Chapter 1

Introduction and definitions

The aim of this chapter is to recall and introduce notions and terms that are used throughout the rest of this thesis. Most of them are known in the framework of standard statistical mechanics. However, some of them have to be redefined (extended) in order to be of use for small [a] systems. Most of these notions recover their usual sense at the thermodynamical limit. It is by no means an exhaustive overview of thermostatistics' realm. Moreover, dynamical issues like ergodicity, mixing or "approach to equilibrium" [Sas85, Kry79] are out of the scope of the present thesis, though arguments based on dynamics and time–scales are used. Finally, for simplicity the definitions are worked out within the classical mechanics framework although the basement of thermostatistics on quantum mechanics is needed as it is done in standard textbooks on statistical mechanics, viz. [LL94, Cal85, DGLR89, Bal82, Hil56]. Nevertheless, once the phase–space volume is given the type of mechanics (either classical or quantum) plays only a marginal role in the rest of the theory as it is shown below.

1.1 Microcanonical ensemble

1.1.1 Definitions

Let us consider an isolated physical system whose (microscopic) state at a given time t is described by a set of N generalized positions and momenta

$$\{\mathbf{q},\mathbf{p}\}(t) \equiv \{\mathbf{q}_1(t),\dots,\mathbf{q}_N(t),\mathbf{p}_1(t),\dots,\mathbf{p}_N(t)\}. \tag{1.1}$$

The set over which $\{\mathbf{q},\mathbf{p}\}$ is defined is called the *total phase space* Ω. Its dimension is usually huge even for a small system, e.g. for a system of N classical particles the dimension of Ω is $6N$. The dynamical evolution of the system is described by its Hamiltonian $\mathcal{H}\left(\{\mathbf{q},\mathbf{p}\}\right)$. For a time–independent (conservative) Hamiltonian [b], this Hamiltonian and an initial state say $\{\mathbf{q}_0,\mathbf{p}_0\} \doteq \{\mathbf{q},\mathbf{p}\}(t=0)$ define a unique trajectory of the microscopic state $\{\mathbf{q},\mathbf{p}\}$ in Ω [c]. This trajectory does not span the whole phase space Ω but it is dense only on a sub–manifold of Ω noted by W. The dimension of W depends on the number and type of the (macroscopic) "*extensive*" dynamical conserved quantities noted

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[a] In the following, the quotation marks around small are dropped if there is no ambiguity.

[b] Here and hereafter only time–independent Hamiltonian are considered.

[c] Since the Hamiltonian is time–independent any point of the trajectory can be taken as the initial state.

by $X \equiv \{X_1, \ldots, X_{\mathcal{M}}\}$ [d,e]. The number of conserved quantities and their nature depend on the system considered. E.g. the total energy E [f], the total linear momentum $\mathbf{P}$ (if $\mathcal{H}$ is invariant by translation), the total angular momentum with respect to the system center of mass $\mathbf{L}$ (if $\mathcal{H}$ is invariant by translation and by rotation), the number of classical particles N, the total charge $\mathcal{Q}$, the system volume V which can be included in the Hamiltonian as a static potential is also a macroscopic conserved quantity [g].

Now if one assumes *ergodicity* [Hil56, LL94, Kry79], i.e. that the time average $\langle\mathcal{O}\rangle_t$ of an observable $\mathcal{O}$ along a trajectory defined by $\{\mathbf{q}_0, \mathbf{p}_0\}$ and $\mathcal{H}$ is equal to $\langle\mathcal{O}\rangle_{W(X_o)}$ the average over $W(X_0)$, where $X_0 \doteq X(\{\mathbf{q}_0, \mathbf{p}_0\})$,

$$\begin{aligned}\langle\mathcal{O}\rangle_t &\doteq \lim_{t\to\infty} \frac{1}{t}\int_0^t d\tau\, \mathcal{O}(\tau) \\ &\equiv \frac{\int_\Omega d\mathbf{q}\, d\mathbf{p}\, \mathcal{O}(\{\mathbf{q},\mathbf{p}\})\, \delta(X(\{\mathbf{q},\mathbf{p}\}) - X_0)}{\int_\Omega d\mathbf{q}\, d\mathbf{p}\, \delta(X(\{\mathbf{q},\mathbf{p}\}) - X_0)} \doteq \langle\mathcal{O}\rangle_{W(X_0)}. \end{aligned} \tag{1.2}$$

I.e. the temporal averaging $\langle\cdot\rangle_t$ for a single state can be replaced by an ensemble of (infinitely) many states averaging $\langle\cdot\rangle_{W(X(t=0))}$ over the accessible phase–space $W(X_0)$. The density probability of the microstates $\{\mathbf{q},\mathbf{p}\} \in W(X_0)$ is *uniform*, i.e. [h]

$$P(\{\mathbf{q},\mathbf{p}\}) = \frac{\delta(X(\{\mathbf{q},\mathbf{p}\}) - X_0)}{\mathcal{W}(X_0)}, \tag{1.3}$$

where $\mathcal{W}$ is the volume of the accessible phase–space W.

Definition 1. *A collection of systems whose probability distribution follows eq. (1.3) is called a microcanonical ensemble.*

Boltzmann's principle

$$\boxed{S(X) \doteq k_B \ln \mathcal{W}(X)}, \tag{1.4}$$

defines the system entropy S as the logarithm of $\mathcal{W}$ times Boltzmann's constant k_B [i].

