CHAPTER 2

Boltzmann entropy of the classical gas

1. Introduction

The origins of statistical mechanics go back to the XIXth century with major contributions by Boltzmann,[1] Gibbs, and Maxwell.[2] The atomic nature of elements was yet unproved, although the idea was floating around. A major theoretical question dealt with the origin of irreversibility. How can we reconcile the observed irreversibility of thermodynamics, while the microscopic Newton laws are reversible? Boltzmann argued that irreversibility arises in a probabilistic way ("statistical"). But his ideas met with strong resistance, as exemplified by the words of his personal friend and scientific foe Ostwald (1895):

> *The actual irreversibility of natural phenomena thus proves the existence of processes that cannot be described by mechanical equations, and with this the verdict on scientific materialism is settled.*

Boltzmann's ideas are entirely accepted nowadays. The domain of physics that deals with deriving macroscopic (thermodynamic) properties of a system, starting with microscopic equations, is statistical mechanics. It applies to many different situations, to systems with classical or quantum particles, localized spins, and combinations of these.

The world is quantum by nature. However, classical mechanics is often a good approximation, and it makes sense to develop a statistical mechanics theory of a gas of classical particles.

2. Physical motivation for the entropy

Let $D \subset \mathbb{R}^3$ be a bounded subset in $\mathbb{R}^d$ (the dimension d being usually equal to 3), and let $V = |D|$ be the volume (i.e. Lebesgue measure) of D. Consider N particles in D. The state of the system is described by $(p_1, q_1), \dots, (p_N, q_N) \in \mathbb{R}^d \times D$, where p_i denotes the momentum of the i-th particle and q_i denotes its position. The overall state space is $(\mathbb{R}^d \times D)^N \simeq \mathbb{R}^{dN} \times D^N$. The energy of the system is given by the Hamiltonian function H,

$$H(\{p_i, q_i\}) = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{1 \leqslant i < j \leqslant N} U(q_i - q_j). \tag{2.1}$$

[1]The Austrian Ludwig Boltzmann (1844–1906) is buried in Vienna. On his tomb is engraved the formula $S = k \log W$. Of a difficult character, he moved to Leipzig because of conflicts with Ernst Mach in Vienna. He had friendly contacts yet scientific disagreements with Wilhelm Ostwald and he attempted suicide in 1901. He was to succeed in 1906.

[2]The Scot James Clerk Maxwell (1831–1879) found in 1873 the equations that describe electromagnetism, and was also the first person to realize that light is an electromagnetic phenomenon.

The first term represents the kinetic energy and the second term represents the interaction energy. We always suppose that $U(q)$ is spherically symmetric, i.e. $U(q)$ is a function of the Euclidean norm $|q|$ of q. The microscopic equations of motion are given by Hamilton equations

$$\begin{cases} \dot{q}_i = \nabla_{p_i} H = \frac{p_i}{m}, \\ \dot{p}_i = -\nabla_{q_i} H = -\sum_{j \neq i} \nabla_{q_i} U(q_i - q_j). \end{cases}$$

The heart of statistical mechanics resides in formulæ that give thermodynamic potentials in terms of microscopic degrees of freedom. Before giving the formula for the entropy, Definition 2.1 below, we discuss the underlying motivation.

Roughly speaking, the entropy measures the "number of available states" of the system. This is better understood when discretizing the state space (momenta and positions). We assume that all p_i's and q_i's take lattice values with respect to some fixed, tiny mesh.

Let $W = W(U, V, N)$ be the number of arrangements of $p_1, \dots, p_N$ and $q_1, \dots, q_N$ that are compatible with U, V, N. That is, the total energy $H(\{p_i, q_i\})$ must be equal to U (up to a tolerance interval), and $q_1, \dots, q_N$ must belong to the cubic box of size $L = V^{1/3}$ centered at the origin. We expect W to be related to the entropy.

If we have two systems described by U_1, V_1, N_1 and U_2, V_2, N_2, the number of arrangements for both systems simultaneously is $W_1 \cdot W_2$. Since the entropy should be extensive, we take the logarithm and define $S = \text{const} \log W$. Consider now two systems that exchange energy. We ignore all details associated with the evolution equations, but we retain the principle of conservation of energy. We concentrate on the number of available states. We want to maximize $W_1(U_1) \cdot W_2(U_2)$ under the condition $U_1 + U_2 = \text{const}$. This amounts to maximizing $S_1(U_1) + S_2(U_2)$, which suggests that S is indeed related to the entropy! The constant in front of the logarithm determines the scale of the absolute temperature; it is Boltzmann constant $k_{\rm B} = 1.38 \cdot 10^{-23}$ J/K.

3. Finite-volume entropy

We now give a precise mathematical definition of the entropy of the classical gas. Its form is motivated by the discussion above, and the reader is encouraged to reflect on similarities. Mathematically oriented readers can accept it as a mathematical definition, that suffices to itself. It would be a pity to miss the deep physical content, however.

