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Non Existence of a Density Expansion of the Transport Coefficients in a Moderately Dense Gas

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Abstract Two examples of developments in Statistical Mechanics, on whose success the experts agreed, are discussed. First and foremost, a systematic generalization of the Boltzmann equation for a dilute gas from binary to higher order particle collisions, expected to lead to a density expansion of the transport coefficients. This would imitate, in nonequilibrium, the density expansion of the thermodynamic quantities in equilibrium. However, by studying concrete models, it became clear that because of the neglect of collective collision effects, not relevant in equilibrium, the purely formal expressions for the transport coefficients obtained this way exhibited divergences. Secondly, a related purely mechanical problem, concerned the question of the maximum number of collisions between three identical hard balls in infinite space. The answer, on intuitively convincing grounds, was generally accepted to be three, as in one dimension. Also this was incorrect, as a computer simulation first showed.

The message here is: beware for common opinions and purely formal or intuitive arguments: test them on concrete models first.

Keywords Divergences · Density expansions · Transport coefficients · Nonequilibrium gas · Maximum collision number · Three hard balls

1 Introduction

After World War II there was a widespread interest in Statistical Mechanics to generalize the Boltzmann Equation for a dilute gas, which takes into account only binary collisions, systematically to higher density gases. This would imply taking into account higher order

This paper is neither a survey nor a historical paper, but a re-collection and interpretation of the author of what happened in what someone called "The Bronze Age of Statistical Mechanics (1956)" (D. Levermore).

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i.e. 3-particle, 4-particle etc. collisions. There was general agreement that such generalization should be possible and would then lead to density (or virial) expansions of the transport coefficients, in close analogy with the corresponding density expansions for the thermodynamic properties of a moderately dense gas in thermal equilibrium.

I. Prigogine organized in 1956 a large meeting to that effect in Bruxelles, which was partially devoted to this question. Almost all leaders in Statistical Mechanics at the time were present, such as J.G. Kirkwood, J.E. Mayer, M.G. Mayer, E.W Montroll, G.E. Uhlenbeck, L. Van Hove and J. Yvon, apart from Prigogine, and many other—especially very active younger participants—such as M.S. Green, J.L. Lebowitz and J. Ross [1].

In particular it was discussed, which of the many different existing derivations of a generalized Boltzmann Equation, was the correct one. There appeared to be no doubt, however, that such a generalization and the ensuing virial expansion of the transport coefficients could be realized.

After two hours of intense discussions of the various proposed derivations of a generalized Boltzmann Equation, D.K.C. MacDonald asked the question: "Could somebody tell me what the Boltzmann Equation precisely is?". To this, G.E. Uhlenbeck described calmly and very briefly, for a somewhat stunned audience, the answer given here:

"The Boltzmann Equation of 1872 is:

$$\frac{\partial f}{\partial t} = -\boldsymbol{v} \cdot \frac{\partial f}{\partial \boldsymbol{r}} + J_2(ff)". \tag{1}$$

Here $f = f(\boldsymbol{r}, \boldsymbol{v}, t)$ is the average number of gas particles around the position $\boldsymbol{r}$, with velocity $\boldsymbol{v}$ at time t, in a unit volume element in a 6 dimensional phase-space (μ-space or $\boldsymbol{r}, \boldsymbol{v}$-space) $\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{v} \equiv \mathrm{d}x\mathrm{d}y\mathrm{d}z\mathrm{d}\mathbf{v}_x\mathrm{d}\boldsymbol{v}_y\mathrm{d}\boldsymbol{v}_z$, centered around $\boldsymbol{r}, \boldsymbol{v}$. The lhs (left-hand side) of (1) gives the rate of change of f as the sum of the two terms on the rhs (right-hand side) of (1).

The first term on the rhs of (1), the streaming term, gives the change, per unit time, in the average number of particles with velocity $\boldsymbol{v}$ in a unit volume element $\mathrm{d}\boldsymbol{r}\ \mathrm{d}\boldsymbol{v}$.

The second term gives the average number, per unit volume and time, of binary, i.e. two particle, collisions in the dilute gas, based on a statistical assumption and on the (collision) dynamics of two particles alone in infinite space, as indicated by the subscript 2 on the J_2, which involves the product of two f-functions, referring to the two colliding particles, respectively.

Before discussing the generalization of the Boltzmann Equation, I will first remind the reader of the "exemplary" density expansion of the thermodynamic properties (e.g. the pressure) of a moderately dense gas in equilibrium.