Note that so far no assumption has been made on the extensive nature of S [j] nor the thermodynamical limit $N \to \infty$, $N/V = const$ has been invoked. S is a purely "mechanical based" quantity defined for any system size. S *may or may not* be extensive.

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[d] This definition of an extensive variable, say X, is different from the conventional one: consider a system where $X = X_0$ and divide it in two equal pieces A and B. X is extensive if $X_A = X_B = \frac{X_0}{2}$ [DGLR89]. At the thermodynamical limit, if it exists, both definitions are equivalent (see sec. 1.2.1). In the following, to avoid cumbersome notations, the dynamical conserved quantities are called "extensive".

[e] To avoid cumbersome notations X refers also to a single "extensive" variable.

[f] As only conservative Hamiltonian are considered, $E = \mathcal{H}$ is a constant of motion. Therefore E is *always* an element of X; $X_1 \equiv E$.

[g] Contrary to e.g. E, the conservation of the volume does not necessarily decrease the dimension of W.

[h] For a quantum system the discrete nature of X leads to [DGLR89]

$$P(\{\mathbf{q},\mathbf{p}\}) = \frac{1}{\mathcal{W}(X_0)}.$$

[i] k_B is set from now on to 1.

[j] In the classical sense $S(X)$ is said to be extensive if X is extensive (see footnote (d)) and if for any $\lambda > 1$

$$S(\lambda X) = \lambda S(X).$$

From now on, the “extensive” variables X are assumed to be continuous [k] (since the following does not apply to discontinues variables), and S is assumed to be a smooth many time differentiable (at least three times) function of X. Moreover, the nature of the mechanics (classical or quantum) governing the system does not matter it is “hidden” in $\mathcal{W}$, the measure of the accessible phase–space [GRO01].

Once the entropy is defined one can introduce new, auxiliary, variables. These *intensive* variables $x \equiv \{x_1, \ldots, x_{\mathcal{M}}\}$ are the conjugate of $X \equiv \{X_1, \ldots, X_{\mathcal{M}}\}$ with respect to the entropy

$$x_i \doteq \frac{\partial S}{\partial X_i},\ i = 1, \ldots, \mathcal{M}. \tag{1.5}$$

E.g. the conjugate of E is β which is *defined* as the inverse temperature, the conjugate of the system volume V is βP where P is *defined* as the pressure.

There is a clear hierarchy among the quantities mentioned above

i. first, the “extensive” dynamically conserved quantities X;

ii. then, the entropy S which is proportional to the logarithm of the space–phase volume accessible to the system at fixed X (i);

iii. finally, the intensive variables derived from S (ii) with respect to the mechanical conserved quantities (i).

All this quantities are well defined and there is no quantity defined *a priori.*

It is worth to notice that the sign of $C_V^{-1} \doteq \frac{\partial \beta^{-1}}{\partial E}$, the microcanonical heat capacity, depends on the sign of the second derivative of S with respect to the energy

$$C_V^{-1} \doteq \frac{\partial \beta^{-1}}{\partial E} = -\frac{\frac{\partial^2 S}{\partial E^2}}{\left(\frac{\partial S}{\partial E}\right)^2}. \tag{1.6}$$

At the thermodynamical limit van Hove’s theorem [vH49] states that $\frac{\partial^2 S}{\partial E^2} \leq 0$ for all E [l], i.e. S is a *concave* function of E. The proof of this theorem relies on the thermodynamical limit. Therefore, it does not apply to small systems. *A priori*, for these systems $\frac{\partial^2 S}{\partial E^2}$ can either be positive or negative, i.e. in small systems there is nothing that forbids negative specific heat capacity regions. This point is of great importance and is further discussed in chapter 2.

1.1.2 On the choice of X

Following the discussion in the previous section one should incorporate in X all and only all the conserved quantities of the considered system. However, in practice one has often to loosen this constraint:

- An isolated system of N classical particles has $6N - 1$ constant of motions. For $N > 2$ their functional form are known only when the system equations of motion are integrated [FER65], which is usually an impossibly difficult task. So, all the

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[k] Or quasi–continuous, e.g. the number of particles N when N is sufficiently large, or any other conserved quantity when the system is described by quantum physics.

[l] In fact, the constraint applies to all X, i.e. $\frac{\partial^2 S}{\partial X_i^2} \leq 0$, $i = 1, \ldots, \mathcal{M}$ for all the values taken by X, see sec. 1.2.3.

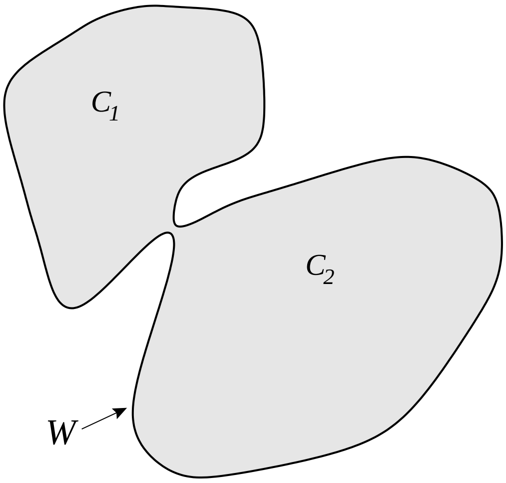

Figure 1.1: Schematic view of W. C can have two "macroscopic" values: C_1 and C_2.

constant of motions cannot be in practice incorporated in X. Nevertheless, seven of these constants are known: the energy, three components for the total linear and the total angular momentum [PAD90]. Moreover, some of them can be less relevant. For example, the total linear momentum can be set to zero by a suitable choice of frame coordinates. Finally, for practical use one is forced to study the system with a small number of parameters. This is the basic historical reason of introducing statistical mechanics.

