

# THE ROLE OF ENTROPY IN THE TIME EVOLUTION OF MACROSCOPIC SYSTEMS

Joel L. Lebowitz

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## Clausius' Macroscopic Entropy

“The second law of thermodynamics forbids perpetual motion of the second kind and implies the existence of a definable entropy for any system in a state that can be reached by a succession of reversible processes. These “thermodynamic” states are typically defined as states of “equilibrium” under specified restraints on composition, energy, and external boundary conditions, in the sense that no spontaneous change can occur in the system as long as the constraints remain fixed.”

L. Onsager, Thermodynamics and Some Molecular Aspects of Biology, in *The Neurosciences, A Study Program*, eds. G. C. Quarton et al. (Rockefeller University Press, New York, 1967) pp. 75–79

The basic formulation of this macroscopic law “the second law of thermodynamics” goes back to Clausius. He stated:

“Two fundamental theorems of the mechanical theory of heat:

1. The energy of the universe is constant.
2. The entropy of the universe tends to a maximum.”

Given an equilibrium system with energy  $E$  and mole (or particle) numbers  $\mathbf{N}$  in a volume  $V$ , there exists a function  $S(E, \mathbf{N}, V)$  such that in a reversible process

$$dS = [dE + pdV - \sum \mu_j dN_j]/T$$

Thermodynamics further states that the entropy of two isolated macroscopic systems, each in equilibrium,

$$\begin{aligned} & S_{1,2}(E_1, \mathbf{N}_1, V_1, E_2, \mathbf{N}_2, V_2) \\ &= S_1(E_1, \mathbf{N}_1, V_1) + S_2(E_2, \mathbf{N}_2, V_2) \end{aligned}$$

Suppose these systems are brought into contact with some time period and then again isolated, then according to the second law,

$$\begin{aligned} S'_{1,2} &= S_1(E'_1, \mathbf{N}'_1, V'_1) + S_2(E'_2, \mathbf{N}'_2, V'_2) \geq S_{1,2} \\ &= S_1(E_1, \mathbf{N}_1, V_1) + S_2(E_2, \mathbf{N}_2, V_2) \end{aligned}$$

Extensivity: *for spatially uniform equilibrium systems,*

$$S(E, \mathbf{N}, V) = V s(e, \mathbf{n}).$$

For systems in “local thermal equilibrium” (LTE)

$$S_{\text{loc.eq.}}(n, \mathbf{u}, e) = \int_V s(e(\mathbf{x}) - \frac{1}{2} m n(\mathbf{x}) \mathbf{u}^2(\mathbf{x}), n(\mathbf{x})) d\mathbf{x}$$

Hydrodynamic evolution of macro-variables,

$$\frac{dS_{\text{loc.eq.}}}{dt} \geq 0; \quad \mathcal{H}\text{-theorem.}$$

## Example

Consider an isolated system in LTE (with  $\mathbf{u} = 0$  and  $n$  constant) with an energy density profile  $e_0(\mathbf{x})$  and corresponding temperature profile  $T_0(\mathbf{x})$

$$\frac{\partial s}{\partial t} = -\frac{\nabla \cdot \mathbf{J}}{T} = -\nabla \cdot (\mathbf{J}/T) + \mathbf{J} \cdot \nabla(1/T),$$

where  $\mathbf{J}$  is the heat flux,  $\mathbf{J}/T$  is the entropy flux, and  $\mathbf{J} \cdot \nabla(1/T)$  is the entropy production.

Integrating yields

$$\frac{dS_{\text{loc.eq.}}}{dt} = \frac{d}{dt} \int_V s d\mathbf{x} =$$

$$\int_V \mathbf{J} \cdot \left(\nabla \frac{1}{T}\right) d\mathbf{x} \geq 0.$$

As  $t \rightarrow \infty$ ,  $T(\mathbf{x}, t) \rightarrow \bar{T}$ , for all  $\mathbf{x} \in V$ , with  $\bar{T}$  determined by energy conservation and  $S_{\text{loc.eq.}}$  approaches its maximum (equilibrium) value  $Vs(\bar{e}, n)$ .

