

On Ruelle’s Construction of the Thermodynamic Limit for the Classical Microcanonical Entropy

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Abstract In 1969 Ruelle published his construction of the thermodynamic limit, in the sense of Fisher, for the quasi-microcanonical entropy density of classical Hamiltonian N -body systems with stable and tempered pair interactions. Here, “quasi-microcanonical” refers to the fact that he discussed the entropy defined with a regularized microcanonical measure as $\ln(N!^{-1} \int \chi_{\{\mathcal{E}-\Delta \leq \mathcal{E} < H < \mathcal{E}\}} d^{6N} X)$ rather than defined with the proper microcanonical measure as $\ln(N!^{-1} \int \delta(\mathcal{E} - H) d^{6N} X)$. Replacing $\delta(\mathcal{E} - H)$ by $\chi_{\{\mathcal{E}-\Delta \leq \mathcal{E} < H < \mathcal{E}\}}$ seems to have become the standard procedure for rigorous treatments of the microcanonical ensemble hence. In this note we make a very elementary technical observation to the effect that Ruelle’s proof (still based on regularization) does establish the thermodynamic limit also for the entropy density defined with the proper microcanonical measure. We also show that with only minor changes in the proof the regularization of $\delta(\mathcal{E} - H)$ is actually not needed at all.

Keywords Classical microcanonical entropy · Thermodynamic limit

The object of interest in this note is Boltzmann’s ergodic ensemble entropy

$$S_{H_{\Lambda}^{(N)}}(\mathcal{E}) = \ln \Omega'_{H_{\Lambda}^{(N)}}(\mathcal{E}), \quad (1)$$

where

$$\Omega'_{H_{\Lambda}^{(N)}}(\mathcal{E}) = \frac{1}{N!} \int \delta\left(\mathcal{E} - H_{\Lambda}^{(N)}(X^{(N)})\right) d^{6N} X \quad (2)$$

is known as the *structure function*; here, the ' means derivative w.r.t. \mathcal{E} of

$$\Omega_{H_{\Lambda}^{(N)}}(\mathcal{E}) = \frac{1}{N!} \int \chi_{\{H_{\Lambda}^{(N)} < \mathcal{E}\}} d^{6N} X, \quad (3)$$

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where $d^{6N}X := d^{3N}p d^{3N}q$ and $\chi_{\{H_\Lambda^{(N)} < \mathcal{E}\}}$ is the characteristic function of the set $\{H_\Lambda^{(N)}(X^{(N)}) < \mathcal{E}\} \subset \mathbb{R}^{3N} \times \Lambda^N$, with $X^{(N)} := (\mathbf{p}_1, \dots, \mathbf{p}_N; \mathbf{q}_1, \dots, \mathbf{q}_N) \in \mathbb{R}^{3N} \times \Lambda^N$, and where

$$H_\Lambda^{(N)}(X^{(N)}) = \sum_{1 \leq i \leq N} \frac{1}{2} |\mathbf{p}_i|^2 + \sum_{1 \leq i < j \leq N} W(|\mathbf{q}_i - \mathbf{q}_j|) + \sum_{1 \leq i \leq N} V_\Lambda(\mathbf{q}_i) \tag{4}$$

is the Hamiltonian of a Newtonian single specie N -body system in $\Lambda \subset \mathbb{R}^3$.¹ The entropy (1) can be evaluated in great detail for the perfect gas Hamiltonian ($W \equiv 0$) [1]. However, for $W \neq 0$ an exact evaluation would seem virtually impossible² and one has to resort to asymptotic analysis for large N [10].