- In some systems there exist several processes (degrees of freedom) with very different time–scales. Hence, some quantities might be considered as constant though there are not formally, i.e. some degrees of freedom may relax very quickly compared to other ones. Then, as an approximation one can build a ME where the degrees of freedom with long relaxation time are considered as fixed. This kind of argument is used in part III and in general to define the statistical mechanics of self–gravitating systems, see for example [HK77, SAS85, CP01]. Of course, terms like "majority", "sensibly", "quickly", etc, have to be carefully discussed and defined for each system depending on e.g. the precision asked.

- It can also happen that the phase space is made of two (or more) "basins" connected with each other by "tunnels" (see Fig. 1.1). If the system is ergodic, the time spent in each basin is simply proportional to their respective volume. In some cases, these basins can unambiguously be labeled with a quantity say $\mathcal{C}$, for example a symmetry [JG00]. Strictly taken the definition of the microcanonical ensemble given in the previous section, one should not use $\mathcal{C}$ as a new parameter in X. However, it is again a matter of time–scales. If in an experiment, one can control $\mathcal{C}$ and prepare a collection of systems having all the same value of $\mathcal{C}$, and if the time of experimentation is smaller than the typical time over which this quantity is conserved (the typical time that the system spends in the corresponding basin), then just like in the previous point, one may consider $\mathcal{C}$ as quasi–conserved and add it in X.

1.2 Canonical ensemble

1.2.1 Definitions

Consider a large isolated system called hereafter HT. Its Hamiltonian and the value of the constant of motions are noted by $\mathcal{H}_{HT}$ and X_{HT}, respectively. Now consider a part of HT, say A, and the rest of HT, say B. $\mathcal{H}_{HT}$ can be written as

$$\mathcal{H}_{HT} = \mathcal{H}_A + \mathcal{H}_B + \mathcal{H}_{AB}, \tag{1.7}$$

where $\mathcal{H}_A$ and $\mathcal{H}_A$ are the Hamiltonian of A and B resp., and $\mathcal{H}_{AB}$ describes the interactions between A and B.

If $\mathcal{H}_{AB}$ can be neglected compared to $\mathcal{H}_A$ and $\mathcal{H}_B$, i.e. if

$$\mathcal{H}_{HT} \simeq \mathcal{H}_A + \mathcal{H}_B, \tag{1.8}$$

then HT can be seen as the union of two independent systems $HT = A \cup B$. The following relation holds

$$X_{HT} \quad = \quad X_A + X_B, \tag{1.9}$$

where X_A and X_B are the values taken by X in A and B. Therefore, X is a set of extensive variables in the conventional sense (see footnote d on page 4). A priori X_A and X_B are not fixed, they can both fluctuate [m]. The volume of the phase space $\mathcal{W}_{HT}$ accessible to HT is written as a folding product

$$\mathcal{W}_{HT}(X_{HT}) = \int_{X_{A\,min}}^{X_{A\,max}} \mathcal{W}_A(X_A)\mathcal{W}_B(X_{HT} - X_A)\, dX_A, \tag{1.10}$$

where $\mathcal{W}_A$ and $\mathcal{W}_B$ are the phase space volumes of A and B, respectively. The bounds of the integral in eq. (1.10) depend on the domains of definition of A and B.

Now if A is small compared to B, i.e. if $\mathcal{H}_A \ll \mathcal{H}_B$ and $X_A \ll X_B$, then B can be seen as a reservoir of X for A, i.e. the exchange of amounts of X between A and B does neither change notably the entropy of B ($\frac{\partial^k S_B}{\partial X^k}|_{X_B} = 0$ for $k = 2, 3, \ldots$) nor the value of X_B. Under those conditions, the probability $P(X_A)$ for the subsystem A to have a given value of X_A is [LL94]

$$P(X_A) = \frac{1}{\mathcal{Z}(x_0)} \exp\left(-x_0 \cdot X_A + S_A(X_A)\right), \tag{1.11}$$

where $\mathcal{Z}(x_0)$ is the normalization constant called the partition function

$$\mathcal{Z}(x) = \int_{X_{A\,min}}^{X_{A\,max}} dX \, \exp\left(-x \cdot X + S_A(X)\right), \tag{1.12}$$

$x_0 = \frac{\partial S_B}{\partial X_B}|_{X_B} \simeq \frac{\partial S_{HT}}{\partial X_{HT}}|_{X_{HT}}$ is imposed to A by the reservoir. $S_A\,(X)$ is the entropy that A would have if it was isolated. The domain of definition of S_A is $[X_{A\,min}, X_{A\,max}]$. Thus the values of the intensive variables are imposed by the reservoir HT on A while its extensive variables are free to fluctuate according to the distribution (1.11). The probability distribution P depends explicitely on x_0. Therefore, in the following, it is noted $P\,(X, x_0)$.

