

Equivalence of statistical-mechanical ensembles: A collection of quotes and notes

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Added to the last version: Lieb 1973

- E. H. Lieb and M. B. Ruskai, A fundamental property of quantum-mechanical entropy, PRL 30, 434, 1973.
 - There are some properties of entropy, such as concavity and subadditivity, that are known to hold (in classical and in quantum mechanics) irrespective of any assumptions on the detailed dynamics of a system.
- G. H. Wannier. *Statistical Physics*. Wiley, New York, 1966.
 - p. 66: [Darwin-Fowler method] Expectation values for all relevant quantities can be obtained for the microcanonical ensemble in the form of contour integrals. If these contour integral can be evaluated by the method of steepest descent, equation (4.16) results for the expectation value of N_i . [Large deviation equation in contraction] This type of evaluation is almost always legitimate. Troublesome exceptions to this situation do arise occasionally.* One faces then the unpleasant fact that the two types of ensembles yield different answers. In these exceptional situations a deeper physical analysis is required; it usually confirms the canonical result.

[References *:

- * C.G. Darwin and R.H. Fowler, Phil. Mag. 44. 450 and 823 (1922).
- * R.H. Folwer, Statistical Mechanics, Cambridge, 1936. Chapter II.
- * M. Lax, Phys. Rev. 97, 1419, 1955.
- * C.C. Yan and G.H. Wannier, J. Math Phys. 6, 1833, 1965.]

- p. 75: It is therefore quite untrue that we know its energy once we are given the temperature. [...] Thus the statement that the energy is a function of temperature acquires only a sense in the limit of large n .
- p. 75: Thus we can see independently from the case of the perfect gases that the energy becomes extremely sharply defined as the number of molecules in a sample gets large.
- p. 84: [...] we have just learned [p. 75] that for a “large” system the energy fluctuation is very small. It follows then that the part of the energy spectrum which is effective within the sum [of the partition function] under given external conditions is also small. Thus, notwithstanding the formal structure of [the partition function], all effective value [of the energy] in this sum are actually very close to U [the microcanonical energy].
- R. H. Fowler. *Statistical Mechanics*. Cambridge University Press, Cambridge, 2nd edition, 1966.
 - p. 36: [Steepest descent approach.]
- D. Ruelle. *Statistical Mechanics: Rigorous Results*. W.A. Benjamin, Amsterdam, 1969.
 - p. 3: It is believed that the various ensembles yield equivalent descriptions in the thermodynamic limit, i.e., for large systems; to prove this is the problem of equivalence of ensembles, which is only incompletely solved.
 - p. 56: [Shows how the free energy is to be calculated from the entropy through Legendre transform, if one assumes differentiability of the entropy. Then mentions:] They [these equations] express here the equivalence of ensembles.
 - p. 52: The transition from microcanonical to canonical [...] amounts, in the thermodynamic limit, to a description of the surface [microcanonical manifold] [...] in terms of its tangent lines and planes (using the so-called Legendre transformations).
- R. S. Ellis. *Entropy, Large Deviations, and Statistical Mechanics*. Springer-Verlag, New York, 1985.
 - p. 77: The microcanonical ensemble with specific energy u is equivalent to the canonical ensemble with inverse temperature $\beta(u)$. [Ellis then goes on to define a canonical entropy.]

- J. W. Gibbs. *Elementary Principles in Statistical Mechanics with Especial Reference to the Rational Foundation of Thermodynamics*. Yale University Press, Yale, C.T., 1902. Reprinted by Dover, New York, 1960.
 - p. xi: For the average square of the anomalies of the energy, we find an expression which vanishes in comparison to the square of the average energy, when the number of degrees of freedom is indefinitely increased. An ensemble of systems in which the number of degrees of freedom is of the same order of magnitude as the number of molecules in the bodies with which we experiment, if distributed canonically, would therefore appear to human observation as an ensemble of systems in which all have the same energy.
 - p. 72: [Positive specific heat.]
 - p. 74: It follows that to human experience and observation with respect to such an ensemble as we are considering, or with respect to systems which may be regarded as taken at random from such an ensemble, when the number of degrees of freedom is of such order of magnitude as the number of molecules in the bodies subject to our observation and experiment $\varepsilon - \bar{\varepsilon}$ [...] would be in general vanishing quantities, since such experience would not be wide enough to embrace the more considerable divergencies from the mean values, and such observation not nice enough to distinguish the ordinary divergencies. In other words, such ensembles would appear to human observation as ensembles of systems of uniform energy [...].
 [Then Gibbs goes on to mention, in the footnote of page 75, a case of ensembles inequivalence related to phase transitions!]
 [More or less the same statement on pages 168-171]
 - p. 115: [Definition of microcanonical ensemble.]
 - p. 116: From a certain point of view, the microcanonical distribution may seem more simple than the canonical, and it has perhaps been more studied, and been regarded as more closely related to the fundamental notions of thermodynamics. [...] It is sufficient here to remark that analytically the canonical distribution is much more manageable than the microcanonical.
 - p. 118: [...] regarding the canonical ensemble as consisting of an infinity of microcanonical ensembles.
 - p. 178: In regard to the naturalness of seeking analogies [connections with experiments] with thermodynamic behavior of bodies in canonical or microcanonical ensembles of systems, much will depend upon how we approach the subject, especially upon the question whether we regard energy of temperature as an independent variable.

