

Response to Review of *Kinetic Theory and Irreversible Thermodynamics*¹

Byung Chan Eu²

Received February 9, 1994

In a tone and style that would put one in sympathy with the ire expressed by the literary master, J. W. von Goethe,⁽¹⁾ toward reviewers, Dorfman has recently given a rather subjective review⁽²⁾ of the above monograph. It is hardly a scientific review; it is an all-out assault against one opposed to his cherished claim, for which the review is unabashed propaganda, of the divergence of transport coefficients, in a review of a subject quite removed from the main thrust of his review. Any review, being a personal opinion, cannot but be subjective to some extent, but Dorfman's review is sadly wanting balance from a more reasoned viewpoint.

The principal aim of the monograph, *Kinetic Theory and Irreversible Thermodynamics*, was, as the title suggests, to study the kinetic theory foundations of irreversible thermodynamics for systems removed far from equilibrium. Under the general aim the mathematical structures of irreversible thermodynamics are studied from the molecular theory viewpoint for dilute classical gases, dilute quantum gases, gases with internal structures, dense monatomic and polyatomic fluids, as well as relativistic gases. These studies make it possible to erect a coherent, comprehensive, and thermodynamically consistent mathematical structure for a theory of irreversible processes in fluids which may be far removed from equilibrium. The generalized hydrodynamic equations underlying the theory of irreversible processes have been shown to be effective for rarefied gas dynamics, non-linear transport processes, rheology of polymers, etc.

Since scattering theory plays an important role in dense fluid kinetic

¹ This book review originally appeared in *J. Stat. Phys.* 73:799–801 (1993).

² Department of Chemistry and Department of Physics, McGill University, Montreal, Quebec H3A 2K6, Canada.

theory, formal theories of many-particle scattering are treated to a considerable depth in a chapter. And to support the kinetic theory employed, a chapter is necessarily devoted to calculations of transport coefficients within the framework of the kinetic theory used to formulate a theory of irreversible processes in dense fluids. It was not the aim of this work to delve deeply into the theories of transport coefficients and time correlation functions which Dorfman wants to be the centerpiece of the part of the book dealing with dense fluids. If he feels so strongly about his theory, he then is free to see that his viewpoints get treated to his satisfaction in a monograph of his own. We all have different motivations and priorities of subjects in our scholarly work and also different opinions on what is correct and appropriate and what is not. As far as the mathematical structures of the theory of irreversible processes are concerned, Dorfman's favorite subject, namely, the divergence property claimed to be associated with the transport coefficients and obviously cherished by him, is incidental. Since he makes this aspect the central point of his review, I am obliged to discuss some facts about it.

Dorfman would like to see the question of the divergence of transport coefficients and time correlation functions put on a pedestal and worshipped as a lasting landmark contribution to the dense fluid kinetic theory. But this cannot be done, since it is founded on shaky mathematical approximations to the many-particle collision operators involved in the dense fluid kinetic theory. Many-particle collision operators have rather intricate mathematical properties that cannot be easily guessed by simply extrapolating the theory of two-particle collision operators to the situations of three or more particles. This fact is well known in many-particle scattering theory and was expounded first by Faddeev⁽³⁾ and Weinberg⁽⁴⁾ and later by many others.⁽⁵⁾ It is unfortunate that these important facts about many-particle collision operators have been lost to most kinetic theorists, to the detriment of the development of dense fluid kinetic theory. The main point of the Faddeev theory⁽³⁾ is that the Lippmann–Schwinger equations for the components of a three-particle operator acquire completely continuous integral kernels only after four iterations of the integral equations, and the lower-order iterates have weak logarithmic-type singularities which get smoothed out on further iterations. Their singular behavior, however, does not mean that the three-particle operator is singular in the wave number (\mathbf{k}) space or does not exist or is divergent. It only means that the lower-order iterates are not mathematically faithful representations of the three-particle operator in question since in fact the three-particle collision operator is bounded in the \mathbf{k} space if the potential energies are nonsingular. The troublesome, weakly singular products of two-particle collision operators (e.g., the lower-order iterates mentioned earlier) appear in the

so-called binary collision expansion for many-particle collision operators. As was pointed out by various authors^(4,6) in scattering theory, the binary collision expansion for the case of $N \geq 4$, where N is the number of particles, has an additional problem stemming from disconnected diagrams which contribute delta functions of momenta. Such delta functions render the integral kernels *not completely continuous* and the resulting series is divergent. Ronis and Oppenheim⁽⁷⁾ considered the $k=0$ matrix element of such an iterate (a product of three two-particle collision operators) in two dimensions and found them singular. Despite their singularity the three-body collision operator, however, is bounded. Therefore, their conclusion does not affect the final result for the bound of the three-particle collision operator. The cure advocated by the divergence school is a resummation of selective terms which could have been avoided altogether if the results of many-particle scattering theory had been used.