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[m] For simplicity, all the components of X are assumed to fluctuate. Of course, depending on the context some of them might be fixed.

Definition 2. *A collection of systems whose extensive variables X are distributed according to the distribution (1.11) is called a canonical ensemble* [n].

In most of the cases the range of X_A in the integral (1.12) can be changed to $[0, +\infty[$. Then $\mathcal{Z}(x)$ becomes the Laplace transform of $\exp(S(X))$. For simplicity, in the following $\mathcal{Z}(x)$ is called the Laplace transform of $\exp(S(X))$. Hereafter, the argument of the exponential in eq. (1.12) is noted by $f(X, x) = -x \cdot X + S(X)$; and $F(x) \equiv -\frac{1}{\beta}\ln(\mathcal{Z}(x))$ is called the free energy, or the thermodynamical potential in CE. Note that one can alternatively write the previous functions of the intensive parameters x (i.e. P, $\mathcal{Z}$, f, F) as functions of the "extensive" parameters X_0 provided that $x_0 = \frac{\partial S}{\partial X}|_{X_0}$. Hence, in the following, $f(X, x_0)$ is also noted $f(X, X_0)$. Note that X_0 is not necessarily unique, i.e. a priori, nothing forbids $X_1 \neq X_0$ from satisfying $x_0 = \frac{\partial S}{\partial X}|_{X_1}$.

1.2.2 Link between ME and CE

Equation (1.12) shows that the main mathematical ingredient that transforms ME to CE is a Laplace transform. In order to facilitate the following discussions it is worth to spend some time to acquire a "pictorial" representation of this transform.

For sake of simplicity let us suppose that E is the only parameter ($X = E$) and that the entropy $S(X)$ is a concave function for all values of X as required by conventional thermodynamics.

Fig 1.2(a) shows the entropy (thick plain line) and the line $x_0 \cdot X$ (thick dashed line). The value of $x_0 (\equiv \beta)$ has been set to $x_0 = \frac{\partial S}{\partial X}|_{X_0}$. The plain line is just $x_0 \cdot X + K$ where K is a constant chosen so that this line touches $S(X)$ at X_0. *By definition* the line $x_0 \cdot X + K$ is tangent to $S(X)$ at X_0

$$\frac{\partial}{\partial X}(x_0 \cdot X + K)|_{X_0} = x_0 = \frac{\partial S}{\partial X}|_{X_0}.$$

$f(X, X_0) = f(X, x_0) = -x_0 \cdot X + S(X)$ is plotted in Fig. 1.2(b). It is the result of the shearing of S by the line of equation $x_0 \cdot X = 0$. By construction, $f(X, x_0)$ has an extremum at X_0

$$\frac{\partial f}{\partial X}|_{X_0} = -x_0 + \frac{\partial S}{\partial X}|_{X_0} = 0.$$

For the present example this extremum is even a maximum since $\frac{\partial^2 f}{\partial X^2}|_{X_0} = \frac{\partial^2 S}{\partial X^2}|_{X_0} < 0$. Note that this extremum is a maximum because S is concave at X_0.

In Fig. 1.2(c) the argument of the integral in Eq. (1.12), i.e. $\exp(f(X, X_0)) \propto P(X, X_0)$ is plotted. As one can see, it is a peaked function with a maximum at X_0. In the canonical ensemble and for this system, the most probable value of X is X_0. The most probable value of X is always X_0 if the entropy S is a strictly concave function of X, i.e. $\frac{\partial^2 S}{\partial X^2} < 0$ for all values of X. It can be shown that in the Gaussian approximation the width of this distribution is proportional to $\beta^{-2} C_V$, where C_V is the heat capacity. C_V is defined *in CE* in the following way

$$C_V \doteq \frac{\partial \langle E \rangle}{\partial T} \propto \langle E^2 \rangle - \langle E \rangle^2, \tag{1.13}$$

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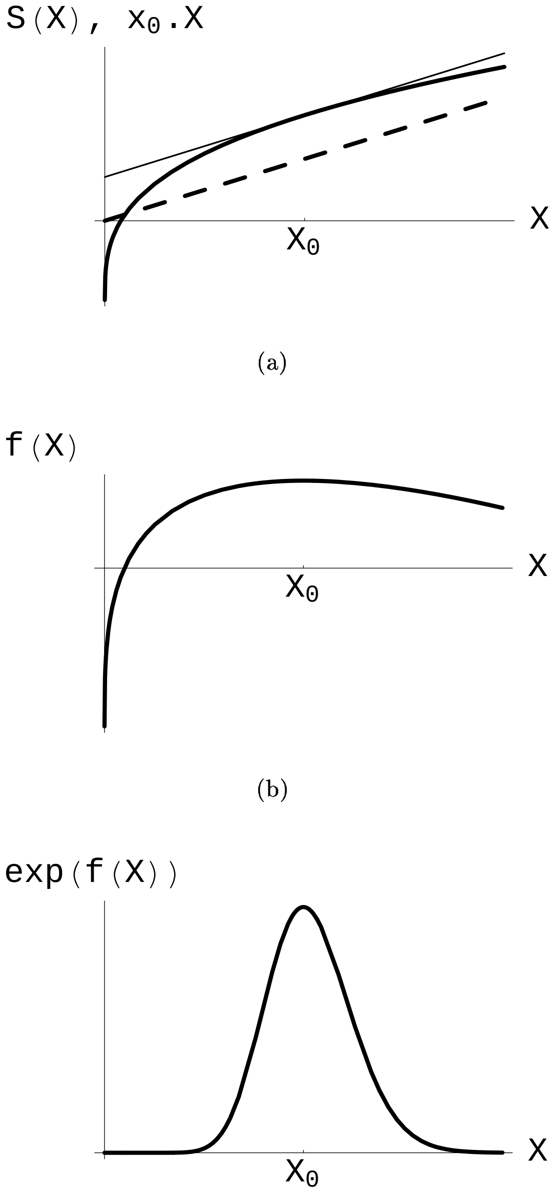
[n] In the conventional canonical ensemble, the only fluctuating extensive parameter is the subsystem energy E_A.