It is very natural to take energy for an independent variable rather than temperature, because ordinary mechanics furnishes us with a perfectly defined conception of energy, whereas the idea of something relating to a mechanical system and corresponding to temperature is notion but vaguely defined.

- pp. 180-183: [How a small part of a microcanonical ensemble is canonically distributed.]
- p. 208: [Equivalence grand-canonical petit-canonical.]
- L. D. Landau and E. M. Lifshitz. *Statistical Physics*, volume 5 of *Landau and Lifshitz Course of Theoretical Physics*. Butterworth Heinemann, Oxford, 3rd edition, 1991.
 - p. 8, §3: [Fluctuations of additive quantities.]
 - p. 82, §29: The possibility of applying the Gibbs distribution [...] to closed systems is also seen from the fact that this distribution hardly differs from the microcanonical distribution, while being very much more convenient for practical calculations. For the microcanonical distribution is, roughly speaking, equivalent to regarding as equally probable all microstates of the body which correspond to a given value of its energy. The canonical distribution is “spread” over a certain range of energy values, but the width of this range (of the order of the mean fluctuation of the energy) is negligible for a macroscopic body.
 - p. 333: [Chapter XII on Fluctuations.]
- R. Balian. *From Microphysics to Macrophysics: Methods and Applications of Statistical Physics*, volume I. Springer-Verlag, Berlin, 1991.
 - p. 34: Notwithstanding the difference of the form of these two probability laws, they are practically equivalent for the evaluation of macroscopic quantities.
 - p. 144: We shall see in §5.5.3 that, in the limit of large systems, the two ways of giving the information which characterizes a state on the macroscopic scale lead to the same predictions for most physical properties. [See also p. 165.]
 - p. 207 §5.5.3: We shall show that, if a system is extensive, we obtain for all, extensive or intensive, macroscopic physical quantities the same value whatever statistical ensemble we are using, be it a microcanonical, canonical [...].

- p. 208: [Equivalence between grand-canonical and petit-canonical.]
 - p. 210: The exponential decrease $e^{-\beta E}$ is thus combined with the very rapid increase in the level density to give rise to a sharp peak which differs little from the microcanonical energy distribution. [About $P_\beta(E)$]
 - p. 222: The smallness of these fluctuations, when the thermodynamic limit exists, enables us to understand intuitively the equivalence between the various ensembles [...].
 - p. 222: Nevertheless, there is one important exception. When a system can undergo a phase transition [...].
 - p. 223: [...] the various ensembles are not equivalent as regards fluctuations when there is a phase transition [...].
- K. Huang. *Statistical Mechanics*. Wiley, New York, 1987.
 - Note: Huang uses the term ‘system’ instead of ‘configuration of the system’; it’s a common use of language for physicists who view, since the work of Gibbs, an ensemble as a collection of systems rather than a collection of the configurations of a system.
 - §7.2, p. 145: We now show that the canonical ensemble is mathematically equivalent to the microcanonical ensemble in the sense that although the canonical ensemble contains systems of all energies the overwhelming majority of them have the same energy.
 - p. 146: As $N \rightarrow \infty$, almost all systems in the ensemble [canonical] have the same energy [...], which is the internal energy. Therefore the canonical ensemble is equivalent to the microcanonical ensemble.
 - p. 147: We have shown that almost all systems in the canonical ensemble have the same energy—namely, the energy that is equal to the internal energy of a system at the given temperature T .
 - p. 148: From a physical point of view, a microcanonical ensemble must be equivalent to a canonical ensemble, otherwise we would seriously doubt the utility of either.
 - p. 148: A macroscopic substance has the extensive property, i.e., any part of the substance has the same thermodynamic property [sic] as the whole substance. Now consider a piece of substance isolated from everything. Any part of the substance must still be in equilibrium with the rest of the substance, which serves as a heat reservoir that defines a temperature for the part on which we focus our attention. Therefore the whole substance must have a well-defined temperature.