Definition 2.1. *The* **finite-volume entropy** *is*

$$\boxed{S(U, D, N) = k_{\rm B} \log \frac{1}{h^{dN} N!} \int_{\mathbb{R}^{dN}} {\rm d}p_1 \dots {\rm d}p_N \int_{D^N} {\rm d}q_1 \dots {\rm d}q_N \, \mathbb{1}_{[H(\{p_i, q_i\}) \leqslant U]}.}$$

In absence of particles, $S(U, D, 0) = 0$.

The constant h is Planck constant; it has dimension distance $\times$ momentum, and it is present *solely* in order that the expression in the logarithm be dimensionless. Changing its value only adds an unimportant constant to the entropy. Notice the factor $1/N!$. It is necessary so that S scales as V in the limit of large volumes. It can be justified by invoking quantum mechanics, where identical particles are described by either symmetric, or antisymmetric complex functions.

It turns out that the major contribution of the integrals in the expression for S comes from a thin neighborhood of the manifold $H(\{p_i, q_i\}) = U$. The physical interpretation of the entropy is thus to measure the volume of the phase space with energy U.

Thermodynamics involves *bulk quantities* only and discard all boundary effects. Boundary terms are present in the expression for S, however. Further, it can be verified that S is not exactly homogeneous. This suggests to consider the **thermodynamic limit** where the extensive quantities are sent to infinity, keeping intensive quantities fixed. So we consider the density of energy u and the density of particles n (both per volume). The thermodynamic entropy is then defined as the limit $D \nearrow \mathbb{R}^d$ of $S(|D|u, D, |D|n)/|D|$. The precise definition of the limit of increasing domains will be given later.

Recall that the Hamiltonian is the sum of kinetic energy, that depends solely on the momenta, and of interaction energy, that depends solely on the positions. It follows that

- If $\int \mathrm{d}q_1 \dots \mathrm{d}q_N \, \mathbb{1}_{\{\sum_{i<j} U(q_i - q_j) \leqslant U\}} = 0$, then $S(U, D, N) = -\infty$.
- If $\int \mathrm{d}q_1 \dots \mathrm{d}q_N \, \mathbb{1}_{\{\sum_{i<j} U(q_i - q_j) \leqslant U\}} > 0$, then $S(U, D, N) > -\infty$, and it is strictly increasing in U.

The entropy can then be inverted so as to give $U(S, D, N)$; it is given by

$$U(S, D, N) = \sup\Big\{U : S(U, D, N) \leqslant S\Big\}. \tag{2.2}$$

Notice that it is decreasing in D, in the sense that $U(S, D, N) \geqslant U(S, D', N)$ when $D \subset D'$. It may take the value $+\infty$. We also set $U(S, D, 0) = 0$.

DEFINITION 2.2. *A potential $U(q)$ is* **stable** *if there exists a constant B such that for any N and any positions $q_1, \dots, q_N \in \mathbb{R}^d$, we have the inequality*

$$\sum_{1 \leqslant i < j \leqslant N} U(q_i - q_j) \geqslant -BN.$$

Nonnegative potentials, $U(q) \geqslant 0$ for any q, are obviously stable. Systems with unstable potential collapse at low energy, in the sense that particles acquire huge negative energy by occupying a small spatial area, instead of spreading in the whole domain as expected.

Let us define the densities of entropy and energy by

$$s_D(u, n) = \frac{S(|D|u, D, |D|n)}{|D|}, \tag{2.3}$$

$$u_D(s, n) = \frac{U(|D|s, D, |D|n)}{|D|}. \tag{2.4}$$

Their qualitative graph is depicted in Fig. 2.1 when the potential is stable.

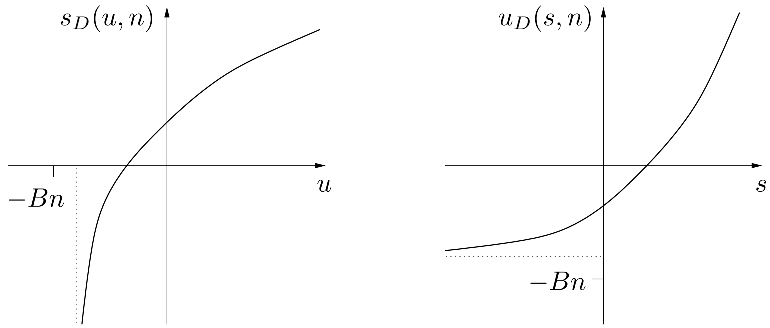

FIGURE 2.1. The entropy density for a stable potential with constant B. It is equal to $-\infty$ if $u < -Bn$. It may have a vertical asymptote, whose location depends on D. The inverse function is the energy. It is bounded below and may have a horizontal asymptote.