The "self-evidence" of the existence of a density expansion was based on the intuitively "obvious" observation that the probability for two-, three-, four-, etc. particle collisions in a unit volume would, "of course", be proportional to corresponding increasing powers of the density i.e. n^2, n^3, n^4 etc., respectively, of the gas.[1]

This was first achieved by J.E. Mayer in 1937 [2] and reads for the pressure $p(n, T)$ of a gas in equilibrium:

$$p(n, T) = k_B T[n + B(T)n^2 + C(T)n^3 + D(T)n^4 + \cdots], \tag{2}$$

where n is the number density and T the absolute temperature of the gas, while k_B is Boltzmann's constant. In this virial (density) expansion of the pressure, the first term on the rhs

[1] If the gas consists of N-particles and is contained in a volume V, then the (number) density of the gas $n = N/V$.

$\sim n$ is the single particle or ideal gas contribution, the second term $\sim n^2$ the contribution of two particles with prefactor $B(T)$, the second virial coefficient, the third term $\sim n^3$, the three particle contribution with prefactor the third virial coefficient $C(T)$ and the fourth term $\sim n^4$, with prefactor the fourth virial coefficient $D(T)$, etc.

The structure of these and all other (higher) virial coefficients is such, that they consist of isolated clusters of an increasing number of particles, which are so constructed, that they are only different from zero, if they have the *cluster property*, i.e. all particles in a cluster must interact with each other and if not, then those contributions to the corresponding virial coefficients vanish.

In this paper I assume additivity of the intermolecular forces and a spherically symmetric intermolecular potential field between two particles 1 and 2, $\varphi(r_{12})$, i.e. only dependent on their distance r_{12}, with a sufficiently short range. Then the second virial coefficient reads:

$$B(T) = -2\pi N \int_0^\infty [\exp -(\varphi(r_{12}))/k_B T - 1] r_{12}^2 dr_{12}. \tag{3}$$

Thus, the integrand on the rhs of (3) vanishes, if there is no interaction between the two particles 1 and 2, i.e. when $\varphi(r_{12}) = 0$. $B(T)$ gives therefore an *extra* contribution to p, not contained in the previous (ideal gas) term. Similarly all the higher virial coefficients $C(T)$ etc. vanish, unless the particles they contain interact at least once with each other and then give, similar to $B(T)$, extra contributions to $p(n, T)$ not present in the previous virial coefficients.

If the potential $\varphi(r_{12})$ is, e.g., a 12-6 Lennard-Jones potential,[2] the integrand in (3) will vanish sufficiently fast for $r_{12} \to \infty$ for the $B(T)$ to exist. The same property obtains for all higher virial coefficients. The finiteness of all the virial coefficients has allowed Ruelle to prove that the virial expansion is a convergent expansion for sufficiently small gas densities n [6].

It is worthwhile to remark that the existence of a virial expansion for a gas in equilibrium is in a way a "miracle", since it allows a property of the entire N-particle gas ($p(n, T)$) to be systematically expressed in terms of an increasing number of small 1, 2, 3, etc. isolated particle clusters. In other words: the daunting N-particle dynamical many body problem has been reduced to static 2, 3, etc. few body (particle) problems.

As said, the general expectation in the Statistical Mechanical community was for a "long" time, that the same had to be true for a gas in a non-equilibrium state.

2 Bogolubov's Generalized Boltzmann Equation

Although many different approaches to obtain such a generalized Boltzmann Equation were attempted, the one originally proposed by N.N. Bogolubov in 1946 appeared to be the most promising, since it mimicked, on the level of μ-space or $\boldsymbol{r}$, $\boldsymbol{v}$-space, the structure of the virial expansion (2) in ordinary space:[3]

$$\frac{\partial f}{\partial t} = -\boldsymbol{v} \cdot \frac{\partial f}{\partial \boldsymbol{r}} + J_2(ff) + J_3(fff) + J_4(ffff) + \cdots, \tag{4}$$

[2]The 12-6 Lennard-Jones potential as written in the standard form by de Boer and Michels [3–5] is: $\varphi(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6]$, where ε is the depth of the potential at its minimum and σ its "diameter", i.e. $\varphi(\sigma) = 0$.

[3]The index n in J_n indicates the number of particles involved in J_n and should not be confused with the average particle number density n (cf footnote 2).

as was particularly emphasized by G.E. Uhlenbeck [7], where the index n of the collision operators $J_n(f \ldots f)$ $(n = 2, 3, 4, \ldots)$ indicates the number of particles in the cluster.

Furthermore, each of the f in a cluster $J_n(f \ldots f)$ in (4) depends on the position and the velocity of one of the cluster particles, respectively, as well as on the time.