Ideally one wishes to show that the entropy density $|\Lambda|^{-1} S_{H_\Lambda^{(N)}}(\mathcal{E})$ converges in the *thermodynamic limit* where $N \rightarrow \infty$ such that Λ grows “evenly” with N (in the sense of Fisher [4]), and such that $N/|\Lambda| \rightarrow \rho$ with $\rho \in \mathbb{R}_+$ fixed, and $\mathcal{E}/|\Lambda| \rightarrow \varepsilon$ with $\varepsilon \in \mathbb{R}$ fixed; furthermore, the limit function $s(\rho, \varepsilon)$ should have the right thermodynamic properties. To avoid a trivial thermodynamic limit (negative infinite entropy per volume) where all particles either end up “at infinity” or else all coalesce to a point, the *configurational Hamiltonian*

$$U_\Lambda^{(N)}(\mathbf{q}_1, \dots, \mathbf{q}_N) = \sum_{1 \leq i < j \leq N} W(|\mathbf{q}_i - \mathbf{q}_j|) + \sum_{1 \leq i \leq N} V_\Lambda(\mathbf{q}_i) \tag{5}$$

is assumed to be stable (bounded below $\propto N$) and tempered (“short range”; for the precise definition, see [4] and [13]). The rôle of the single particle potential V_Λ is merely to confine the N particles to the domain Λ , so one can take $V_\Lambda(\mathbf{q}) = +\infty$ whenever $\mathbf{q} \notin \Lambda$, and $V_\Lambda(\mathbf{q}) = 0$ else. Pair potentials W of interest in chemical and condensed matter physics, such as hard sphere or Lennard-Jones interactions, satisfy the postulated conditions on $U_\Lambda^{(N)}$.³

In Chap. 3 of his book [13], Ruelle proved that under the above mentioned conditions, when ε and ρ are fixed in an admissible joint domain Θ , then the thermodynamic limit of the *quasi-microcanonical* ensemble entropy

$$S_{H_\Lambda^{(N)}}^-(\mathcal{E}) = \ln \Omega_{H_\Lambda^{(N)}}(\mathcal{E}), \tag{6}$$

taken per volume, exists and is a concave continuous increasing function $s_{\text{tot}}(\rho, \varepsilon)$ on Θ . He also showed that the same result is obtained if $\Omega_{H_\Lambda^{(N)}}(\mathcal{E})$ in (6) is replaced by $\Omega_{H_\Lambda^{(N)}}(\mathcal{E}) - \Omega_{H_\Lambda^{(N)}}(\mathcal{E} - \Delta\mathcal{E})$; however, *this* argument works only for $\Delta\mathcal{E} > 0$ and does not capture (1).

Replacing the microcanonical measure $\delta(\mathcal{E} - H_\Lambda^{(N)}(X^{(N)}))$ by a quasi-microcanonical measure $\chi_{\{\mathcal{E} - \Delta\mathcal{E} < H_\Lambda^{(N)} < \mathcal{E}\}}$ or $\chi_{\{H_\Lambda^{(N)} < \mathcal{E}\}}$ goes back at least to [6] and seems to have become the standard procedure for rigorous treatments of the microcanonical ensemble [8, 9, 13]. The purpose of this brief note is to point out that no regularization of the classical microcanonical measure is necessary, and actually never was. We first make an elementary technical observation which shows that Ruelle’s proof basically establishes the thermodynamic limit

¹We use units of k_B for entropy, mc^2 for energy, mc for momentum, h/mc for length, where m is the particle mass, c the speed of light, k_B Boltzmann’s and h Planck’s constant.

²Hard sphere interactions merit special mention because they allow one to compute at least the \mathcal{E} -dependence of (1) exactly (as for the perfect gas).

³Like Ruelle [13], in (5) we could also allow irreducible higher-order many-body interactions which are permutation symmetric, translation-invariant, stable and tempered.

for Boltzmann’s ergodic ensemble entropy (1) per volume; a key formula in this proof is still based on the regularized measures. A minor variation on the theme of Ruelle’s proof finally shows that the regularization is not needed.