- p. 148: [...] it matters little whether we specify the energy of the system or the temperature of the system, for specifying one fixes the other.
- F. Reif. *Fundamentals of Statistical and Thermal Physics*. McGraw-Hill, New York, 1965.
 - p. 110: Since the number of particles is so very large, fluctuations in any macroscopic parameters [...] are ordinarily utterly negligible.
 - p. 220: If a macroscopic system A is in contact with a heat reservoir, the relative fluctuations in the energy of A are exceedingly small. Suppose now that A is removed from contact with the heat reservoir and is thermally insulated; then its total energy cannot change at all. But the distinction between this situation and the previous one is so small that it is really utterly irrelevant for most purposes; in particular, the mean values of all physical quantities (e.g., of the mean pressure or the mean magnetic moment of A) remain quite unaffected. Hence it makes no difference whether these mean values are calculated by considering the system to be isolated so that it has equal probability of being in any one of its states of accurately specified fixed energy, or by considering it to be in contact with a heat reservoir so that it is distributed over all its states in accordance with a canonical distribution.
- J. J. Binney, N. J. Dowrick, A. J. Fisher, and M. E. J. Newman. *The Theory of Critical Phenomena: An Introduction to the Renormalization Group*. Oxford University Press, Oxford, 1992.
 - p. 41: Note that since the heat capacity [...] grows linearly with the size of the system, the fractional energy fluctuations $\delta U/U$ fall as the square root of the system size. They therefore become negligible in the limit that the size goes to infinity. Because of this, this limit is called the thermodynamic limit. The exception to this is when the heat capacity of the system diverges, as it does at a critical point. Then the fluctuations do not go away as the system becomes larger, but are present on all scales.
 - p. 99: [...] the rms variation in the energy H increases only as the square root of the system's volume V , while the internal energy $U = \langle H \rangle$ increases as V [...]. Hence in the thermodynamic limit of infinite V the only states which contribute to thermal averages are those for which $H = U$. So unless we are very close to T_c , where the heat capacity [...] is very large, the microcanonical average [...] provides a valid estimate of the thermal average.

- L. E. Reichl. *A Modern Course in Statistical Physics*. Edward Arnold Publishers, London, 1980.
 - p. 246 [Chap. 9, §2]: In the thermodynamic limit, most microstates will have an energy approximately equal to the average energy $U = \langle E \rangle$ and the canonical ensemble becomes equivalent to the microcanonical ensemble.
- G. Gallavotti. *Statistical Mechanics: A Short Treatise*. Springer, New York, 1999.
 - Note: Gallavotti uses the terms ‘orthodic’ or ‘orthodes’ in the following sense: an ensemble is orthodic if the energy per particle (more precisely the equilibrium energy per particle) can be written in that ensemble as a function of the temperature (p. 19). This definition is quite unclear; it seems to be more or less equivalent to the requirement of equivalence of ensembles, but Gallavottidoes not actually equate orthodic ensembles with equivalent ensembles.
 - p. 59: Therefore the “theory of ensembles” poses three questions:
 - (1) existence and description of orthodic ensembles;
 - (2) equivalence of the thermodynamics that they describe;
 - (3) comparison of the equations of state computed from the ensembles and the corresponding ones obtained experimentally.
 - p. 60: We shall see that while the canonical ensemble is *already* orthodic in finite volume, the microcanonical ensemble is orthodic “only” in the “thermodynamic limit” $N \rightarrow \infty, U \rightarrow \infty, V \rightarrow \infty$ so that $U/N = u, V/N = v$ stay constant (or tend to a constant).
 - p. 68: [§2.3: Equivalence Between Canonical and Microcanonical Ensembles]
 - p. 69: We shall see that “in general” for each *given* system there is equivalence (in the thermodynamic limit) between canonical and microcanonical ensembles *if* the constant k_B [Boltzmann’s constant] appearing in the theory of the two ensembles is taken to be the same.
 - pp. 70-71: [‘Proof’ of equivalence of ensembles based essentially on the Laplace approximation applied to the canonical partition function.]
 - p. 73: [§2.4: Non-equivalence of the Canonical and Microcanonical Ensembles. Phase Transitions. Boltzmann’s Constant]
 - p. 73: [...] the proof (rigorous or not) of equivalence between the canonical and microcanonical ensembles *no longer works, in general, if the maximum*

in (2.3.11) [Integral defining the partition function] is reached on an interval (u_-, u_+) , $u_- < u_+$ rather than at a single point.