Finally the $J_n(f \ldots f)$ in (4) are integrals over infinite space over the positions and velocities of all $(n-1)$ particles in the cluster, except over particle 1, and posses the *cluster property* i.e., each particle in a cluster must have at least one collision with another cluster particle (including particle 1); if not, their contributions to J_n vanish (cf. Fig. 1(b)).

Comparing the equilibrium virial expansion (2) with the expansion (4), one sees that the right-hand sides of these two expansions exhibit a certain formal correspondence in structure and that the role of the equilibrium density n is, in non-equilibrium, taken over by the non-equilibrium single particle distribution function $f(\boldsymbol{r}, \boldsymbol{v}, t)$. "Collide" means in (4) a real dynamical collision, not just a (static) interaction of particles as e.g. in (3).

It should be emphasized again that the structure of the J_n is similar to that of the corresponding virial coefficients in equilibrium involving n interacting particles, in that they have both the *cluster property*, i.e. they vanish unless all n particles interact or collide at least once with another particle in the cluster. Therefore the term J_n contains only *extra* contributions to $\frac{\partial f}{\partial t}$ from n colliding particles, which were not contained in the previous J_m with $m < n$.

I will restrict myself here to a brief discussion of Bogolubov's work [8, 9]. Bogolubov actually arrived at an equation of a much more complicated form than (4). He obtained his generalized Boltzmann Equation as a special solution of the basic Liouville equation for the N-particle system in the $6N$ dimensional phase space $\Gamma = \{\boldsymbol{r}_1, \boldsymbol{v}_2, \ldots, \boldsymbol{r}_N, \boldsymbol{v}_N\}$ of the entire N-particle system. By integrating the Liouville Equation successively over the phases $\boldsymbol{r}, \boldsymbol{v}$ of an increasing number of particles, leads then to a hierarchy of coupled equations for all the distribution functions, which depend on $1, 2, 3, \ldots$ particles, respectively, while taking also the limits $N, V \to \infty$ with $N/V = n$. For details I refer to the literature [7]. This hierarchy was called by Uhlenbeck, the B-B-G-K-Y-hierarchy, named alphabetically, but not chronologically, after a number of (but not all) authors, who derived this hierarchy independently from the Liouville Equation: Bogolubov, Born and Green, Kirkwood and Yvon, where the latter was also the first [8–12].

In order then to obtain a single *closed* equation for $f(\boldsymbol{r}, \boldsymbol{v}, t)$, Bogolubov *assumed* that, after a characteristic time of the order of the duration of a collision, all higher order distribution functions of the gas in this hierarchy of coupled equations would, as far as their time evolution was concerned and depend only on that of the first (Boltzmann's) distribution function $f(\boldsymbol{r}, \boldsymbol{v}, t)$.

One should emphasize, that Bogolubov's original generalized Boltzmann equation was recursive, in that the n-particle collision term he obtained, was expressed as a sum of $m \leq n$ particle collision contributions. It did not have therefore the obvious, virial-like, structure as (4) [13]. Later the much simpler formal virial-like expansion of (4) was derived [14].[4]

[4] In fact, non-equilibrium cluster expansions can be constructed formally [14] similar to those employed in equilibrium statistical mechanics to obtain density expansions of distribution functions or thermodynamic properties. Using those, the recursive Bogolubov expressions for the collision operators can be rewritten in a much more transparent form like (4), as a sum of diagrams for each particle cluster, which is identical to those appearing in the corresponding equilibrium virial coefficients for the thermodynamic properties, when expressed in terms of linear (Husimi) graphs [15]. In these graphs then, the vertices represent instead of the equilibrium density n, the Boltzmann distribution functions $f(\boldsymbol{r}, \boldsymbol{v}, t)$ of the various particles in the cluster, while the lines connecting the vertices represent instead of equilibrium (static) Boltzmann factors, non-equilibrium (dynamical) streaming operators [7]. It is this simplified form of the generalized Boltzmann

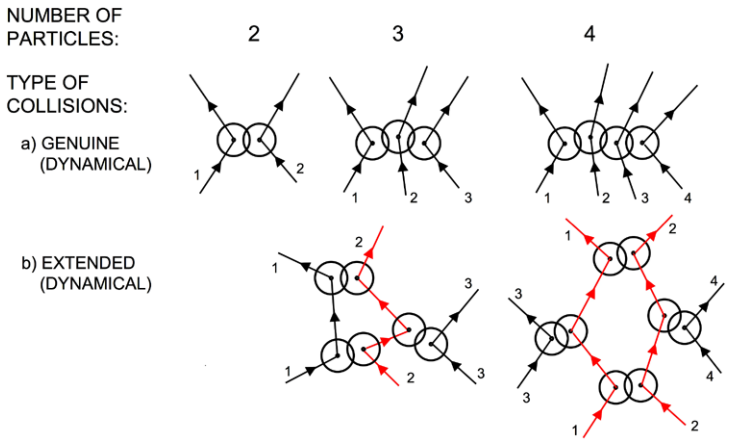

Fig. 1 (**a**) genuine two, three and four particle collisions, where all particles overlap; (**b**) extended three and four particle collisions. *Overlapping circles* represent particles at collision, interacting with a finite range interparticle potential. The velocities of the particles are indicated by *arrows*