A key ingredient in Ruelle’s proof is the reduction of the (\mathbf{p}, \mathbf{q}) -space problem to two separate problems, one in \mathbf{p} -space and the other in \mathbf{q} -space. Namely, since the characteristic function of an interval of \mathbb{R} is a non-negative, bounded, piecewise continuous function, it is the upper limit of a sequence of continuous functions, and as such weakly lower semi-continuous. Therefore the convolution integral with a δ function is well-defined and yields the identity

$$\chi_{\{H_\Lambda^{(N)} < \mathcal{E}\}} = \int \chi_{\{U_\Lambda^{(N)} < \mathcal{E} - E\}} \delta(E - K^{(N)}) dE, \tag{7}$$

where we introduced the abbreviation $K^{(N)}$ for the kinetic Hamiltonian, i.e.

$$K^{(N)}(\mathbf{p}_1, \dots, \mathbf{p}_N) = \sum_{i=1}^N \frac{1}{2} |\mathbf{p}_i|^2, \tag{8}$$

so $H_\Lambda^{(N)} = K^{(N)} + U_\Lambda^{(N)}$. Integrating (7) w.r.t. $d^{6N} X$ and interchanging with the dE integration on the so integrated r.h.s. (7), then multiplying by $N!^{-1}$, yields Ruelle’s (4.3) in Sect. 3.4 of [13],

$$\Omega_{H_\Lambda^{(N)}}(\mathcal{E}) = \int \Omega_{U_\Lambda^{(N)}}(\mathcal{E} - E) \Omega'_{K^{(N)}}(E) dE, \tag{9}$$

where

$$\Omega_{U_\Lambda^{(N)}}(\mathcal{E}) = \frac{1}{N!} \int \chi_{\{U_\Lambda^{(N)} < \mathcal{E}\}} d^{3N} q \tag{10}$$

and

$$\Omega'_{K^{(N)}}(\mathcal{E}) = \int \delta(\mathcal{E} - K^{(N)}) d^{3N} p; \tag{11}$$

note that multiplying $\Omega'_{K^{(N)}}(\mathcal{E})$ by a factor $|\Lambda|^N / N!$ gives the structure function of the perfect gas. Thanks to (9), the proof that the thermodynamic limit exists for the logarithm of l.h.s. (9), taken per volume, reduces to proving that the thermodynamic limit exists separately for the logarithm of (10) and of (11), each taken per volume. For (11) this is easy. The \mathbf{p} -space integrations in (11) can be carried out explicitly as for the perfect gas, yielding

$$\Omega'_{K^{(N)}}(\mathcal{E}) = \frac{(2\pi)^{3N/2}}{\Gamma(3N/2)} \mathcal{E}^{\frac{3N}{2}-1} \chi_{\{\mathcal{E} > 0\}}, \tag{12}$$

and so one can take the thermodynamic limit of $|\Lambda|^{-1} \ln \Omega'_{K^{(N)}}(\mathcal{E})$, giving

$$\lim_{N \rightarrow \infty} \frac{1}{|\Lambda|} \ln \Omega'_{K^{(N)}}(\mathcal{E}) = \frac{3}{2} \rho \ln \left(\frac{4\pi e \mathcal{E}}{3 \rho} \right) \equiv s_{\text{kin}}(\rho, \mathcal{E}) \tag{13}$$

(cf., (4.4) in Sect. 3.4 of [13]), which differs from the entropy density of the perfect gas by an added $\rho \ln(\rho/e)$, due to the absence of the factor $|\Lambda|^N / N!$ in (11). All the hard technical work, which we won’t repeat here (and don’t need to), now goes into analyzing the configurational integral (10). Ruelle proves (Theorem 3.3.12): *If $\Lambda \rightarrow \mathbb{R}^3$ (Fisher) when $N \rightarrow \infty$,*

such that $\mathcal{E}/|\Lambda| \rightarrow \varepsilon$ and $N/|\Lambda| \rightarrow \rho$ with ε and ρ fixed in an admissible joint domain Θ , then the limit for the configurational (interaction) entropy density exists,

$$\lim_{N \rightarrow \infty} \frac{1}{|\Lambda|} \ln \Omega_{U_\Lambda^{(N)}}(\mathcal{E}) = s_{\text{int}}(\rho, \varepsilon), \tag{14}$$