(a)

(b)

(c)

Figure 1.2: Schematic illustration of the integral in Eq. (1.12) on page 7 (see text). (a) Entropy $S(X)$ (thick line); $x_0 \cdot X \doteq \frac{\partial S}{\partial X}|_{X_0} \cdot X$ (dashed line) and $x_0 \cdot X + K$ (thin line) where K is chosen so that $x_0 \cdot X_0 + K = S(X_0)$. (b) Result of the shearing of S by $-x_0 \cdot X$, i.e. $f(X) = -x_0 \cdot X + S(X)$. (c) Unnormalized probability distribution of X $P(X, X_0) \propto \exp\left(f(X, X_0)\right)$.

where

$$\langle E \rangle \equiv -\frac{1}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial \beta} \tag{1.14}$$

is the mean value of the energy in CE, and

$$\langle E^2 \rangle \equiv \frac{1}{\mathcal{Z}} \frac{\partial^2 \mathcal{Z}}{\partial \beta^2} \tag{1.15}$$

is the mean value of the energy squared in CE. From the definition of the canonical heat capacity eq. (1.13), it immediately follows that it is a *positive* quantity. This is in sharp contrast with ME where nothing forbids *a priori* the entropy to have a convex part for finite size systems and consequently a region of *negative* heat capacity. If one identifies the two definitions of C_V then S *must* be a concave function of X. However, when CE and ME are not equivalent this identification is simply no longer legitimated (see sec. 1.2.3).

In order to generalize the previous results to multidimensional parameter spaces, first H_S is defined as the Hessian matrix of S

$$H_s \doteq \left\| \frac{\partial^2 S}{\partial X_i \partial X_j} \right\|, \, i,j = 1, \ldots, \mathcal{M}. \tag{1.16}$$

H_S is a $\mathcal{M} \times \mathcal{M}$ symmetric matrix. Therefore, one can always find a basis $\{\mathbf{v}_1, \ldots, \mathbf{v}_{\mathcal{M}}\}$ where H_S is diagonal. Its $\mathcal{M}$ eigenvalues are $\lambda_1 \geq \lambda_2 \geq \ldots \geq \lambda_{\mathcal{M}}$. Furthermore, $D_S = \lambda_1 \cdot \lambda_2 \cdots \lambda_{\mathcal{M}}$ is the determinant of H_S also called the Hessian of S. Note that H_f the Hessian matrix of f is equal to H_S since f is S plus a linear function of X.

In one hand, when $\lambda_1 < 0$ holds at $X = X_0$, then $S(X)$ is said to be a concave function at X_0 (it is a *local* property). In the other hand, when $\lambda_{\mathcal{M}} > 0$ at X_0 then $S(X_0)$ is locally convex.

Now in the case of a multidimensional parameter space, $f(X, x_0)$ is the result of the shearing of S by a plane of equation $x_0 \cdot X$. In the Gaussian approximation, the fluctuation of the full parameter–vector $\sqrt{\langle X^2 \rangle - \langle X \rangle^2}$ is proportional to $\left((-1)^{\mathcal{M}+1} D_S\right)^{-1}$. Again, this implies that $(-1)^{\mathcal{M}+1} D_S$ is positive. One can even show that *all* the eigenvalues of H_S have to be negative, i.e. $\lambda_1 < 0$ [GV00, FG01]. Or on other words, S must be concave at X_0. This generalizes the constraint of a positive heat capacity for a system with $\mathcal{M} = 1$.

1.2.3 Equivalence conditions

At the thermodynamical limit, CE and ME are said to be equivalent at $X = X_0$ if the following conditions hold

1. $\langle X \rangle_{CE} = X_0$,

2. $\lim_{N \to \infty} \langle X^2 \rangle - \langle X \rangle^2 \sim N$,

where

$$\langle X \rangle_{CE} = -\frac{1}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial x} |_{x_0 = \frac{\partial S}{\partial X}|_{X_0}}, \tag{1.17}$$

is the mean value of X in CE, and

$$\langle X^2 \rangle_{CE} = \frac{1}{\mathcal{Z}} \frac{\partial^2 \mathcal{Z}}{\partial x^2} |_{x_0 = \frac{\partial S}{\partial X}|_{X_0}}. \tag{1.18}$$

Condition (2) ensures the specific heat capacity to be a *finite and positive* quantity.