In addition, the generalized Boltzmann Equation (4) is purely formal and it was tacitly assumed that this equation made physical sense. In fact, as will be shown in Sect. 4, it did not. To see this, a much more detailed analysis of the J_n with $n > 2$ in terms of the type of collisions between the n-particles in each J_n was needed first, than the formal manipulations used so far. I will restrict myself here to a very simplified presentation of what is involved here.

In Fig. 1, a binary and two different types of three and four particle collisions, are sketched for interparticle potentials with a finite range.

Except for binary collisions, for collisions between more than 2 particles there are a number of different classes of contributing collisions to the J_n of (4). The first class, illustrated in Fig. 1(a), is analogous to the "collisions" occurring in the equilibrium virial expansion: it is a "genuine" three or four etc. particle collision, where each cluster particle interacts "simultaneously" with all other particles in the cluster. However, as is illustrated in Fig. 1(b) for J_3 and J_4, there is another class of collisions, where two particles 1 and 2, say, collide, separate, but then after a finite time a third particle 3, collides with one of the original two particles, 2, causing a re-collision of the original pair 1, 2. The structure of the J_3-term is such that this type of (re) collision also makes a non-vanishing contribution to J_3 and similarly for J_4.[5]

A sketch of some such collisions between three and four particles, contributing to J_3 and J_4, respectively, is given in Fig. 1(b). The corresponding J_3-, J_4- etc. operators involve then integrals over all possible positions and velocities of the 3, 4, etc. particles, respectively, (except of particle 1) in their combined phase space.

Equation, exhibited formally in (4) which is amenable to treatment. It could, in principle, be used to obtain the *short* time behavior of the distribution function $f(\boldsymbol{r}, \boldsymbol{v}, t)$ for times $t/t_{\mathrm{mfp}} = O(1)$ of a moderately dense gas, where t_{mfp} is the duration of a mean free path.

[5]There are in addition, other types of collisions, which contribute to the J_n, e.g. collision sequences which prevent recollisions to take place between two particles, due to the "unfortunate" interception of one of the two particles by another particle in an "unfortunate deflecting" collision, so that the recollision never takes place. For more details, see [16].

Therefore the Bogolubov expansion has the same property as the equilibrium virial expansion, in that a property of the entire N-particle system, $\frac{\partial f}{\partial t}$, is expressed in terms of the dynamical (collision) properties of isolated groups of 2, 3, -particles in infinite space thus reducing the many particle dynamical problem to a sequence of dynamical problems of increasing numbers $(2, 3, 4, \ldots)$ of particles. The three particle collision term $J_3(fff)$ was first obtained by Bogolubov, almost 75 years after the two particle collision term $J_2(ff)$ of Boltzmann.

3 Expected Virial Expansion of Transport Coefficients

With the generalized Boltzmann equation of Bogolubov in the form (4) it appeared that a virial expansion of the transport coefficient had in principle been obtained. All that was further needed, was to go from a mesoscopic description of the gas in terms of $f(\boldsymbol{r}, \boldsymbol{v}, t)$ in $(\boldsymbol{r}, \boldsymbol{v})$ space to a macroscopic description of the gas in terms of the first five velocity moments of f, the five hydrodynamical quantities:

$$\text{the local density} \quad n(\boldsymbol{r}, t) = \int d\boldsymbol{v} f(\boldsymbol{r}, \boldsymbol{v}, t), \tag{5}$$

$$\text{the local velocity} \quad \boldsymbol{u}(\boldsymbol{r}, t) = \int d\boldsymbol{v}\boldsymbol{v} f(\boldsymbol{r}, \boldsymbol{v}, t), \tag{6}$$

$$\text{the local temperature} \quad \frac{3}{2} n(\boldsymbol{r}, t) T(\boldsymbol{r}, t) = \int d\boldsymbol{v} \frac{1}{2} m \boldsymbol{V}^2(\boldsymbol{r}, t) f(\boldsymbol{r}, \boldsymbol{v}, t). \tag{7}$$

Here the so-called peculiar velocity $\boldsymbol{V}(\boldsymbol{r}, t) = \boldsymbol{v} - \boldsymbol{u}(\boldsymbol{r}, t)$, is the velocity of a particle $\boldsymbol{v}$ with respect to the average local velocity at $\boldsymbol{r}$, $\boldsymbol{u}(\boldsymbol{r}, t)$, which is relevant for the proper definition of the transport coefficients.