and $s_{\text{int}}(\rho, \varepsilon)$ is concave and continuous on Θ . Having (13) and (14) Ruelle now applies Laplace’s method⁴ to (9) and finds (Sects. 3.4.1 and 3.4.2)

$$\lim_{N \rightarrow \infty} \frac{1}{|\Lambda|} \ln \Omega_{H_\Lambda^{(N)}}(\mathcal{E}) = \sup_{\tilde{\varepsilon} \in (0, \varepsilon - \varepsilon_0(\rho))} \{s_{\text{kin}}(\rho, \tilde{\varepsilon}) + s_{\text{int}}(\rho, \varepsilon - \tilde{\varepsilon})\} \equiv s_{\text{tot}}(\rho, \varepsilon), \tag{15}$$

where $\varepsilon_0(\rho) = \inf\{\pi_2(\rho, \varepsilon) | \rho \text{ fixed}\}$ is a boundary point of Θ . The continuity, concavity, and increase of $s_{\text{tot}}(\rho, \varepsilon)$ on Θ follow from (15). Ruelle also shows (see Sect. 3.3.14) that $s_{\text{int}}(\rho, \varepsilon)$ remains unchanged if in (14) one replaces $\Omega_{U_\Lambda^{(N)}}(\mathcal{E})$ by $\Omega_{U_\Lambda^{(N)}}(\mathcal{E}) - \Omega_{U_\Lambda^{(N)}}(\mathcal{E} - \Delta\mathcal{E})$ with $\Delta\mathcal{E} > 0$. It follows that the same is also true for $s_{\text{tot}}(\rho, \varepsilon)$ in (15). This completes our summary of Ruelle’s proof of the thermodynamic limit of the quasi-microcanonical entropy per volume.

Interestingly enough, by taking the derivative w.r.t. \mathcal{E} of the representation (9), one obtains Gibbs’ equation (303) [6],

$$\Omega'_{H_\Lambda^{(N)}}(\mathcal{E}) = \int \Omega'_{U_\Lambda^{(N)}}(\mathcal{E} - E) \Omega'_{K^{(N)}}(E) dE, \tag{16}$$

with $\Omega'_{U_\Lambda^{(N)}}(\mathcal{E})$ generally defined only in the distributional sense. But exchanging \mathcal{E} and E derivatives under the integral in (16), integrating by parts, then taking logarithms, now yields the following representation for (1):

$$S_{H_\Lambda^{(N)}}(\mathcal{E}) = \ln \int \Omega_{U_\Lambda^{(N)}}(\mathcal{E} - E) \Omega''_{K^{(N)}}(E) dE. \tag{17}$$

Next, (12) shows that in (13) we can replace $\Omega'_{K^{(N)}}(\mathcal{E})$ by $\Omega''_{K^{(N)}}(\mathcal{E})$ and still get $s_{\text{kin}}(\rho, \varepsilon)$, and this fact plus the limit (14) plus an easy adaptation of the Laplace method arguments in Sects. 3.4.1 and 3.4.2 of [13] now prove:

The thermodynamic limit for Boltzmann’s entropy per volume exists and has all the right monotonicity, continuity and concavity properties. This limit coincides with Ruelle’s $s_{\text{tot}}(\rho, \varepsilon)$ given by the variational principle (15), thus

$$\lim_{N \rightarrow \infty} \frac{1}{|\Lambda|} \ln \Omega'_{H_\Lambda^{(N)}}(\mathcal{E}) = s_{\text{tot}}(\rho, \varepsilon). \tag{18}$$

This concludes our demonstration that Ruelle’s treatment of (6) basically achieves control over (1). This entirely elementary observation may well have been made before; yet the author is not aware of anyone having pointed it out.

Armed with hindsight, we now inquire into whether (17) can be obtained directly from (1), i.e. without first proving (9) for the regularized ensemble entropy (6) and then taking the derivative of (9). At the purely formal level this is quite straightforward. Rather than from

⁴For background material on this method, cf. [3, Sect. II.7].