4. Entropy of the ideal gas

Let us compute explicitely the entropy of the ideal gas in dimension $d = 3$. Here, "ideal gas" refers to the absence of interactions, i.e. we set $U(q) \equiv 0$. Since $H(\{p_i, q_i\}) = \sum \frac{p_i^2}{2m}$, the integrals over $p_1, \dots, p_N$ yield the volume of the ball of radius $\sqrt{2mU}$ in $3N$ dimensions. Further, the integrals over $q_1, \dots, q_N$ yield $|D|^N$. Recall that the volume of the n-dimensional unit ball is $\pi^{n/2}/\Gamma(\frac{n}{2}+1)$ with the Gamma function satisfying $\Gamma(n+1) = n!$ for integer n. We obtain

$$S(U,D,N) = k_{\mathrm{B}} \log\Big\{ \frac{1}{h^{3N}} \frac{|D|^N}{N!} \frac{\pi^{\frac{3N}{2}}}{\Gamma(\frac{3N}{2}+1)} (2mU)^{\frac{3N}{2}} \Big\}.$$

In order to get the thermodynamic limit we use **Stirling inequality**:[3] for all $n \geqslant 1$,

$$\sqrt{2\pi n}\, n^n \,\mathrm{e}^{-n} \,(1 + \tfrac{1}{12n}) \leqslant n! \leqslant \sqrt{2\pi n}\, n^n \,\mathrm{e}^{-n} \,(1 + \tfrac{1}{12n} + \tfrac{1}{288n^2}).$$

It is enough for our purpose to retain $n! \approx n^n \,\mathrm{e}^{-n}$. It follows that

$$\tfrac{1}{|D|} \log \tfrac{|D|^N}{N!} = \tfrac{N}{|D|} \log \tfrac{|D|}{N} + \tfrac{N}{|D|} + \tfrac{1}{|D|} \log \tfrac{N^N \,\mathrm{e}^{-N}}{N!} \to -n \log n + n.$$

Similarly,

$$\tfrac{1}{|D|} \log \tfrac{(2mU)^{\frac{3N}{2}}}{\Gamma(\frac{3N}{2}+1)} = \tfrac{3N}{2|D|} \log \tfrac{4mU}{3N} + \tfrac{3N}{2|D|} + \tfrac{1}{|D|} \log \tfrac{(\frac{3N}{2})^{\frac{3N}{2}} \,\mathrm{e}^{-\frac{3N}{2}}}{\Gamma(\frac{3N}{2}+1)}$$
$$\to \tfrac{3}{2} n \log \tfrac{u}{n} + \tfrac{3}{2} n \log \tfrac{4m}{3} + \tfrac{3}{2} n.$$

We thus find

$$s(u,n) = \lim_{D \nearrow \mathbb{R}^3} \tfrac{1}{|D|} S(|D|u, D, D|n) = \tfrac{3}{2} n \log \tfrac{u}{n} - n \log n + \mathrm{const}\, n. \qquad (2.5)$$

[3]Stirling formula is due to Abraham de Moivre (1667–1754), a French Protestant who lived in England because of persecutions from the Catholic king Louis XIV. De Moivre could improve the formula thanks to comments from the Scot James Stirling (1692–1770), who was from a Jacobite family and therefore had difficulties with the English (Jacobites were supporters of the king James II of Britain, who was deposed because of his Catholic faith and who went into exile in France).

It is identical to the entropy of the ideal gas computed in Chapter 2 using thermodynamic relations only! In other words, we have derived the ideal gas law and the law of Dulong and Petit, showing in particular that $c_V = \frac{3}{2}k_{\rm B}$. The factor comes from the integrals over momenta and it takes this value because particles are represented by points for a monoatomic gas. In the case of diatomic particles, the kinetic energy involves the angular velocity as well, and the resulting integrals yield the factor $\frac{5}{2}$.

5. Subbaditivity of the energy

The proof of the pointwise convergence of $u_D(s,n)$ as $D \nearrow \mathbb{R}^d$ is a tricky but fundamental result of mathematical physics, which was obtained in the 60's by Ruelle and Fisher. These notes follow [Ruelle, 1969] rather closely. We alleviate the notation by neglecting physical constants, i.e. by setting $k_{\rm B} = h = 2m = 1$.

We start by the claim that the energy is essentially *subadditive*.