This transition from $(\boldsymbol{r}, \boldsymbol{v})$ space to $\boldsymbol{r}$-space and then to hydrodynamics was accomplished much earlier for the Boltzmann Equation, independently by Chapman and Enskog (1916, 1917), using different but equivalent methods [17]. The same Chapman-Enskog procedure can be used to obtain a solution of the generalized Boltzmann Equation (4) and leads then to the five hydrodynamical equations for $n(\boldsymbol{r}, t)$, $\boldsymbol{u}(\boldsymbol{r}, t)$ and $T(\boldsymbol{r}, t)$.

The basic assumption here is similar to that made by Bogolubov to obtain the generalized Boltzmann Equation, in that after a characteristic time much larger than the mean free time t_{mfp} between two successive collisions of a gas particle, $f(\boldsymbol{r}, \boldsymbol{v}, t)$ would only depend on t via $n(\boldsymbol{r}, t)$, $\boldsymbol{u}(\boldsymbol{r}, t)$, $T(\boldsymbol{r}, t)$, the five hydrodynamical variables.

The Chapman-Enskog solution of the Boltzmann Equation (1), or of the generalized Boltzmann Equation (4), is obtained by considering a special solution of this equation. It is assumed then, that the space and time dependence of $f(\boldsymbol{r}, \boldsymbol{v}, t)$ after a time $t \gg t_{\text{mfp}}$, (cf. (4)), is only *via* the first five (hydrodynamic) moments of f, so that with: $f(\boldsymbol{r}, \boldsymbol{v}, t) = f(\boldsymbol{r}, \boldsymbol{v} \mid n(\boldsymbol{r}, t), \boldsymbol{u}(\boldsymbol{r}, t), T(\boldsymbol{r}, t))$ and one has:

$$\frac{\partial f}{\partial t} = \frac{\partial f}{\partial n} \cdot \frac{\partial n}{\partial t} + \frac{\partial f}{\partial \boldsymbol{u}} \cdot \frac{\partial \boldsymbol{u}}{\partial t} + \frac{\partial f}{\partial T} \cdot \frac{\partial T}{\partial t}, \tag{8}$$

where in the last equation the arguments $\boldsymbol{r}, \boldsymbol{v}, t$ have been dropped. If one then makes an expansion in the spatial gradients of $n, \boldsymbol{u}, T$, i.e. in $\frac{\partial n}{\partial \boldsymbol{r}}$, $\frac{\partial \boldsymbol{u}}{\partial \boldsymbol{r}}$, $\frac{\partial T}{\partial \boldsymbol{r}}$, then to lowest order in these gradients, the Euler equations, while to first order in the gradients, the Navier-Stokes equations of hydrodynamics are found, respectively, [13]. Suffice it here to say that the latter

express the time derivatives of $n(\boldsymbol{r},t)$, $\boldsymbol{u}(\boldsymbol{r},t)$ and $T(\boldsymbol{r},t)$ in terms of their first order spatial derivatives or gradients.

There are only two basic ingredients in the hydrodynamic equations for the five hydrodynamical quantities (5)–(7). (1) The five conservation laws of mass, momentum and energy and (2) A linear assumption of the relation between the momentum or the heat currents (flows) and their corresponding gradients. In particular, the xy-component P_{xy} of the pressure tensor (i.e. the flow of x-momentum in the y-direction in a shearing fluid), is then given by

$$P_{xy} = -\eta \frac{\partial u_x}{\partial y}, \tag{9}$$

while the heat flow vector $\boldsymbol{J}$ is given by

$$\boldsymbol{J} = -\lambda \frac{\partial T}{\partial \boldsymbol{r}}. \tag{10}$$

Here the coefficients of proportionality between the currents and the gradients are the transport coefficients: the shear viscosity η, and the thermal or heat conductivity λ, respectively. The $\boldsymbol{r},t$ dependences of η and λ via $n(\boldsymbol{r},t)$ and $T(\boldsymbol{r},t)$ are here, and from now on, suppressed.

The Chapman-Enskog solution of the generalized Boltzmann Equation leads then to a formal density expansion of the transport coefficients, in particular for the shear viscosity, of the form:

$$\eta(n,T) = \eta_0(T) + \eta_1(T)n^* + \eta_2(T){n^*}^2 + \cdots, \tag{11}$$

where a dimensionless density n^*, has been used which e.g. for hard balls of diameter σ in d dimensions equals $n\sigma^d$.