But what is entropy? *Microscopically*

## Microstates: classical

The complete microscopic (or micro) state of an isolated classical system of  $N$  point particles of unit mass is specified at any time  $t$  by a point  $X$  in its phase space  $\Gamma$ ,

$$X = (\mathbf{r}_1, \mathbf{v}_1, \dots, \mathbf{r}_N, \mathbf{v}_N), \quad \mathbf{r}_i \in \mathbf{V} \subset \mathbb{R}^d, \quad \mathbf{v}_i \in \mathbb{R}^d.$$

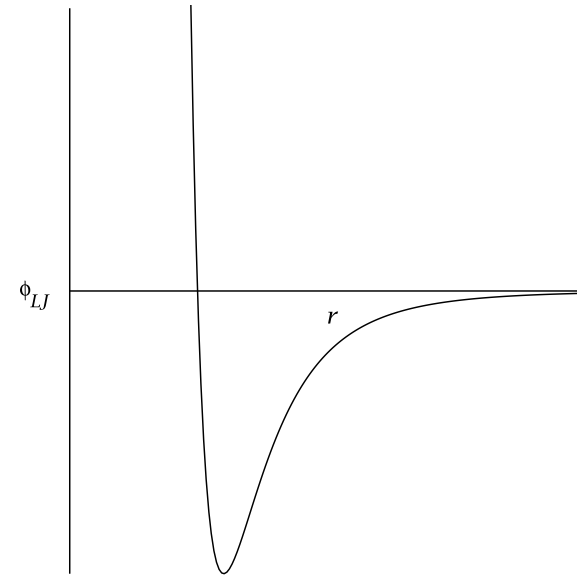
Given an  $X$  at some time  $t_0$ , the microstate at any other time  $t \in \mathbb{R}$ ,  $X(t)$ , is given (as long as the system stays isolated) by the Hamiltonian evolution which takes place on an energy surface,  $\Gamma_E$ , specified by  $H(X) = E$ .

A typical (effective, non-relativistic) Hamiltonian for a simple fluid, say Argon, has the form

$$H(X) = \frac{1}{2} \sum \mathbf{v}_i^2 + \frac{1}{2} \sum_{i \neq j} \phi(\mathbf{r}_{ij}).$$

A representative interaction is given by the Lennard-Jones potential

$$\phi_{LJ}(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right].$$



The equations of motion

$$\dot{\mathbf{r}}_i(t) = \mathbf{v}_i(t), \quad \dot{\mathbf{v}}_i(t) = - \sum_{j \neq i} \frac{\partial}{\partial \mathbf{r}_i} \phi(\mathbf{r}_{ij}),$$

with appropriate boundary conditions on  $\partial V$  preserve the energy and the projection of the Liouville volume,  $d\Gamma = \prod d\mathbf{r}_i d\mathbf{v}_i$ , on  $\Gamma_E$ .

## Macrostates

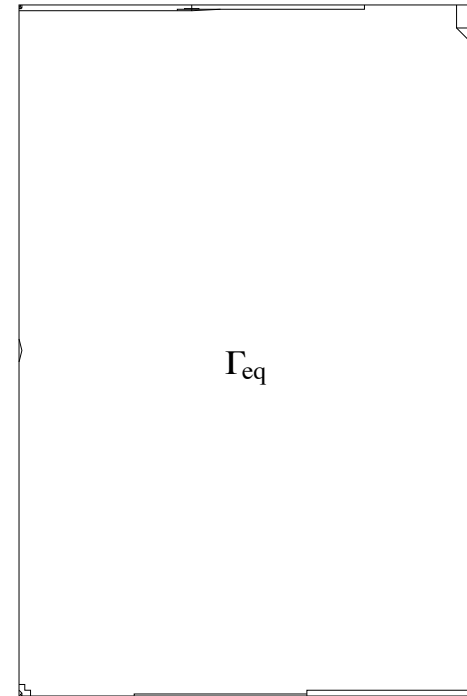
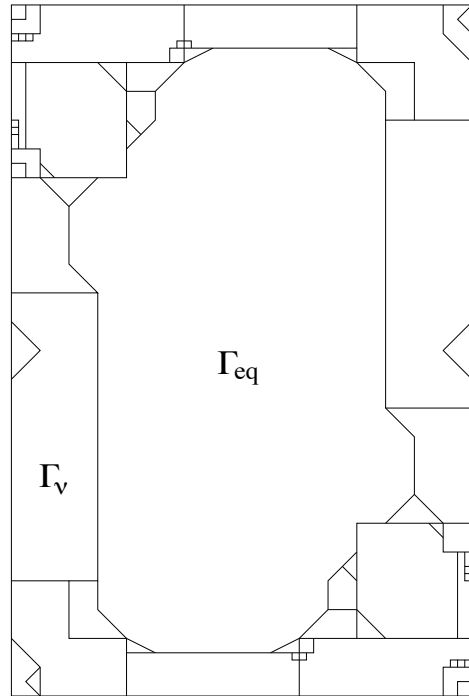
To describe the macroscopic state of a system of  $N$  atoms in a box  $V$ , say  $N \gtrsim 10^{20}$ , we make use of a much cruder description than that provided by the microstate  $X$ . We shall denote by  $M$  such a macroscopic description of a macrostate. As an example we may divide  $V$  into  $K$  cells, where  $K$  is large but still  $K \ll N$ , and specify the number of particles, the momentum and the amount of energy in each cell, with some tolerance.