At the limit $N \to \infty$, if ME and CE are equivalent then $\frac{X}{N}$ does not fluctuate in CE. Its distribution function $P\left(\frac{X}{N}, \frac{X_0}{N}\right)$ as a function of the specific "extensive" variables is a δ–Dirac distribution, i.e.

$$P\left(\frac{X}{N}, \frac{X_0}{N}\right) = N\delta\left(X - X_0\right). \tag{1.19}$$

For finite systems, as $\frac{X}{N}$ fluctuates one needs a set of "weaker" conditions where small fluctuations are allowed

0'. $\mathcal{Z}\left(x_0\right) = \int dX \exp\left(-x_0 \cdot X + S\left(X\right)\right) < +\infty$,

1'. $X_0 - \Delta X_0 < \langle X \rangle_{CE} < X_0 + \Delta X_0$,

2'. $\langle X^2 \rangle - \langle X \rangle^2 < \delta X_0$,

where $x_0 = \frac{\partial S}{\partial X}|_{X_0}$. δX_0 and ΔX_0 are two arbitrary positive constants. For small systems a zeroth condition must be added: $\mathcal{Z}$ must be finite. This condition holds for all systems at the thermodynamical limit since their entropies are everywhere concave as van Hove's theorem states it [o]. In part III, a model is presented for which condition (0') does not hold for some values of X_0 and a particular choice of intensive parameters (see section 6.4.4).

In order to fulfill these equivalence conditions at X_0, $f\left(X, X_0\right)$ must have a global maximum at X_0. Locally this means that f and therefore S must be concave at X_0. I.e. CE and ME can be equivalent for small systems at X_0 only if $\lambda_1\left(X_0\right) < 0$. But if the plane $x_0 \cdot X + K(X_0) = 0$ touches more than one time the entropy surface then at least condition (2') is not satisfied, consequently CE is not equivalent to ME at X_0. Hence, the equivalence at X_0 implies that $\lambda_1(X_0) < 0$, whereas the converse proposition is not always true.

1.3 Microcanonical or canonical ensemble?

As ME and CE are equivalent at the thermodynamical limit (except at phase transitions, see below in section 2.2), the choice of the ensemble used to describe the infinite system is only a matter of conveniency. The canonical description is commonly preferred because therein the computations are usually "reduced" to optimization problems. They are in most of the cases technically easier to handle and faster to solve than computing averages over the whole microcanonical phase spaces. Moreover, the notion of heat bath is well defined and the assumptions made in sec. 1.2.1 on page 7 in order to define CE are valid.

For small systems the situation is dramatically different. CE relies on the assumption that the interactions between the system A and its reservoir B can be neglected and that the conserved quantities are extensive. These assumptions generally do not hold for small systems, i.e. when the range of the forces is of the order of the range of the system. For a small system the interactions between A and B dramatically affect the whole system A [GRO97, SCH97, CP01, SSHT00, STH00].

Nevertheless, one can go on and simply *assume* a canonical distribution for the "extensive" variables. This in order to benefit from technical advantages of CE compared to ME. In this respect, the canonical ensemble can be seen as a trick (as already noticed by Ehrenfest eighty years ago [EE12]). But, if one uses this trick, one would loose a lot of information about the physics of the system near and at phase transitions. This information

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[o] To be more precise, when $N \to +\infty$ it is $\mathcal{Z}^{1/N}$ which is a finite quantity.

is accessible to ME. Some information is lost because the equivalence conditions (1') or (2') do not hold near and at phase transitions (see section 2.2, see also [GV00] where half of the parametric space is in practice lost after the Laplace transform [p]). One could not observe for example multifragmentation of nuclei [CGD00, DGC$^+$00, DBB$^+$99, Gro90] or of metallic clusters [GMS97, SKM$^+$97, GM97, MHGS97]. In a model presented in part III, all the phenomena of astrophysical interest are overlooked by CE.

As there is a hierarchy of system parameters, $X \rightarrow x$ (see page 5) there is a hierarchy of ensembles ME → CE with a loss of information from ME to CE [CH88, GM97].

In summary, ME is the proper ensemble to describe small systems and information is lost in the transformations ME ↔ CE.

For all these reasons *the microcanonical description of a small system should be preferred to the canonical one.*

1.4 Toy models

In chapter 2 the definitions of phases and phase transitions are illustrated by the following simple analytical entropy-models. The model considered as one–dimensional $S(X) = S(E)$ is adapted from [Hül94a]. The two dimensional model is the one of a gas in the van der Waals approximation. In sec. 1.4.2 some classical results for this model are recalled [LL94, DGLR89].

1.4.1 1–D toy model

Hüller introduced in [Hül94a] several models of typical density of states (or entropy), in order to illustrate the smearing of information in CE. In the following chapter, one of these 1–dimensional entropy model is used to illustrate (a) the influence of the surfaces through the surface entropy S_{surf} and (b) the behavior of the caloric curve towards the thermodynamical limit. The entropy-model S_1 is defined as

$$S_1(\epsilon) = S_\infty(\epsilon) + N^{2/3} S_{surf}(\epsilon), \tag{1.20}$$

where ϵ is the specific energy $\epsilon = E/N$. $s_\infty(\epsilon) = \frac{S_\infty(\epsilon)}{N}$, the "infinite" system specific entropy (the volume part of S_1) as a function of the specific energy ϵ is given by

$$s_\infty(\epsilon) = \beta_t \epsilon - \begin{cases} 0 & \text{if } -d < \epsilon < d, \\ a_4 \left(|\epsilon| - d\right)^4 & \text{else,} \end{cases} \tag{1.21}$$

with the constants $\beta_t = 1$, $a_4 = 0.04$, and $d = 0.5$. As required by van Hove's theorem $\frac{\partial^2 s_\infty}{\partial \epsilon^2} \leq 0$ for all ϵ [vH49]; $\frac{\partial^2 s_\infty}{\partial \epsilon^2} = 0$ for a range of energies $-d < \epsilon < d$.