(7) we start from the “identity”

$$\delta \left(\mathcal{E} - H_{\Lambda}^{(N)} \right) = \int \delta \left(\mathcal{E} - E - U_{\Lambda}^{(N)} \right) \delta \left(E - K^{(N)} \right) dE, \tag{19}$$

which happens to be the formal derivative w.r.t. \mathcal{E} of the identity (7); we now formally integrate by parts on the r.h.s. (19) to obtain the “identity”

$$\delta \left(\mathcal{E} - H_{\Lambda}^{(N)} \right) = \int \chi_{\{U_{\Lambda}^{(N)} < \mathcal{E} - E\}} \delta' \left(E - K^{(N)} \right) dE; \tag{20}$$

next we integrate (20) w.r.t. $d^{6N} X$, and in the so integrated r.h.s. (20) we formally interchange $d^{6N} X$ and dE integrations, multiply by $N!^{-1}$, then take logarithms, et voilà: out pops (17). Unfortunately, these are all only symbolic manipulations.⁵ A slightly different plan of attack leads to conquest, though.

We note that the \mathbf{p} -space integrations involved in (1) can be carried out in the same fashion as for the perfect gas. The problem then becomes to study the large N asymptotics of the resulting \mathbf{q} -space integrals. Thus, carrying out the \mathbf{p} integrations in $\Omega'_{H_{\Lambda}^{(N)}}(\mathcal{E})$ given by (2), with $H_{\Lambda}^{(N)}$ given by (4), Boltzmann’s entropy (1) becomes (cf. (305) in [6])

$$S_{H_{\Lambda}^{(N)}}(\mathcal{E}) = \ln \left(\frac{2^{3N/2}}{3N} \left| \mathbb{S}^{3N-1} \right| \Psi'_{U_{\Lambda}^{(N)}}(\mathcal{E}) \right) \tag{21}$$

with

$$\Psi'_{U_{\Lambda}^{(N)}}(\mathcal{E}) = \frac{3/2}{(N-1)!} \int \left(\mathcal{E} - U_{\Lambda}^{(N)}(\mathbf{q}_1, \dots, \mathbf{q}_N) \right)^{\frac{3N}{2}-1} \chi_{\{U_{\Lambda}^{(N)} < \mathcal{E}\}} d^{3N} \mathbf{q}. \tag{22}$$

The primitive of (22),

$$\Psi_{U_{\Lambda}^{(N)}}(\mathcal{E}) = \frac{1}{N!} \int \left(\mathcal{E} - U_{\Lambda}^{(N)}(\mathbf{q}_1, \dots, \mathbf{q}_N) \right)^{\frac{3N}{2}} \chi_{\{U_{\Lambda}^{(N)} < \mathcal{E}\}} d^{3N} \mathbf{q}, \tag{23}$$

in turn obtains when carrying out the \mathbf{p} integrations in $\Omega_{H_{\Lambda}^{(N)}}(\mathcal{E})$ given in (3), so that the entropy (6) reads (cf. (304) in [6])

$$S_{H_{\Lambda}^{(N)}}^{-}(\mathcal{E}) = \ln \left(\frac{2^{3N/2}}{3N} \left| \mathbb{S}^{3N-1} \right| \Psi_{U_{\Lambda}^{(N)}}(\mathcal{E}) \right). \tag{24}$$

The integral (22) is obviously not more complicated than (23). Since Ruelle controlled (6), which is (24), he effectively controlled (23), and this means that his arguments control (22), the miniscule difference between the powers $3N/2$ and $(3N/2) - 1$ at the integrands of (23) and (22), and between their factors $1/N!$ and $(3/2)/(N-1)!$ hardly making a difference at all.