Clearly there are many  $X$ 's (in fact a continuum) which correspond to the same  $M$ . Let  $\Gamma_M$  be the region in  $\Gamma_E$  consisting of all microstates  $X$  corresponding to a given macrostate  $M$  and denote by  $|\Gamma_M|$  its Liouville volume projected on  $\Gamma_E$ . Since we are dealing with macroscopic systems, we should actually think of  $\Gamma_E$  as an energy shell of thickness  $\delta E \ll E$ .

For  $N$  large enough and any reasonable choice of  $M$ 's, there exists an equilibrium macrostate,  $M_{eq}$ , for which  $|\Gamma_{M_{eq}}| \sim |\Gamma_E|$ , the volume of the whole energy shell. When  $M$  specifies a nonequilibrium state,  $|\Gamma_M|$  is much smaller. Thus if a dilute gas contains  $N$  atoms in a volume  $V$  then the ratio of  $|\Gamma_{M_{eq}}|$  for the macrostate  $M_{eq}$  in which there are  $(\frac{1}{2} \pm 10^{-10})N$  particles in the left half of the box to  $|\Gamma_M|$ , corresponding to a macrostate  $M$  in which all the particles are in the left half, is of order  $2^N$ . The result is similar if we use  $K \ll N$  boxes. We will still have that for  $N$  large enough  $|\Gamma_{M_{eq}}| \sim |\Gamma_E|$ . In fact, we expect that

$$\frac{|\Gamma_E \setminus \Gamma_{M_{eq}}|}{|\Gamma_E|} \sim e^{-cN}.$$

## Pictorially



The second picture is slightly more faithful. Neither shows the topology or differences in relative sizes of the different  $\Gamma_M$ 's.

The fact that  $|\Gamma_{eq}| \sim |\Gamma_E|$  explains why typical properties of macroscopic equilibrium systems, i.e. those true for almost all  $X \in \Gamma_{eq}$ , are also typical for all  $X \in \Gamma_E$  and can thus be obtained from the microcanonical ensemble. N.B. We did not have to invoke ergodicity to justify use of the microcanonical ensemble.

## Approach to Equilibrium

Boltzmann (also Maxwell, Kelvin, ...) argued that given this disparity in the sizes of the  $\Gamma_M$  corresponding to the various macrostates, the evolution of a typical microstate  $X$  specified to be at  $t = t_0$  in the phase space region  $\Gamma_M$ , will be such that  $|\Gamma_{M(X(t))}|$  will increase for  $t > t_0$  in a way which *explains* and describes the evolution towards equilibrium of macroscopic systems which start in the macrostate  $\Gamma_M$ ,  $M \neq M_{eq}$ , and are kept (effectively) isolated afterwards.

Typical here means that for any  $\Gamma_M$  the relative volume of the set of microstates  $X$  in  $\Gamma_M$  for which this is false during some time period  $\tau$  during which the macrostate undergoes a macroscopically noticeable change, but no bigger than the age of the universe, goes to zero exponentially in the number of atoms in the system.

## Boltzmann's Entropy

To make a connection with the Second Law of Thermodynamics, enunciated by Clausius in 1855, Boltzmann defined the entropy of a macroscopic system in a microstate  $X$  as

$$S_B(X) = k \log |\Gamma_{M(X)}| = S_B(M)$$

and showed that (for a dilute gas) in an equilibrium macrostate  $M_{eq}$ ,  $S_B(M_{eq})$  is proportional to the thermodynamic entropy of Clausius. Following O. Penrose, I shall call  $k \log |\Gamma_M(X)|$  the Boltzmann entropy of a system in the macrostate  $M(X)$ .

Thus calling  $S(E) = k \log |\Gamma_E|$ , we have the Boltzmann-Einstein formula

$$\text{Prob}(X \in \Gamma_M) \sim e^{-[S(E) - S_B(M)]} \sim e^{-[S_{eq} - S_B(M)]} \sim e^{-N\delta_M}$$

i.e.,  $\delta_M$  is a large deviation function (LDF) for macrostates  $M$  in the microcanonical measure.

## Quantum systems: microstates

Let me turn now to the quantum world, which is, to the best of our knowledge, the world we live in. The first question to answer is: what takes the place of the point  $X \in \Gamma$  as the microstate of a macroscopic system?

Sad to say there is not, at the present time (almost a century after the Bohr atom), a satisfying generally accepted answer to this question. What "everyone" does agree on is that the wave function  $\Psi$ ,  $\Psi \in \mathcal{H}$ , the Hilbert space of the system, is an important ingredient of the microstate. Let us assume for the present that  $\Psi$  is a sufficiently good description, i.e. it will give, via the usual rules, the properties of our isolated system.