The surface effects are described by an entropy S_{surf} modeled in the following way

$$S_{surf}(\epsilon) = -a \cos(\pi \epsilon), \tag{1.22}$$

where $a = 0.01$.

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[p] Formally $\mathcal{Z}$ contains the same information as S. But in practice, the inverse Laplace transform, needed to recover S from $\mathcal{Z}$, is a very unstable transformation when finite precision is used [CH88]. Moreover, in CE the quantities are mostly computed thanks to some optimization algorithms (e.g. maximization of free energy, or f, etc.). Hence, the information near minima ($\lambda_1(X_0) > 0$) is overlooked by those methods.

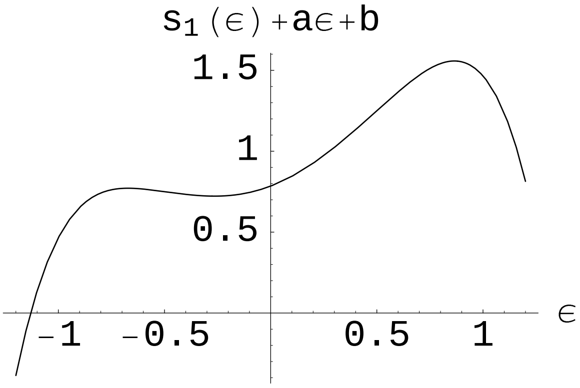

Figure 1.3: Specific entropy $s_1(\epsilon)$. A linear term in ϵ is added to $s_1(\epsilon)$ in order to emphasize the convex intruder ($a = -0.5$, $b = 1$ and $N = 100$). For finite N the specific heat capacity is negative for $\epsilon \in]-0.5, 0.5[$ and positive elsewhere.

For N finite, s_1 has a convex intruder ($\frac{\partial^2 s_\infty}{\partial \epsilon^2} > 0$) for a range of energies $-d < \epsilon < d$. See for an illustration fig. 1.3. As shown in the next chapter, this negative specific heat signals a first order phase transition [Gro97]. At the thermodynamical limit, $s_1 = S_1/N$ must satisfy van Hove's theorem, so the influence of surface effects must decrease relatively to the volume ones. A reasonable assumption is that the scaling of the surface effects should be $\sim N^{2/3}$ as already written in eq. (1.20) on the facing page. This scaling implies that $\lim_{N\to\infty} s_1 = s_\infty$, thus s_1 satisfies van Hove's theorem.

1.4.2 2–D toy model: the van der Waals approximation

The second model is the van der Waals gas [DGLR89, LL94]. It is a simple analytical model that presents first and second order phase transitions. Its *microcanonical* specific entropy ($s = \frac{S}{N}$) as a function of the specific energy ϵ and the specific volume $v = \frac{V}{N}$ is (up to an additive constant that does not depend on ϵ and v)

$$s(\epsilon, v) = \ln(v - b) + \frac{3}{2}\ln\left(\epsilon + \frac{a}{v}\right), \tag{1.23}$$

where a and b are two phenomenological constants. Their values depend on the fluid: a is linked to the interaction potential acting in the mean on one particle, b is an approximation for the avoided volume per particle [q].

With a suitable choice of units, i.e. $\epsilon\frac{b}{a} \to \epsilon$ and $\frac{v}{b} \to v$, eq. (1.23) becomes

$$s(\epsilon, v) = \ln(v - 1) + \frac{3}{2}\ln\left(\epsilon + \frac{1}{v}\right). \tag{1.24}$$

In these units β the inverse temperature is

$$\beta \doteq \frac{\partial s}{\partial \epsilon} = \frac{3}{2}\frac{1}{\epsilon + \frac{1}{v}}, \tag{1.25}$$

and the pressure p

$$\beta p \doteq \frac{\partial s}{\partial v} = \frac{1}{v-1} - \frac{3}{2}\frac{1}{v^2\left(\epsilon + \frac{1}{v}\right)}. \tag{1.26}$$

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[q] For a discussion on the avoided volume see app. A.