By the general properties of concave functions, one can see that this possibility can be realized *only* for exceptional values of β (and precisely for a set of values forming “at most” a denumerable set). This means that for exceptional values of β , *i.e.* of the temperature, corresponding elements of the canonical and microcanonical ensembles *may be not equivalent*. [Partially wrong: It is known that the canonical ensemble is always realized within the microcanonical ensemble. The main point of the theory of nonequivalent ensembles is that the microcanonical ensemble can be richer than the canonical ensemble.]

- p. 74: [...] *rather than being an obstacle* to the microscopic formulation of thermodynamics, [the phenomenon of nonequivalent ensembles] *shows* the possibility that statistical mechanics can be the *natural frame* in which to study the *phase transition* phenomenon.

[...]

Hence cases in which there is no equivalence between corresponding elements of the two ensembles, or more generally when there are corresponding but nonequivalent elements in two orthodic ensembles, can be taken as signaling a phase transition: this is in fact the definition of phase transition that is commonly accepted today. [Should add here: *first-order* phase transitions.]

- p. 75: [...] the possible nonequivalence *cannot be considered a defect of the theory*, but it can be ascribed to the fact that, when equivalence fails, the elements of the two statistical ensembles that should be equivalent [!] are not because they describe two different phases that may coexist (or different mixtures of coexisting phases).
 - p. 81: [Discussion of nonequivalent ensembles as signaling first-order phase transitions, metastable states, etc.]
- O. E. Lanford III. Entropy and equilibrium states in classical statistical mechanics. In A. Lenard, editor, *Statistical Mechanics and Mathematical Problems*, volume 20 of *Lecture Notes in Physics*, pages 1–113, Berlin, 1973. Springer-Verlag.
 - pp. 44-47: Discussion of the equivalence of the microcanonical and canonical ensembles for a non-interacting system.
 - p. 50: The heuristic basis of the analysis we will give is the following: One wants to show that, except for exceptional values of β , the function

$\frac{U(q_1, \dots, q_N)}{N}$ on Λ^N is for large Λ , N , nearly constant with respect to the canonical probability measure μ_β . This means that, except for some set of configuration[s] of small probability, all configurations have approximately the same energy. For these configurations, the weight factor $e^{-\beta U}$ is nearly constant, so one would expect [expect] that the canonical probability measure is much the same as the one obtained by assigning equal weight to all configurations with approximately the right value for $\frac{U}{N}$ and weight zero to all other configurations, i.e., the canonical probability measure should be in some sense equivalent to the one obtained by normalizing the restriction of the Lebesgue measure to be [the] appropriately chosen “thickened energy surface.”

- p. 63: Many of the results we have obtained so far in this section come under the general heading of equivalence of ensembles for thermodynamic functions. That is, we have seen how to replace the independent variable ε by β ; we have seen the relation between the free energy as a function of (v, β) [v = specific volume] and the entropy as a function of (v, ε) , and we have seen that there are two distinct ways of computing the entropy, one giving it as a function of (v, β) , the other giving it as a function of (v, ε) .
- p. 63: [Macrostate level of equivalence] We turn next to the consideration of the equivalence of ensembles for observables, i.e., we want to see what can be said about the relation between the distribution of a given observable f/N with respect to the canonical probability measure [...] and its distribution with respect to the micro-canonical probability measure for some very thin energy surface [...].
- pp. 63-69: Macrostate (observable) equivalence of ensembles.
- Note: Lanford implicitly avoids the subject of nonconcave entropies because he is interested in finite-range observables having (as he proves) concave entropies. I believe that if Lanford had been told about nonconcave entropies, he would have understood the problem of nonequivalent ensembles immediately.
- H. S. Leff. On the connections between thermodynamics and statistical mechanics. *Am. J. Phys.*, 37(1):65–67, 1969
 - Defines a canonical entropy from the Legendre transform definition of the equilibrium energy associated with a given temperature.