## Macrostates: quantum

The next question then is: what takes the place of the  $\Gamma_M \subset \Gamma$ . The answer, as given by von Neumann, is to first "round" the operators corresponding to the macro variables so they all commute, then let  $\mathcal{H}_\nu$  be the linear subspace of  $\mathcal{H}$  specified by their simultaneous eigenvalues,  $\nu$ . Thus  $\Psi \in \mathcal{H}_\nu$  corresponds to the system being in the macrostate  $M_\nu$ . We then have

$$\mathcal{H}_E = \bigoplus \mathcal{H}_\nu$$

with the  $\mathcal{H}_\nu$  forming an orthogonal decomposition of the very large but still finite dimensional Hilbert space  $\mathcal{H}_E$ , with a basis given by the energy eigenstates  $|\phi_\alpha\rangle$  with  $E_\alpha \in [E, E + \delta E]$ .

To what extent this “rounding” can actually be done mathematically is still an open problem. For example, for a macroscopic system of Heisenberg spins on a lattice,

$$\underline{\sigma}_a = (\sigma_i^x, \sigma_i^y, \sigma_i^z), i = 1, \dots, N,$$

how well can we find three commuting operators  $m_N^\alpha, \alpha = x, y, z$ , such that

$$\left\| m_N^\alpha - \frac{1}{N} \sum_i \sigma_i^\alpha \right\| \rightarrow 0$$

as  $N \rightarrow \infty$  in a suitable norm? Physically, it certainly seems very reasonable that we can specify simultaneously all three spin components  $\frac{1}{N} \sum_i \sigma_i^\alpha$  with arbitrary small error,  $\epsilon_N \rightarrow 0$ , as  $N \rightarrow \infty$ .

Accepting this rounding, the orthogonal decomposition of  $\mathcal{H}$  corresponds to the classical decomposition of the energy shell  $\Gamma_E$  into regions  $\Gamma_M$  with  $\Gamma_E = \cup \Gamma_M$ . The analog to the Liouville volume  $|\Gamma_M|$  is the dimension of  $\mathcal{H}_\nu$ , denoted by  $|\mathcal{H}_\nu|$ . The Hamiltonian time evolution preserving Liouville volume now corresponds to the unitary evolution, obtained from the solution of the Schrödinger equation, which preserves the dimension of subspaces of  $\mathcal{H}$ .

The linear subspace,  $\mathcal{H}_{eq}$ , corresponding to the equilibrium macrostate is again (like in the classical case) characterized by the fact that its dimension is, for a macroscopic system, almost the same as the dimension of the whole (microcanonical) Hilbert space,

$$|\mathcal{H}_{eq}| \approx |\mathcal{H}_E|.$$

All other  $|\mathcal{H}_\nu|$  are much, much smaller.

The analog of the Boltzmann entropy for the system with a wave function  $\Psi \in \mathcal{H}_\nu$  would then be, according (more or less) to von Neumann\*, given by

$$S_B(\nu) = \log |\mathcal{H}_\nu|.$$

Using this prescription, the reasoning of Boltzmann about the approach to equilibrium and the microscopic origin of the second law for classical systems goes through, essentially unchanged, also for macroscopic quantum systems.

The only "fly in the ointment" in this analysis is that while for classical systems the microstate  $X$  uniquely specifies the macrostate  $M(X)$  (with possible exceptions of Lebesgue measure zero which can generally be ignored) this is no longer true in quantum mechanics:

A "typical" wave function  $\Psi$  will (in general) not be just in one linear subspace but will have projections  $P_\nu|\Psi\rangle \neq 0$ , for essentially all  $\nu$ .

\*One always talks of von Neumann's Gibbs entropy  $S_G = -\text{tr}(\rho \log \rho)$  which gives zero entropy to a pure state and never of his Boltzmann entropy discussed in chapter 5 of his book Foundations of Quantum Mechanics.

Thus, giving  $\Psi$  does not uniquely specify the macrostate of the system. This is the paradox of Schrödinger's cat, where the  $\Psi$  of the cat clearly corresponds to a superposition of incompatible macrostates: one in which the cat drank the milk and one in which it did not.

My only answer to this, at the moment, is that there is always a "fact of the matter" about macrostates, i.e. of whether the cat has drunk its milk or has not. How this "fact of the matter" for macrostates is to be understood or reconciled with the autonomous Schrödinger evolution of the wave function is still very much (as far as I am concerned) an unsettled matter. I quote from J. S. Bell's talk in 1989 on the occasion of Julian Schwinger's 70th birthday celebration.