The first term $\eta_0(T)$ on the rhs of (11) is the Chapman-Enskog result for the Boltzmann Equation (1). An explicit expressions for $\eta_0(T)$ in terms of the interparticle forces (cf footnote 2), which determine the dynamics of the binary collisions contained in the Boltzmann Equation, were obtained by Chapman and Enskog in 1917, which agrees for a realistic (e.g. Lennard-Jones-like potential (see footnote 2)) very well with experiment. Choh and Uhlenbeck were the first to obtain a formal expression, based on the formal term $J_3(fff)$, for $\eta_1(T)$ in 1957, forty years later than Chapman and Enskog did for $\eta_0(T)$ based on $J_2(ff)$. For hard spheres $\eta_1(T)$ agrees well with computer simulations for moderate gas densities [18, Fig. 1]. $\eta_2(T)$ contains the contributions of four particle collisions in $J_4(ffff)$ in (4) etc.

Comparing the expansion in (11) for the non-equilibrium transport coefficient η in powers of n^* with the expansion in (2) for the equilibrium thermodynamics quantity p in powers of n, one sees that they are formally identical.

4 Divergences in the Non-equilibrium Virial Expansion

For about ten years after the Brussels meeting, the various approaches to a derivation of a generalized Boltzmann Equation converged to the result of Bogolubov and the formal expression obtained by Choh and Uhlenbeck for the three particle correction of the viscosity, $\eta_1(T)$ stood as an explicit, though formal, expression for a transport coefficient in a gas beyond the dilute gas regime. However, when attempts were made to evaluate explicitly

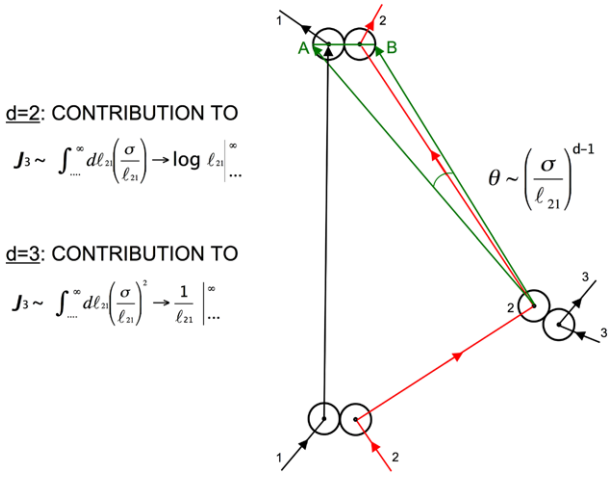

Fig. 2 An extended sequence of 3 collisions between three identical hard disks 1, 2 and 3, contributing to $J_3(fff)$: (12) (23) (12) (cf Fig. 1(b)). Without the intermediate (23) collisions, there would be no contribution to $J_3(fff)$. In $d = 2$ the necessary (12) recollision for a contribution to $J_3(fff)$ can only take place if particle 3 directs, after its collision with 2, particle 2 to collide with (far away) particle 1, thus creating a recollision between particles 1 and 2. The (1, 2) recollision can only occur if particle 3 directs particle 2 to hit the line AB, which will require a target scattering angle $\theta \sim \sigma/\ell_{21}$, where ℓ_{21} is the distance between the (2, 3) and the (1, 2) recollision. Since the motion of the 3 particles is in the *infinite* plane the contribution to $J_3(fff)$ of these type of collisions will be $\sim \int_{...}^{\infty} (\sigma/\ell_{21}) d\ell_{21}$. Although the integral decreases with increasing ℓ_{21}, it does not decrease fast enough, so that a logarithmic divergent contribution results in $d = 2$. However, in $d = 3$, where an extra dimension perpendicular to the plane of the figure exists, the decrease for a recollision will be $\sim (\sigma/\ell_{21})^2$, which leads then to a finite contribution to $J_3(fff)$

the Choh-Uhlenbeck expression for e.g. a simple but concrete particle model, unexpected difficulties occurred.