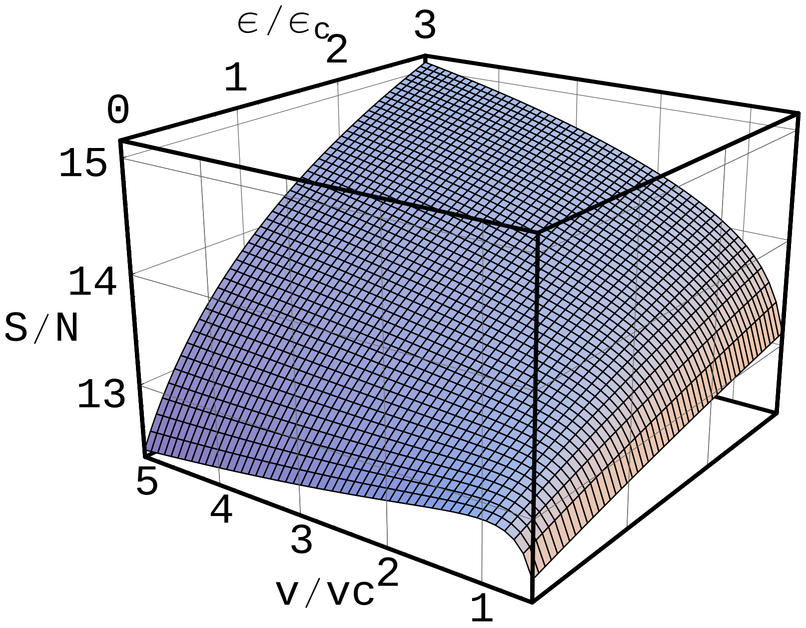


Figure 1.4: Specific entropy surface of the van der Waals model as a function of the specific energy ϵ and volume v. ϵ_c and v_c are the specific critical energy and volume.

This model has a critical point (second order phase transition) at $\epsilon_c = \frac{1}{9}$, $v_c = 3 \Rightarrow \beta_c = \frac{27}{8}$, $p_c = \frac{1}{27}$. At this critical point the following relations hold [DGLR89, LY52B]

$$\frac{\partial p}{\partial v}|_{\beta=cst} = 0, \tag{1.27}$$

$$\frac{\partial^2 p}{\partial v^2}|_{\beta=cst} = 0. \tag{1.28}$$

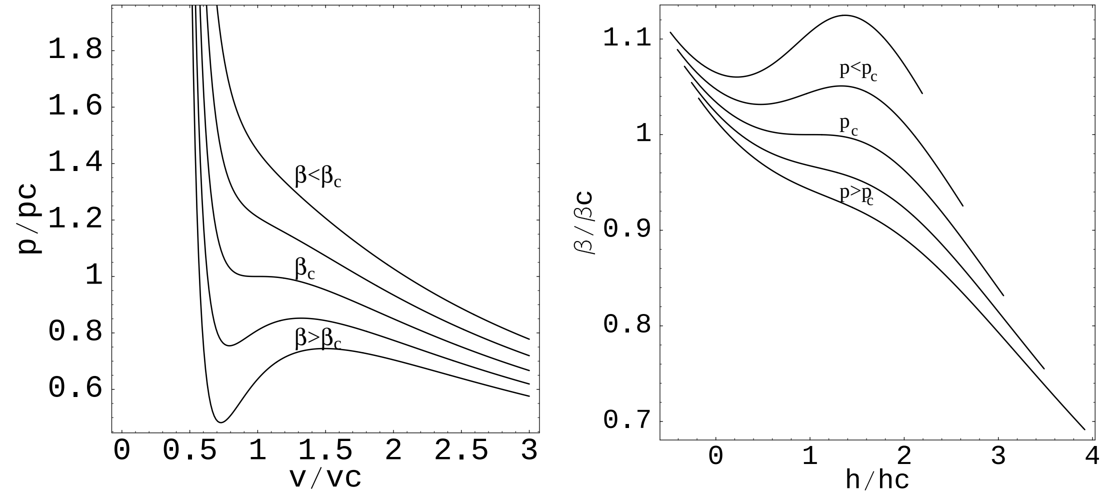
All quantities written in the following, for this model, are normalized by these critical values.

Fig. 1.4 shows the specific entropy s as a function of ϵ and v.

In fig. 1.5(a) on the next page isotherms are plotted in the plane (p, v) for different temperatures. At large volumes, the compressibility $\chi \doteq -\frac{\partial v}{\partial p}$ is large like in a gas. At small volumes, χ is small like in a liquid. Below β_c, the isotherms have a loop, i.e. there is a region of negative χ. In other words, the equation $p(v) = p_0$ has one solution above β_c and three below β_c. This loop is classically interpreted as a signal of a first order transition with phase coexistence [DGLR89]. Along the critical isotherm ($\beta = \beta_c$), the compressibility diverges at $v = v_c$. This divergence signals a second order phase transition.

In fig. 1.5(b) isobars are plotted in the plane (β, h), where $h = \epsilon + pv$ is the specific enthalpy. At low pressure and for a given isotherm, β is a multiple valued function of h. On the critical isobar ($p = p + c$), $\frac{\partial \beta}{\partial h}$ diverges at h_c.

The domain of physical validity of the van der Waals (vdW) approximation is smaller than the domain of definition of its entropy ($v > -1$ and $\epsilon > -\frac{1}{v}$, see eq. (1.24)). E.g. in the phase transition region, where for a real liquid–gas phase transition the density is no longer uniform, in contrast with the uniform density assumption made in the vdW approximation. Another region where the physical validity of eq. (1.24) breaks down is



(a) Isotherms: pressure vs volume. From top to bottom increasing β.

(b) Isobars: β vs enthalpy. From top to down increasing pressure.

Figure 1.5: Isotherms and isobars of the van der Waals model.

where the pressure becomes negative, i.e. $\frac{\partial s}{\partial v} < 0$ (see fig. 1.4 at $\epsilon = 0$ and $v \gtrsim 1$, see also eq. (1.26)). Moreover, S does not have a proper thermodynamical limit since the region of negative compressibility remains even at the limit $N \to \infty$. However, for illustration in the following the underlying physical system is forgotten and s is taken as it is. It is simply used as an entropy-model.