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From Classical Mechanics to Statistical Mechanics

In this chapter and the following one, the main concepts of statistical physics of equilibrium systems will be derived from a dynamical perspective that focuses on the observation of a single system over the course of time. With a few assumptions and facts, this approach will lead us to the mean values of fluctuating observables and, moreover, to their distributions. We will obtain microscopic expressions for naive concepts like temperature and pressure and for more sophisticated ones like chemical potential and entropy, which characterize macroscopic systems within classical thermodynamics. A further main virtue of this approach emphasizing trajectories is that it can be extended quite naturally to systems undergoing nonequilibrium processes, which will become the main focus of stochastic thermodynamics.

1.1 Histograms from Trajectories: Mesoscopic and Macroscopic Observables

In this section, we introduce three paradigmatic systems that highlight the difference between mesoscopic observables that refer to systems coupled to a much larger macroscopic system or embedded into one, and genuine macroscopic observables.

1.1.1 Brownian Motion of a Suspended Microsphere in Air

A classical example of a trajectory of a single particle is the erratic motion of micron-sized particles first observed on a qualitative level by Robert Brown in 1827. A quantitative experimental analysis of this phenomenon, later called Brownian motion, was achieved by Perrin in 1907. Since a discussion of the original Brownian motion goes beyond the concepts formulated in this introduction, we postpone its analysis to Chapter 9.

About 100 years after Perrin's experiments, it became possible to analyze not only the position of a Brownian particle but also its velocity, which can indeed serve as a paradigm for a mesoscopic observable. In this experiment by

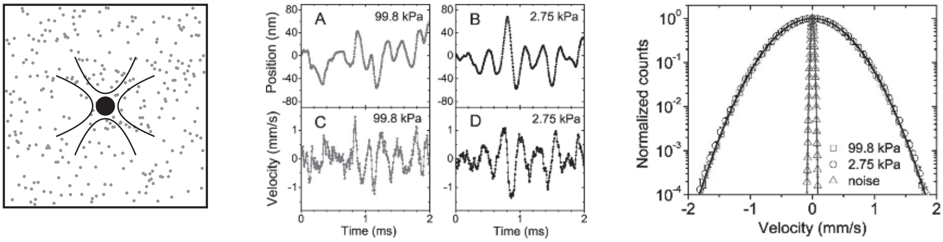

Figure 1.1 Measurements of Brownian motion of a microsphere in air at room temperature. *Left panel:* Sketch of a micron-size sphere in an optical trap undergoing collisions with air molecules. *Middle panels:* Trajectories of position (A,B) and velocity (C,D) of the microsphere. (A,C) are taken at atmospheric pressure (99.8 kPa), (B,D) at a much lower pressure (2.75 kPa). *Right panel:* Histogram of the velocity. The Gaussian distribution is independent of the pressure. Middle and right panels from T. Li *et al.*, *Science* **328** 1673 (2010). Reprinted with permission from AAAS.

Li et al. (2010), a microsphere is trapped in air by an effectively harmonic potential created with modern laser technology; see Figure 1.1.

Collisions of the colloidal particle with the surrounding air molecules generate an apparently random trajectory along one Cartesian coordinate, $X(t)$, leading to a velocity $V(t)$. Due to this random character, the particular value of $V(t)$ at a certain time t is not informative. More interesting is the **histogram**[1]

$$p^{\exp}(V) = \frac{1}{T}\int_0^T dt\delta(V(t) - V) \tag{1.1}$$

that can be extracted from such experimental data.[2] For sufficiently large observation time T, such an experimental histogram becomes stationary, i.e., independent of T.

This histogram can be interpreted as a probability distribution. Given such a trajectory $V(t)$ recorded over a total time T and a time t chosen randomly in the interval $0 \leq t \leq T$, the probability that $V(t)$ lies in the interval $V \leq V(t) \leq V + dV$ is

$$p(V \leq V(t) \leq V + dV) \approx p^{\exp}(V)dV \tag{1.2}$$

for small dV.

The important experimental observations that have to be explained by theory are, first, that the histogram for the velocity becomes a Gaussian, with, second, a width, i.e., a variance, that is independent of the density of the surrounding air.