PROPOSITION 2.1. *Suppose that* $|U(q)| \leqslant |q|^{-\eta}$ *when* $|q| > R$. *Let* $D_1, \dots, D_m$ *be disjoint bounded domains in* $\mathbb{R}^d$ *such that* $\operatorname{dist}(D_k, D_\ell) \geqslant R$ *if* $k \neq \ell$. *Then*

$$U\Bigl(\sum_{k=1}^m S_k, \bigcup_{k=1}^m D_k, \sum_{k=1}^m N_k\Bigr) \leqslant \sum_{k=1}^m U(S_k, D_k, N_k) + \sum_{1 \leqslant k < \ell \leqslant m} \operatorname{dist}(D_k, D_\ell)^{-\eta} N_k N_\ell.$$

PROOF. Let $S = \sum S_k$, $D = \cup D_k$, $N = \sum N_k$, and $W = \sum_{k<\ell} \operatorname{dist}(D_k, D_\ell)^{-\eta} N_k N_\ell$. From the expression (2.2) for the energy,

$$\begin{aligned} U(S,D,N) - W &= \sup\bigl\{U - W : S(U,D,N) \leqslant S\bigr\} \\ &= \sup\bigl\{U : S(U+W,D,N) \leqslant S\bigr\}. \end{aligned}$$

We now restrict the integrals over $({\rm d}q_i)_{i=1}^N$ so that there are N_1 particles in D_1, N_2 in D_2, and so on... The set of U's in the expression above becomes bigger, hence the supremum is higher. The integrand is invariant under permutations of particles, and the number of ways of ordering N particles in m groups of $N_1, \dots,$ N_m is $\frac{N!}{N_1! \dots N_m!}$. We get

$$U(S,D,N) - W \leqslant \sup\Bigl\{U : \log \frac{1}{N_1! \dots N_m!} \Bigl[\prod_{k=1}^m \int_{\mathbb{R}^{dN_k}} ({\rm d}p_i^{(k)})_{i=1}^{N_k} \int_{D_k^{N_k}} ({\rm d}q_i^{(k)})_{i=1}^{N_k}\Bigr] \\ 1\!\!1_{\{H(\cdot) \leqslant U+W\}} \leqslant S\Bigr\}. \tag{2.6}$$

Now

$$H\bigl(\{p_i^{(k)}, q_i^{(k)}\}_{\substack{1 \leqslant k \leqslant m \\ 1 \leqslant i \leqslant N_k}}\bigr) \leqslant \sum_{k=1}^m H\bigl(\{p_i^{(k)}, q_i^{(k)}\}_{1 \leqslant i \leqslant N_k}\bigr) + \sum_{1 \leqslant k < \ell \leqslant m} \operatorname{dist}(D_k, D_\ell)^{-\eta} N_k N_\ell, \tag{2.7}$$

so that

$$\begin{aligned} 1\!\!1_{\{H(\cdot) \leqslant U+W\}} &\geqslant 1\!\!1_{\{\sum_{k=1}^m H(\{p_i^{(k)}, q_i^{(k)}\}_{1 \leqslant i \leqslant N_k}) \leqslant U\}} \\ &\geqslant \prod_{k=1}^m 1\!\!1_{\{H(\{p_i^{(k)}, q_i^{(k)}\}_{1 \leqslant i \leqslant N_k}) \leqslant U_k\}}. \end{aligned} \tag{2.8}$$

The last inequality holds for any numbers that satisfy $U_1 + \cdots + U_m = U$. Let U_k^* be the maximizer in $\sup\{U_k : S(U_k, D_k, N_k) \leqslant S_k\}$, and let $U^* = \sum U_k^*$. We can choose $U_k = U_k^* + \frac{U-U^*}{m}$ in the equation above. We obtain

$$U(S,D,N) - W \leqslant \sup\Big\{U : \sum_{k=1}^m S(U_k^* + \tfrac{U-U^*}{m}, D_k, N_k) \leqslant \sum_{k=1}^m S_k\Big\}. \tag{2.9}$$

Since S is increasing in U, the supremum is reached by $U = U^*$, and this proves the proposition. □

We can use Proposition 2.1 to derive an upper bound for the energy, that complements the lower bound $U(S,D,N) \geqslant -BN$.

Corollary 2.2. *Suppose that D contains N disjoint cubes of size L centered at $x_1, \dots, x_N \in [(L+R_0)\mathbb{Z}]^d$, with $R_0 > R$. Then*

$$U(S,D,N) \leqslant N \frac{(S/N)^{\frac{2}{d}}}{\pi\Gamma(\frac{d}{2}+1)^{\frac{2}{d}} L^2} + \tfrac12 N R_0^{-\eta} \sum_{z\in\mathbb{Z}^d\setminus\{0\}} |z|^{-\eta}.$$

Notice that the latter sum is convergent for $\eta > d$. The bound is proportional to N when S/N is held constant. To get this corollary, use the decreasing property of U in order to replace D by the union of cubes located on the vertices of the lattice $[(L+R_0)\mathbb{Z}]^d$. Then apply Proposition 2.1 with $S_k = \frac{S}{N}$ and $N_k = 1$. Notice that $U(S,D,1)$ can be exactly computed.