In fact, in 1965, J. Weinstock [19], R. Goldman and E.A. Frieman [20] and J.R. Dorfman and E.G.D. Cohen [21, 22] found independently that divergences of the non-equilibrium virial coefficients occurred. In particular, for a two dimensional system of a gas of hard disks, $\eta_1(T)$ was found to diverge logarithmically, due to the unboundedness of the occurrence of extended three particle collisions, as sketched in Fig. 2 and is discussed in its caption. As the same figure indicates, for hard spheres there is convergence "by the skin of one's teeth", so that $\eta_1(T)$ then exists and consequently also three dimensional hydrodynamics with $\eta_0(T) + \eta_1(T)n^*$ as viscosity, could be used for a gas of sufficiently low density. In fact, using the above mentioned simplified expressions instead of the original Bogolubov expressions for the $\boldsymbol{J}_n$ and consequently also for the corresponding transport coefficient virial coefficients η_{n-2}, one can argue that the divergences decrease with increasing dimension, but are present for all $\boldsymbol{J}_n$ and η_{n-2} for $n \geq 4$.

5 Origin of the Divergences and Its Consequences

The physical reason that extended collisions in a non-equilibrium gas diverge is that they are collisions between a number of particles inside an *isolated* (from all other particles in the gas) cluster of particles in infinite space. It was the "miracle" of the corresponding virial coefficients in equilibrium, that, although they also involved integrals over infinite

space, actually they only extended over distances of the order of the (short) range of the interparticle forces. This occurred because the entire problem was static in the sense that it did not contain the time and therefore no dynamics and only "instantaneous" interaction or overlap contributions of particles were needed. To the contrary, collisions contributing to the (non-equilibrium) transport coefficients, do involve the time and the dynamics of the particles.

Although for the "genuine" n-particle collisions, when all particles collide simultaneously and therefore only have, a local, spatially restricted, time dependence, no divergent contributions to the transport coefficients can occur also in nonequilibrium, for the *extended* collisions they do, since unlimited infinitely long free paths are possible then between successive collisions (cf Fig. 1(b) and Fig. 2).

However, for any gas of finite density, on the average, no free path can exceed the mean free path very much. In fact, the mean free path is a *many* particle (collective) property of the entire (N-particle) gas and involves collisions not only between the particles inside conveniently constructed isolated clusters consisting of a "small" number of particles, but between *all* N gas particles. The mean free path is therefore a "many particle" not an "individual particle" effect. Thus for the transport—and presumably all other—physical properties of a non-equilibrium gas *no* reduction of the many (N-) particle gas to those of only (small) isolated groups of particles, can be made.

A consequence of the necessity of considering the mean free path as a cut-off of the free path between extended collisions is, that it implies, in the case of the two dimensional hard disk gas, that factors logarithmic in the density will appear. This, because in a real gas $\log t$ (cf Fig. 2) could not much exceed $\log t_{\rm mtp}$ and, since $t_{\rm mfp}$ is inversely proportional to the density of the gas: $t_{\rm mfp} \sim 1/n\sigma^d$, this leads to a term $\sim \log n^*$, logarithmic in the gas density.

Thus one would expect density expansions of the transport coefficients, illustrated here for the viscosity of the form:

$$d=2 \quad \eta(n,T) = \eta_0(T) + \eta_1'(T)n^* \log n^* + \eta_1''(T)n^* + \cdots, \tag{12}$$

$$d=3 \quad \eta(n,T) = \eta_0(T) + \eta_1(T)n^* + \eta_2'(T)n^* \log n^* + \eta_2''(T){n^*}^2 + \cdots, \tag{13}$$

of these expansion coefficients, η_1', η_1'' and η_2' have been computed analytically for a gas of hard disks ($d=2$) and a gas of hard spheres ($d=3$) explicitly to a high degree of approximation, between 1966 and 1983 by J.V. Sengers et al. [23–25] , respectively. The expansion (12) shows that the number of three particles collisions is—because of the "inner structure" of the extended collisions (cf Fig. 1(b))—not $\sim {n^*}^2$ but $\sim {n^*}^2 \log n^*$. Despite vigorous attempts, no convincing experimental confirmation of a term $\sim n^* \log n^*$ in $\eta(n,T)$ for $d=3$ has been achieved as yet [18].

6 Maximum Number of Collisions

The extended collisions also suggest a purely dynamical question, which in its simplest form reads: "What is the maximum number of collisions between 3 identical hard balls in d dimensions?"