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[1] Strictly speaking, the notion of a histogram requires binning of the data. We will work with the idealized limit of an infinitesimal bin size, which renders the histogram continuous.

[2] Readers not familiar yet with the delta and the theta functions should consult Appendix A.1 first.

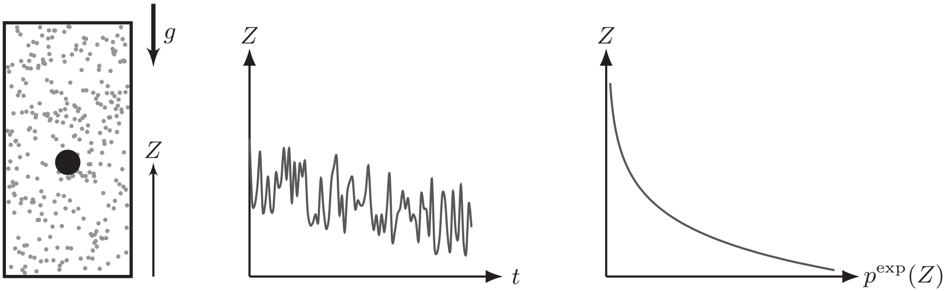

Figure 1.2 Brownian particle under gravity with a typical trajectory for the height $Z(t)$ and the corresponding histogram $p^{\mathrm{exp}}(Z)$.

1.1.2 Brownian Particle in the Gravitational Field

Another variant of such a system is a Brownian particle that is slightly denser than the surrounding liquid; see Figure 1.2. In an idealized experiment, the histogram for the height Z would become roughly exponential (as we will derive in Section 2.2.2). One characteristic of such a histogram is that its most likely value $\hat{Z}$, i.e., the peak of the histogram, differs from its mean value $\langle Z\rangle \equiv \int dZ p^{\mathrm{exp}}(Z)Z$.

1.1.3 Macroscopic Observables

Observables characterizing a macroscopic system show a quite different behavior. For a paradigmatic system, consider a homogeneous fluid of N particles in an isolating box of volume V. Under these conditions, the total energy E of the fluid is constant. The partitioning between kinetic energy and potential energy, however, will fluctuate as a function of time. Even though such a measurement cannot be realized, we anticipate that if it could, a typical trajectory $E_{\mathrm{k}}(t)$ of the kinetic energy would lead to an extremely narrow histogram for which the most likely value $\hat{E}_k$ and the mean value $\langle E_k\rangle$ would practically be the same. Likewise, if one could measure the instantaneous number $N_l(t)$ of particles in the left half of the box, its histogram would exhibit similar characteristics, i.e., tiny fluctuations around the most likely value $\hat{N}_l = N/2$. We will later show that the relative fluctuations of such extensive macroscopic observables are of the order $1/\sqrt{N} \simeq 10^{-12}$ for samples with the size of centimeters.

The two observables just discussed may sound somewhat contrived. For a more accessible macroscopic observable, consider the same fluid but now with the top plate movable under a mass subject to gravity that exerts an external pressure on the confined fluid; see Figure 1.3. In equilibrium, the position Z of this top plate may appear constant. In fact, however, it is subject to tiny fluctuations $\delta Z(t) \equiv Z(t) - \langle Z\rangle$, which will be shown to be of relative order $1/\sqrt{N}$.

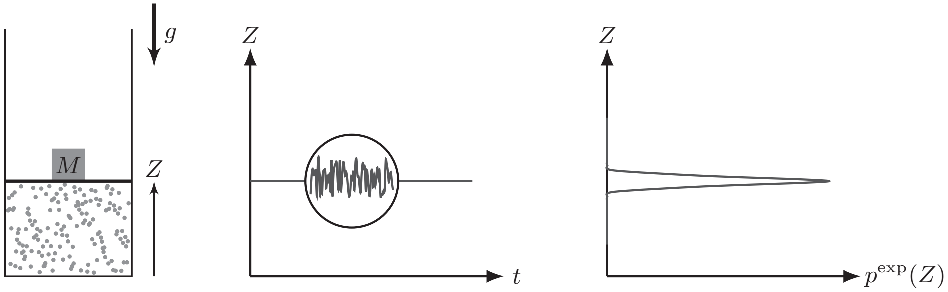

Figure 1.3 Container with a fluid confined by a mass under gravity. The height $Z(t)$ shows tiny fluctuations and a very narrow histogram $p^{\exp}(Z)$.