6. Identifying the thermodynamic limit

We consider now a special sequence of increasing cubes and establish the thermodynamic limit for the energy density. We also prove that the limiting function is convex. We suppose that the potential is stable, and that $|U(q)| \leqslant |q|^{-\eta}$ for $|q| > R$, for some $\eta > d$. Let r such that $2^{\frac{d}{\eta}} < r < 2$, and, for $m \geqslant 1$,

$$L_m = 2^m - r^m.$$

Let D_m be the cube of size L_m. One can put 2^d translates of D_m into D_{m+1} in such a way that they are separated by the distance

$$R_m = L_{m+1} - 2L_m = (2-r)r^m.$$

See Fig. 2.2. Notice that $R_m \to \infty$ as $m \to \infty$. It is useful to remember that D_m is roughly a cube of size 2^m and volume 2^{dm}.

Proposition 2.3. *Let $Q \subset \mathbb{R}^2$ be the set of points (s,n) such that $2^{dm} n \in \mathbb{N}$ for some integer m. Then*

$$2^{-dm} U(2^{dm}s, D_m, 2^{dm}n)$$

converges pointwise to a function $u(s,n) : Q \to \mathbb{R}\cup\{\infty\}$. This function is convex on Q.

Since Q is dense, u can be extended to a convex function in $\mathbb{R}\times\mathbb{R}_+$. The extension is unique except on the boundary of its essential domain. Setting $u(s,n) = \infty$ for negative n, we obtain a convex function on $\mathbb{R}^2$.

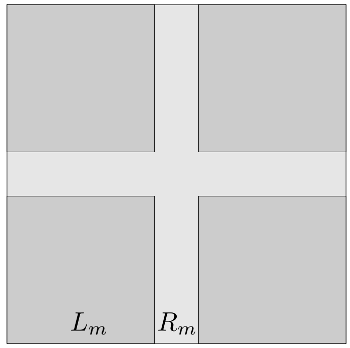

FIGURE 2.2. The domain D_{m+1} contains 2^d translates of the domain D_m separated by distance R_m.

PROOF. Let $(s,n) \in Q$ and let m_0 be large enough so that $2^{dm_0} n \in \mathbb{N}$ and $R_{m_0} > R$. For $m \geqslant m_0$, we have by Proposition 2.1 (U subbadititive):

$$2^{-d(m+1)} U(2^{d(m+1)} s, D_{m+1}, 2^{d(m+1)} n) \leqslant 2^{-dm} U(2^{dm} s, D_m, 2^{dm} n) + \frac{2^d - 1}{2(2-r)^\eta} n^2 (2^d r^{-\eta})^m. \quad (2.10)$$

Consider the sequence

$$c_m = 2^{-dm} U(2^{dm} s, D_m, 2^{dm} n) - \sum_{k=m_0}^{m-1} \frac{2^d - 1}{2(2-r)^\eta} n^2 (2^d r^{-\eta})^k. \quad (2.11)$$

Inequality (2.10) is $c_{m+1} \leqslant c_m$. Recall that $|D|^{-1} U(S, D, N)$ is bounded below by $-BN$. Then (c_m) is a monotone decreasing sequence with a lower bound and therefore it converges. The series in (2.11) is convergent, because $2^d r^{-\eta} < 1$, so $2^{-dm} U(2^{dm} s, D_m, 2^{dm} n)$ also converges. We let $u(s,n)$ denote the limit; it may be infinite. But if it is finite, then $U(2^{dm} s, D_m, 2^{dm} n)$ is finite for all m large enough.

Let $(s_1, n_1), (s_2, n_2) \in Q$. It follows from Proposition 2.1 (U subbadititive) that

$$\begin{aligned} &2^{-d(m+1)} U\big(2^{d(m+1)} (\tfrac{1}{2} s_1 + \tfrac{1}{2} s_2), D_{m+1}, 2^{d(m+1)} (\tfrac{1}{2} n_1 + \tfrac{1}{2} n_2)\big) \\ &\quad\leqslant 2^{-dm-1} U(2^{dm} s_1, D_m, 2^{dm} n_1) + 2^{-dm-1} U(2^{dm} s_2, D_m, 2^{dm} n_2) \\ &\qquad + \frac{2^d}{4(2-r)^\eta} (n_1 + n_2)^2 (2^d r^{-\eta})^m. \end{aligned} \quad (2.12)$$

(We used $\sum_{k<\ell} N_k N_\ell \leqslant \frac{1}{2} (\sum_k N_k)^2$.) As $m \to \infty$, we get

$$u(\tfrac{1}{2} s_1 + \tfrac{1}{2} s_2, \tfrac{1}{2} n_1 + \tfrac{1}{2} n_2) \leqslant \tfrac{1}{2} u(s_1, n_1) + \tfrac{1}{2} u(s_2, n_2). \quad (2.13)$$

This relation is not sufficient for convexity. But because $u(s,n)$ is increasing in s, and because the n's are of the form $2^{-dm} N$, (2.13) implies that $u(s,n)$ is convex on Q. □

7. Thermodynamic limit of the energy density

In the previous section we have identified a candidate for the thermodynamic limit, $u(s,n)$. We now consider a very general sequence of increasing domains.