At the same time of the belief in a generalized Boltzmann Equation and of a virial expansion of the transport coefficients, there was also a strong opinion, represented, amongst others, by Wigner and Uhlenbeck that the maximum number of the above mentioned collisions had to be 3. Their argument was simple (cf Fig. 3): in $d=1$, on a line, two hard

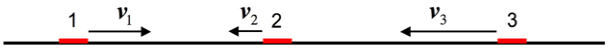

Fig. 3 Collisions between 3 hard rods: 1, 2, 3 (*red*) in $d = 1$, with velocities $\boldsymbol{v}_1, \boldsymbol{v}_2$ and $\boldsymbol{v}_3$, respectively, indicated by *black arrows*. A maximum of 3 collisions can occur, before the particles move away from each other, never to collide again

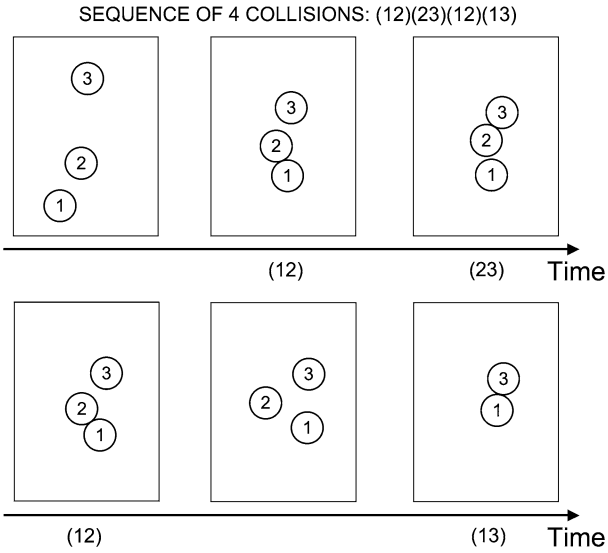

Fig. 4 Example of four collisions between 3 hard disks 1, 2 and 3 in $d = 2$. At and between the first three collisions (12), (23), and (12), particle 2 is always to the *left* of particles 1 and 3. This makes a fourth collision (1, 3) to the right of particles 1 and 3 possible i.e. a sequence of 4 collisions (12) (23) (12) (13). The distance between the first three almost simultaneous collisions (12) (23) (12) and the last, the fourth, (13) collision, is of the order of 5.5 particle diameters in this case. After these four collisions the 3 particles move away from each other, never to collide again. The sketched four collision sequence and its time reverse, (13) (12) (23) (12), are the only possible four collision sequences between 3 hard disks in $d = 2$. Note that in $d = 1$ (cf Fig. 3), particle 2 has *no* other choice than to be just between particles 1 and 3, so that no fourth collision, between 1 and 3, can occur

rods (particles), once directed towards a collision, cannot "escape" each other, i.e. they must collide and one easily proves that the maximum number is 3.[6] Therefore, a fortiori, in $d > 1$, where there is much more space for motion available and collisions are much more difficult to "arrange", the maximum number cannot be > 3.

There is, however, in principle, a possible counter argument, that in a space of dimension $d > 1$, more and other kinds of collisions could be possible than in $d = 1$. In fact, it was first found by J.D. Foch in 1964 numerically that indeed 3 hard disks in $d = 2$ could suffer 4 rather than 3 collisions. Soon afterwards, T.J. Murphy in 1965 provided an analytical proof that the maximum number of collisions of 3 identical hard balls in any dimension $d > 1$ was 4. For details I refer to the literature [26, 27]. This is illustrated in Fig. 4, for hard

[6]The simplest proof is perhaps using an x, t diagram, where, ignoring the finite size of the rods, the theorem follows immediately from the fact that three straight lines can intersect in the plane only a maximum of three times. This is based on the dynamics of hard rods in one dimension, where the laws of momentum and energy conservation for two colliding hard rods lead to an exchange of the velocities of the two colliding particles, so that one particle continues after a collision with the velocity of the other particle before the collision.

disks in $d = 2$ where a sequence of 4 successive collisions is (12) (23) (12) (13) occurs. One should notice that at and between the first 3 collisions (12) (23) (12), particle 2 is always to the left of the particles 1 and 3. Therefore, in $d = 2$, contrary to in $d = 1$—where particle 2 is necessarily always between the particles 1 and 2 (cf Fig. 3)—particle 2 can now "escape" from between 1 and 3, because of the extra dimension, thus making an "extra" (13) collision possible. The above mentioned sequence and its time reversed are the only possible sequences of 4 collisions between 3 hard balls in any dimension $d > 1$.

7 Epilogue

There is, in my opinion, a moral in the examples discussed in this paper of "obvious" general physical results, which were both incorrect, in spite of the fact that they were nourished by many, including outstanding, physicists. I want to end therefore with three recommendations for the younger generation of physicists:

1. Be cautious with "common, fashionable beliefs and opinions"!
2. Test formal developments and intuitive arguments on concrete models!
3. The latter was, in my opinion, beautifully expressed by Oswald Avery of the Rockefeller University, the discoverer of DNA as the seat of genetic information in 1944, when he told his students: "To do research, you must blow bubbles, **but**, you have to prick them yourself"!

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