Such weakly singular terms, consisting of products of three or four two-particle collision operators, usually appear in the binary collision expansion for transport coefficients or related autocorrelation functions, which, for example, Dorfman and his collaborators have studied and claimed to be divergent. They eliminate the divergence by a suitable resummation of divergent series. In scattering theory, ways to avoid such a divergence difficulty have been known since the work by Weinberg⁽⁴⁾ and later by others.⁽⁵⁾ The main ingredient is a cluster expansion which ensures that the integral kernels consist of connected products of collision operators only. In Chapter 9 of my monograph, the important points of the cluster expansion are discussed together with a review of salient points of the Faddeev theory.⁽³⁾ It does not make an easy reading, but then the subject matter is complicated. Anyone with the time and energy to examine the question in detail would know that the divergence claim by Dorfman and others lacks a rigorous mathematical support. And, based on my studies over the years, I find that there is mathematically no substance to it. Therefore, it should not be surprising that the divergence question is not given a prominent place in the monograph, contrary to what Dorfman thinks. It is necessary to point out that the logarithmic density dependence, which is one of the important consequences of the divergence of the binary collision expansion for the many-particle collision operator, has not been proven experimentally, since the most precise measurement of shear viscosity and a careful statistical analysis⁽⁸⁾ of the data by one of the proponents of the logarithmic divergence of transport coefficients were not able to support it. Therefore, Dorfman's complaints in connection with the divergence question and the binary collision expansion stem from a conclusion drawn without a firm mathematical basis, since the modern theory of many-particle scattering theory does not support it and it is without experimental

support. Anyone who will study in detail the development of dense fluid kinetic theory in the future will find that the divergence claim by “the divergence school” is a negative contribution that has been, in my opinion, detrimental to the genuine development of a kinetic theory of matter. It cannot be considered firmly established beyond doubt. Certainly, it cannot be accepted blindly like a religious dogma, since it has not been sufficiently scrutinized in the public domain and there is a contrary opinion in the literature.⁽⁹⁻¹¹⁾ Unfortunately, my own experience teaches me that only the foolhardy would tackle it in the clear view of hostile peer review processes. The book review by Dorfman is an example which shows no tolerance for a slight sign of an opposing viewpoint. I do not believe that the divergence viewpoint is in the mainstream today as he seems to insinuate, and, based on what I have studied in the subject, I do not see why it should be treated as such. One should also remember that meaningful science is not necessarily done in the mainstream of the time. Ah, the mainstream..., whatever it may be, is so fleeting a segment in the vast expanse of natural phenomena. It has a very little meaning. Besides, it is liable to be full of flotsam and jetsam.

This monograph is not meant to supplant the existing monographs such as those by de Groot and Mazur, Chapman and Cowling, Keizer, or Cercignani. They have their own aims and ranges of subjects and my monograph is meant to study different aspects not studied by them. However, it would be an unintended contribution of this monograph if it did give the statistical mechanics community notice that the divergence question under dispute is not cut and dried, since there is no experimental proof for it and it is laden with mathematical problems. For the sake of a healthy development of dense fluid kinetic theory it is worthwhile to have further studies made and an alternative procedure is given in the monograph. I hope that mathematically minded workers will study the question to a greater depth in the future. I have not made a study of the divergence in the time domain. Therefore, I cannot make a comment on it. Nevertheless, one may make inferences on it from what I said earlier in connection with the density dependence of transport coefficients.

REFERENCES

1. W. Goethe, Reviewer (1776), in *Great Writings of Goethe*, S. Spender, ed. (Meridian-New American Library, New York, 1977), p. 46.
2. J. R. Dorfman, *J. Stat. Phys.* **73**:799 (1993).
3. L. D. Faddeev, *Mathematical Aspects of the Three-Body Problem in the Quantum Mechanics* (Daniel Davey, New York, 1965).
4. S. Weinberg, *Phys. Rev. B* **133**:232 (1964).

5. V. A. Alessandrini, *J. Math. Phys.* **7**:215 (1966); O. A. Yakubovskii, *Sov. J. Nucl. Phys.* **5**:937 (1969); I. H. Sloan, *Phys. Rev. C* **6**:1945 (1972); G. J. Bencze, *Nucl. Phys. A* **210**:568 (1973); E. F. Redish, *Nucl. Phys. A* **225**:16 (1974); W. N. Polyzou and E. F. Redish, *Ann. Phys. (N.Y.)* **119**:1 (1979); R. Goldflam and W. Tobocman, *Phys. Rev. C* **20**:904 (1979); G. Cattapanand and V. Vanzani, *Nuovo Cimento A* **72**:333 (1982); **89**:29 (1985).
6. R. Aaron, R. D. Amado, and B. W. Lee, *Phys. Rev.* **121**:319 (1961).
7. D. Ronis and I. Oppenheim, *Physica* **84A**:620 (1976).
8. J. Kestin, E. Paykoc, and J. V. Sengers, *Physica* **54**:1 (1971).
9. S. Fujita, *Proc. Natl. Acad. Sci. USA* **56**:16, 794 (1966); *Phys. Lett.* **22**:425 (1966); **24A**:235 (1967).
10. E. Braun and A. Flores, *J. Stat. Phys.* **8**:155, 167 (1973); E. Braun, A. Flores, and G. Coutino, *J. Stat. Phys.* **10**:49 (1974).
11. B. C. Eu, *J. Chem. Phys.* **60**:1906 (1974).