Given $D \subset \mathbb{R}^d$, let ∂D denote teh boundary of D, and $\partial_h D$ denote the enlarged boundary

$$\partial_h D = \{x \in \mathbb{R}^d : \operatorname{dist}(x, \partial D) \leqslant h\}. \tag{2.14}$$

Recall that the diameter of a set is $\operatorname{diam}(D) = \sup_{x,y\in D} \operatorname{dist}(x,y)$.

Definition 2.3. *The bounded domains D converge to $\mathbb{R}^d$* **in the sense of Fisher***, which we denote $D \nearrow \mathbb{R}^d$, if*

- $\lim |D| = \infty$;
- *as* $\varepsilon \to 0$,

$$\sup_D \frac{|\partial_{\varepsilon \operatorname{diam}(D)} D|}{|D|} \to 0.$$

See the exercises for some intuition.

Proposition 2.4. *Consider domains D converging to $\mathbb{R}^d$ in the sense of Fisher, and numbers satisfying $s_D \to s$, $n_D \to n$ (with $|D| n_D \in \mathbb{N}$), such that (s,n) belongs to* $\operatorname{Ess}(u)$. *Then*

$$\lim_{D\nearrow\mathbb{R}^d} \frac{1}{|D|} U(|D|s_D, D, |D|n_D) = u(s,n).$$

Proof. First, we show that

$$\limsup_{D\nearrow\mathbb{R}^d} \frac{1}{|D|} U(|D|s_D, D, |D|n_D) \leqslant u(s,n). \tag{2.15}$$

The strategy is illustrated in Fig. 2.3 and consists in using subadditivity to compare the energy for D with that for cubes inside D. There are technical complications because Proposition 2.3 garantees the convergence of $2^{-dm} U(2^{dm}s, D_m, 2^{dm}n)$ only for (s,n) in Q.

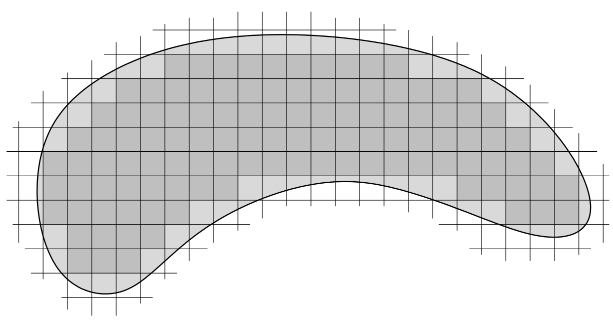

Figure 2.3. The large domain D contains M smaller cubes of size ξL_m.

Let $\xi > 1$, and let L_m be as in the previous section. Supposed that $\mathbb{R}^d$ is paved with translates of cubes of size ξL_m. The volume of cubes inside D is at least $|D| - |\partial_{\sqrt{d}\xi L_m} D|$. The number of cubes M satisfies therefore

$$\frac{|D|}{(\xi L_m)^d} \geqslant M \geqslant \frac{|D|}{(\xi L_m)^d} \Big(1 - \frac{|\partial_{\sqrt{d}\xi L_m} D|}{|D|}\Big). \tag{2.16}$$

Let $n_0 > n$ in Q. We put $2^{dm} n_0$ particles in M' cubes, where M' is the largest integer such that

$$M' 2^{dm} n_0 \leqslant |D| n_D. \tag{2.17}$$

From (2.16) and (2.17) we have $M' \leqslant M$, provided that $\xi^d < \frac{n_0}{n}$ and that D is large enough. We also have $M' > \frac{|D| n_D}{2^{dm} n_0} - 1$. The remaining $|D| n_D - M' 2^{dm} n_0 < 2^{dm} n_0$ particles are put in the remaining $M - M'$ cubes.

By Proposition 2.1, we get

$$\frac{1}{|D|} U(|D| s_D, D, |D| n_D) \leqslant \frac{M'}{|D|} U(2^{dm} s, D_m, 2^{dm} n_0) + \frac{M - M'}{|D|} 2^{dm} n_0 c(s) + \tfrac{1}{2} \frac{M}{|D|} 2^{2dm} n_0 \sum_{z \in \mathbb{Z}^d \setminus \{0\}} |(\xi - 1) L_m z|^{-\eta}. \quad (2.18)$$

The second term in the right side is a bound for the energy of the remaining cubes, obtained using Corollary 2.2; $c(s)$ depends on s only. The last term is less than $\text{const}(\xi - 1)^{-\eta} L_m^{-\eta}$.

