrium for the distribution function itself, $f(v, t)$, is not monotonic since for some values of $v$, $\partial f / \partial v$ changes sign at a certain point in time. Yet the $H$ function is monotonic in all the derivatives that we calculated. The solution, (3), starts off very far from equilibrium with no particles of zero velocity.

This is the first solution of the true BE that has been shown to satisfy (2) to such high order of differentiation. We present our results in the hope that they will stimulate further work that will yield a rigorous proof of (2) for the solution that we have considered.

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# Effective-Medium Approximation for Diffusion on a Random Lattice

Itzhak Webman
*Departments of Mathematics and Physics, Rutgers University, New Brunswick, New Jersey 08903*
(Received 11 September 1981)

A self-consistent effective-medium approximation is presented for the problem of diffusion and ac conductivity on a lattice characterized by random values of transfer rates between pairs of nearest-neighbor sites. The approximation is applied to a percolation model in which only a fraction of the bonds are assigned a finite transfer rate. The results reflect the existence of a percolation threshold in the system, and are consistent with the properties of clusters of bonds in the critical region.

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There is a rapidly growing interest in the problem of classical diffusion in random systems.[1-3] It is relevant to a number of physical processes in disordered media such as dispersive hopping transport in amorphous semiconductors[1,2,4] and the migrations of localized electronic excitations among guest molecules in a host.[5,6] The main current theoretical approach to these phenomena is based on the continuous-time random-walk theory.[1,2,4,7] Alternative methods were recently used to study the problem of one-dimensional systems where some aspects of it can be treated more rigorously.[3,8,9]

In this communication a new self-consistent effective-medium approximation (EMA) is proposed for the related problem of diffusion on a lattice characterized by random values of transfer rate $W_{n'n} = W_{nn'}$ between pairs of nearest-

 