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Response to Book Review: *Statistical Mechanics*, 2nd ed.[1]

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It is probably obvious that any author will find parts of any critical review of his own book misleading. There are some statements of Dorfman's that I find erroneous, while other statements, although fully correct, still require comment.

The first edition of *Statistical Mechanics* was written in the late thirties. The number of published articles in the field since that first writing exceed by more than a factor of ten those published in all preceding time. The publisher asked for a second edition no more voluminous than the first, and with the same title. Detailed treatment of nonequilibrium processes was nonexistent in the thirties. It, and many other important recent developments, were omitted in the second edition, largely to limit volume.

The book was composed with the conviction that a thorough understanding of the treatment of systems composed of relatively simple molecules in well-defined single thermodynamic phases—gas, liquid, and crystal—was the necessary basis of an understanding of more recently treated, and more specialized, problems.

Now to my more serious complaints.

Dorfman in his third paragraph states that "equal a priori probabilities (of quantum states are) referred to in the book as the ergodic hypothesis...". Now this is incorrect. The equal a priori probability is rigorously *derived* in Section 4c, p. 88 of the book from a simple but uncritical statement of the ergodic hypothesis: namely that every quantum state **K** of the system can be reached from every other state **K'** by a chain of allowed transitions. The ergodic hypothesis is then discussed later on p. 126 in considerable detail.

Contrary to Dorfman's statement in his fourth paragraph, the concept of random fluctuations at the walls plays *no role whatever* in the derivation of the microcanonical ensemble beginning on p. 88.

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[1] This book was reviewed in *J. Stat. Phys.* **18** (4) (1978).

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Peculiarly enough, Dorfman does outline a "proper statistical mechanical description of the approach to equilibrium" which is exactly met by the mathematical analysis given in Section 6j of the book, pp. 146–154, which by itself has *no* reference to random fluctuations and is the only discussion in the book (and a very abstract one) of time-dependent processes. A probably legitimate criticism of that section is that I do not make clear that fluctuations from the walls are *not* essential, or used, in the description of what actually happens to the observable properties of the system.

The "random fluctuations," which Dorfman and many others obviously dislike, are used *only* to justify the definition of entropy by $-S/k$ = sum (or integral) of $W_{\mathbf{K}} \ln W_{\mathbf{K}}$, with $W_{\mathbf{K}}$ the probability of state **K**.

The analysis in Section 6j is carried out on the classical probability density in fixed volume $W(\mathbf{p}^{(N)}, \mathbf{q}^{(N)})$ [but can be extended to the quantum Wigner $W(\mathbf{p}^{(N)}, \mathbf{q}^{(N)})$]. Orthogonal normalized functions $\Psi_{n,m}(\mathbf{p}^{(N)}, \mathbf{q}^{(N)})$ are then defined modifying W_{eq} whose amplitudes $a_{n,m}(t)$ under the Liouville operator change with time. At low displacements from equilibrium the excess negentropy $-\Delta S/k$ is the sum of the square amplitudes $\sum_{n,m} a_{n,m}^2$, which sum stays constant in time if the system were *absolutely* isolated. The functions of small n, m values determine the observable properties such as energy, energy flux, number density, and flux, and these only have nonzero values in the initial, properly prepared ensemble. The functions $\Psi_{n,m}$ are so constructed that if $a_{n,m}$ is nonzero, a finite amplitude for larger n', m' begins to grow, and since the sum $\sum a_{n,m}^2$ stays constant in time, the values for the small n's and m's decreases.

The actual macroscopic behavior of the ensemble depends in no way on the interactions with entities outside of the system volume if the experimental setup conforms to the ensemble prescription of isolation, but if negentropy is *defined* by $-S/k$ equal to the sum $W \ln W$, then only the eventual growth of $a_{n+\nu,m+\mu}^2$ for functions $\Psi_{n+\nu,m+\mu}(\mathbf{p}^{(N)}, \mathbf{p}^{(\nu)}, \mathbf{q}^{(N)}, \mathbf{q}^{(\nu)})$, with ν, μ referring to molecules (or possibly photons or phonons) outside the V, can account for a negative $d(-S/k)/dt$.

Section 6j concludes with a plausibility argument concerning a real classical experiment involving heat flow and/or molecular diffusion in a temperature or composition gradient in an isolated system; which is indeed hardly the way one would ever make such a measurement. The suggestion is made that if the real $\sum a_{n,m}^2(t)$ could possibly be measured, it would differ negligibly from the integral in V of the conventionally inferred $-s(\mathbf{r})/k$, with $s(\mathbf{r})$ the entropy density at the position $\mathbf{r}$. However, this conclusion is drawn only after a caution based on spin-echo that (at least if the displacement from equilibrium is large) feedback from macroscopically unobservable functions $\Psi_{n,m}$ to those that influence macroscopic observables can do so periodically.

The reviewer devoted a very considerable amount of space discussing my papers in the thirties on cluster and virial development and the errors in attempting at that time to predict conclusions about the critical region. The new edition discusses the use of the development for a single-phase dense gas system, for which the early papers were primarily intended. It also discusses condensation: van der Waals; a statistical interpretation of the phenomenon; Yang–Lee theory; and the cluster limit, which is correct at sufficiently low temperatures and probably for all below critical, although not proved mathematically.

There is also a short discussion of the mathematical error of taking a limit in reverse order for the $\sum b_n z^n$ series, which leads to the erroneous "Derby hat" prediction.

Somehow the reviewer seems to leave the impression that the cluster development is now obsolete and little used. It certainly is obsolete in treatments of critical phenomena.

I am disappointed that the reviewer did not choose to review Chapter 13 on the density matrix. This chapter includes three sections, 13j–13l, pp. 447–458, in which the Wigner approach of 1932 for the equilibrium matrix is extended for a potential which is a sum $\sum \sum_{i \leqslant i < j \leqslant N} u(r_{ij})$ to all powers of h^2/T. As far as I know, this is completely new and is numerically usable for dense, monatomic systems.