Now we take the limsup with $D \nearrow \mathbb{R}^d$ in the sense of Fisher. The right side becomes

$$\frac{n}{n_0} 2^{-dm} U(2^{dm} s_0, D_m, 2^{dm} n_0) + \Big[\Big(\frac{2^m}{\xi L_m} \Big)^d n_0 - n \Big] c(s) + \text{const} \Big(\frac{2^{2m}}{\xi L_m} \Big)^d (\xi - 1)^{-\eta} L_m^{-\eta}.$$

For the second term, we used

$$\frac{M - M'}{|D|} 2^{dm} \leqslant (\frac{2^m}{\xi L_m})^d - \frac{n_D}{n_0} + \frac{2^{dm}}{|D|}.$$

Next, we take the limit $m \to \infty$ and we get

$$\frac{n}{n_0} u(s, n_0) + [\xi^{-d} n_0 - n] c(s).$$

Finally, we let $\xi \to 1$ and $n_0 \to n$. This proves (2.15).

There remains to show that the liminf is bounded below by $u(s, n)$ as well. A funny argument allows to combine Proposition 2.1 and (2.15). Because of the Fisher limit, there exists $C > 0$ such that for any D, we can find m and a translate of D_m that contains D, such that

$$C \leqslant \frac{|D|}{|D_m|} \leqslant \tfrac{1}{2}.$$

Let D' be the set of points in D_m at distance larger than r^m from D. As $D \nearrow \mathbb{R}^d$, we have $m \to \infty$ and $|D_m|^{-1}(|D| + |D'|) \to 1$. Let n_0 of the form $2^{-dm} N$. Since U is decreasing in D and using Proposition 2.1, we have

$$U(2^{dm} s, D_m, 2^{dm} n_0) \leqslant U(|D| s_D, D, |D| n_D) + U\big(2^{dm} s - |D| s_D, D', 2^{dm} n_0 - |D| n_D\big) + \tfrac{1}{2} 2^{2dm} n_0^2 r^{-\eta m}. \quad (2.19)$$

For the last term, we used $N_1 N_2 \leqslant \frac{1}{2}(N_1 + N_2)^2$. It vanishes as $m \to \infty$. We then obtain

$$\liminf_{D \nearrow \mathbb{R}^d} \frac{1}{|D|} U(|D| s_D, D, |D| n_D) \geqslant \liminf_{D \nearrow \mathbb{R}^d} \Big[\frac{|D_m|}{|D|} |D_m|^{-1} U(2^{dm} s, D_m, 2^{dm} n_0) - \frac{|D'|}{|D|} |D'|^{-1} U\big(2^{dm} s - |D| s_D, D', 2^{dm} n_0 - |D| n_D\big) \Big]. \quad (2.20)$$

We can use (2.15) for the second term of the right side. For any $\varepsilon > 0$, there exists n_0 close to n and D_ε such that if $D \supset D_\varepsilon$,

$$\liminf_{D \nearrow \mathbb{R}^d} \frac{1}{|D|} U(|D|s_D, D, |D|n_D) \geqslant \liminf_{D \nearrow \mathbb{R}^d} \frac{|D_m| - |D'|}{|D|} [u(s,n) - \varepsilon]. \tag{2.21}$$

This completes the prrof since $\lim \frac{|D_m| - |D'|}{|D|} = 1$. □

8. Thermodynamic limit of the entropy density

The claim of Proposition 2.4 can be summarized as follows: Suppose that u_D, s_D, n_D satisfy

$$u_D = \frac{1}{|D|} U(|D|s_D, D, |D|n_D) \quad \Leftrightarrow \quad s_D = \frac{1}{|D|} S(|D|u_D, D, |D|n_D), \tag{2.22}$$

and that $s_D \to s$ and $n_D \to n$. Then $u_D \to u(s,n)$. See Fig. 2.4.

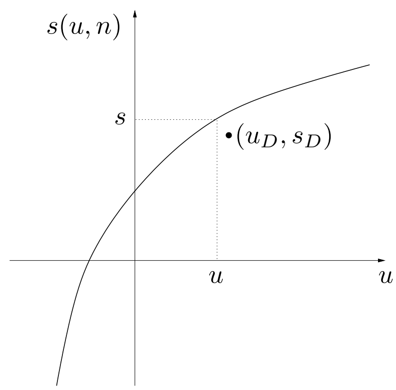

FIGURE 2.4. As $D \nearrow \mathbb{R}^d$, the point (u_D, s_D) moves towards the curve.

Now consider u_D, s_D, and n_D related as in (2.22), with $u_D \to u$ and $n_D \to n$. If $s_D \not\to s(u,n)$, there exists a subsequence of increasing domains D' such that $s_{D'} \to s' \neq s(u,n)$. By Proposition 2.4, the sequence $u_{D'}$ must converge to $u(s',n) \neq u$. Contradiction.

It is time to summarize the results of this chapter.