All we need to do is to show how Ruelle’s control of $\Omega_{U_{\Lambda}^{(N)}}(\mathcal{E})$ given in (10) implies the control of $\Psi_{U_{\Lambda}^{(N)}}(\mathcal{E})$ given in (23), and this will pave the way for the control of $\Psi'_{U_{\Lambda}^{(N)}}(\mathcal{E})$ given in (22). In the spirit of Ruelle’s proof, we seek a convolution representation

⁵However, one can see why the ease with which such formal manipulations apparently lead to the correct result does make it desirable to seek their rigorous foundation [2].

of $\Psi_{U_\Lambda^{(N)}}(\mathcal{E})$ and $\Psi'_{U_\Lambda^{(N)}}(\mathcal{E})$ involving $\Omega_{U_\Lambda^{(N)}}(\mathcal{E})$. Through integration by parts and Fubini's theorem one easily verifies that

$$\int (\mathcal{E} - U_\Lambda^{(N)})^P \chi_{\{U_\Lambda^{(N)} < \mathcal{E}\}} d^{3N}q = P \int_0^{\mathcal{E}-\mathcal{E}_g} E^{P-1} \int \chi_{\{U_\Lambda^{(N)} < \mathcal{E}-E\}} d^{3N}q dE \tag{25}$$

for any power $P > 0$, and so the desired convolutions read

$$\Psi_{U_\Lambda^{(N)}}(\mathcal{E}) = \frac{3N}{2} \int_0^{\mathcal{E}-\mathcal{E}_g} \Omega_{U_\Lambda^{(N)}}(\mathcal{E} - E) E^{\frac{3N}{2}-1} dE, \tag{26}$$

respectively

$$\Psi'_{U_\Lambda^{(N)}}(\mathcal{E}) = \frac{3N}{2} \left(\frac{3N}{2} - 1 \right) \int_0^{\mathcal{E}-\mathcal{E}_g} \Omega_{U_\Lambda^{(N)}}(\mathcal{E} - E) E^{\frac{3N}{2}-2} dE. \tag{27}$$

Inserting (26) into (24) and recalling (12) gives us the log of r.h.s. (9), and we are back full circle to the last stage of Ruelle's proof. In the same vein, inserting (27) into (21), and again recalling (12), we get for Boltzmann's entropy (1) the representation (17), and are back to our elementary observation made there that Ruelle's proof handles (17) as well.

The upshot is: the \mathbf{p} -space integrations are already so regularizing that no “ $\Delta\mathcal{E}$ regularization” is needed. Indeed, (22) shows explicitly that the \mathbf{p} integrations in $\Omega'_{H_\Lambda^{(N)}}(\mathcal{E})$ given by (2), with $H_\Lambda^{(N)}$ given by (4), automatically produce the characteristic function $\chi_{\{U_\Lambda^{(N)} < \mathcal{E}\}}$ which is the integrand of $\Omega_{U_\Lambda^{(N)}}(\mathcal{E})$ given in (10). Therefore it was never necessary to replace Dirac's $\delta(\mathcal{E} - H_\Lambda^{(N)})$ by a characteristic function $\chi_{\{H_\Lambda^{(N)} < \mathcal{E}\}}$ or $\chi_{\{\mathcal{E} - \Delta\mathcal{E} < H_\Lambda^{(N)} < \mathcal{E}\}}$ in the first place.⁶

Needless to stress: the mathematical reasoning presented in this note has no bearing on quantum statistical mechanics [7, 13], nor on the classical statistical mechanics of lattice systems [13]. Both involve discrete energies, which raises not just technically but also conceptually different questions.

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⁶Of course, this observation is meaningless for continuous classical quasi-particle systems like point vortices whose Hamiltonian is missing the kinetic $K^{(N)}(\mathbf{p}_1, \dots, \mathbf{p}_N)$ term, and in which case one needs to control $\Omega'_{U_\Lambda^{(N)}}(\mathcal{E})$ [12]. Interestingly, for overall neutral point vortex systems this feat has been accomplished outside the thermodynamic limit regime, with $(\mathcal{E} - \frac{1}{2}N \ln N) = \varepsilon N$ scaling [11], while their thermodynamic limit regime has so far been treated only with the regularized $\Omega_{U_\Lambda^{(N)}}(\mathcal{E}) - \Omega_{U_\Lambda^{(N)}}(\mathcal{E} - \Delta\mathcal{E})$, see [5].

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