THEOREM I. *Suppose the potential is stable with constant B and it satisfies $|U(q)| \leqslant |q|^{-\eta}$ for $|q| > R$ and $\eta > d$. There exists a concave function $s(u,n) : \mathbb{R}^2 \to \mathbb{R} \cup \{-\infty\}$ which is increasing in u, and is $-\infty$ if $u < Bn$ or if $n < 0$. If (u,n) belongs to the interior of the essential domain of s, then*

$$\lim_{D \nearrow \mathbb{R}^d} \frac{S(|D|u_D, D, |D|n_D)}{|D|} = s(u,n)$$

whenever $u_D \to u$ and $n_D \to n$. Convergence of $\frac{1}{|D|} S(|D|u, D, |D|n)$ is uniform on compact sets.

We have thus established most of the second law of thermodynamics for the case of the ideal gas. We still need to show that $s(u,n)$ is C^1; this will follow from the equivalence of ensembles that we discuss in the next chapter. Uniform convergence means the following property, valid for any compact set C in the interior of the essential domain of s. For any $\varepsilon > 0$, there exists a (bounded) D_ε such that

$$\Big| \frac{1}{|D|} S(|D|u, D, |D|n) - s(u,n) \Big| < \varepsilon \tag{2.23}$$

for any $D \supset D_\varepsilon$ in the sequence of increasing cubes, and any $(u,n) \in C$. This can be proved *ab absurdo*: Otherwise there exists $\varepsilon > 0$, a sequence of domains $D^{(k)}$ converging to $\mathbb{R}^d$, and $(u^{(k)}, n^{(k)}) \in C$ such that

$$\Big| \frac{1}{|D^{(k)}|} S(|D^{(k)}|u^{(k)}, D^{(k)}, |D^{(k)}|n^{(k)}) - s(u^{(k)}, n^{(k)}) \Big| > \varepsilon \tag{2.24}$$

for all k. Since C is compact, there exists a converging subsequence $(u^{(k_i)}, n^{(k_i)})$, and the bracket above goes to 0 as $i \to \infty$ because of Theorem I; contradiction.

The proof of existence of the thermodynamic limit is very intricate. It is quite general, though. Once Proposition 2.1 has been established, things do not depend much on the model under study — the proof applies to any continuous system for which subadditivity of the energy can be proved. So we are rewarded by a straightforward extension of this theorem to quantum systems.

Exercise 2.1. Give a partial proof of Stirling formula. For instance, try to prove that $\lim_{n\to\infty} \frac{n!}{\sqrt{2\pi n} n^n \,\mathrm{e}^{-n}} = 1$.

Exercise 2.2. Consider an interaction potential $U(q)$ of the form

$$\begin{cases} U(q) = \infty & \text{if } |q| < R_0, \\ \Phi(q) & \text{if } |q| \geqslant R_0, \end{cases}$$

where $\Phi(q)$ is a bounded function with bounded support. Show that $U(q)$ is stable.

Exercise 2.3. Consider the interaction potential

$$\begin{cases} U(q) = \infty & \text{if } |q| < R_0, \\ -|q|^{-\eta} & \text{if } |q| \geqslant R_0. \end{cases}$$

Show that $U(q)$ is stable if η is large, and is unstable if η is small.

Exercise 2.4. Suppose that $f : \mathbb{R}^d \to \mathbb{R} \cup \{\infty\}$ satisfies

$$f\big(\alpha x + (1-\alpha)y\big) \leqslant \alpha f(x) + (1-\alpha) f(y),$$

for any $\alpha \in [0,1] \cap \mathbb{Q}$.

(a) Show that f is not necessarily convex.
(b) Assume in addition that $\mathrm{Ess}(f)$ has non empty interior (in other words, there exists an open set where f is finite). Show that f is convex.

Exercise 2.5. Let Q be dense in $\mathbb{R}^d$, and let $f : Q \to \mathbb{R} \cup \{\infty\}$ be convex on Q:

$$f\big(\alpha x + (1-\alpha)y\big) \leqslant \alpha f(x) + (1-\alpha) f(y),$$

for any $x, y \in Q$, and any $\alpha \in [0,1]$ such that $\alpha x + (1-\alpha)y \in Q$. Let $\mathrm{Ess}(f) = \overline{\{x \in Q : f(x) < \infty\}}$. Show that f has a convex extension in $\mathbb{R}^d$, and that it is unique except at the boundary of $\mathrm{Ess}(f)$.

Exercise 2.6. Let $D \subset \mathbb{R}^d$ be a bounded open domain that contains the origin, and with a smooth boundary. Let D_m be the dilation by m, i.e. $D_m = \{mx : x \in D\}$. Show that D_m converges to $\mathbb{R}^d$ in the sense of Fisher as $m \to \infty$.

Exercise 2.7. If $D \nearrow \mathbb{R}^d$ in the sense of Fisher, then $|D| > \text{const} \cdot \text{diam}(D)^d$ for a constant independent of D. Why?

Exercise 2.8. Let $d = 2$, and $D^{(k)} = \{(x, y) : 0 \leqslant x \leqslant k^2, 0 \leqslant y \leqslant k\}$. Show that $D^{(k)}$ does *not* converge to $\mathbb{R}^d$ in the sense of Fisher.