1.2 Foundations

We will build a theory for calculating the histograms obtained from such trajectories on a few basic assumptions and facts. This approach will work for both types of observables: for mesoscopic ones that show broad histograms, and for macroscopic observables for which these are extremely narrow.

1.2.1 Classical Mechanics for the Total Isolated System

We assume that any of the systems we have just introduced, consisting of molecules in a liquid or gas phase, additional colloidal particles, i.e., Brownian ones, and, possibly, a macroscopic weight, can be considered to be fully isolated, i.e., not interacting with any further dynamical degrees of freedom (like, e.g., a radiation field). Interaction with a static external potential arising from gravity or an electric field is allowed. Furthermore, we assume that the total system obeys classical mechanics rather than quantum mechanics. While the intermolecular forces are certainly determined by quantum-mechanical effects, it should be consistent to assume these forces to be given and then to let the molecules move classically under their action. We thus assume a classical Hamiltonian $H(\boldsymbol{\xi})$, where $\boldsymbol{\xi}$ refers to all degrees of freedom, momenta and positions, i.e., to a point in the huge phase space of the total system.[3]

The dynamical trajectory $\boldsymbol{\xi}^t \equiv \boldsymbol{\xi}(t)$ then is, at least in principle, uniquely determined by the unknown (and unobservable) initial phase point $\boldsymbol{\xi}^0$, i.e., $\boldsymbol{\xi}^t = \boldsymbol{\xi}^t(\boldsymbol{\xi}^0)$. By following this theory, the histogram for any variable $A(\boldsymbol{\xi})$ becomes

$$p^{\text{the}}(A|T,\boldsymbol{\xi}^0) \equiv \frac{1}{T}\int_0^T dt\delta(A(\boldsymbol{\xi}^t)-A), \tag{1.3}$$

where we have made the dependence on the initial point and the length T of the trajectory explicit.

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[3] For a brief summary of Hamiltonian dynamics, see Appendix B. An excellent textbook is Jose and Saletan (1998).

1.2.2 The Fundamental Principle

From a theoretical perspective, it is tempting to focus on the limit $T \to \infty$. This limit eliminates the dependence on T, which leaves the dependence on the initial phase point $\boldsymbol{\xi}^0$.[4] We write for this long-time limit

$$p_\infty^{\text{the}}(A|\boldsymbol{\xi}^0) \equiv \lim_{T\to\infty} p^{\text{the}}(A|T,\boldsymbol{\xi}^0). \tag{1.4}$$

The framework of statistical physics follows by exploring the consequences of the one fundamental hypothesis that for physical observables A this histogram (in this long-time limit) is independent of the initial point $\boldsymbol{\xi}^0$ taken from the energy shell at fixed E. Since E is a constant of motion in an isolated system, it is obvious that the latter dependence is relevant and must be kept. We write this hypothesis in the form

$$p_\infty^{\text{the}}(A|\boldsymbol{\xi}^0) \to p(A|E) \tag{1.5}$$

for all $\boldsymbol{\xi}^0$ with $H(\boldsymbol{\xi}^0) = E$.

As an intuitive justification for this hypothesis, assume, in a thought experiment, that for the system with the Brownian particle we have just discussed the initial velocities and positions of a few fluid particles (and possibly even those of the Brownian particle) are modified slightly at fixed E. It is hard to imagine that such a change would affect the experimental histogram in the long-time limit. In fact, repeating the experiment, which necessarily implies starting from a different initial phase point, yields the same experimental Gaussian histogram for the velocity. Still, this hypothesis has not yet been proven for a generic many-body system. In fact, it is known not to hold true for small isolated systems with only a few degrees of freedom for which typically the energy shell contains regions that confine the trajectories starting there.[5] Consequently, in such systems, the initial state matters for the long-time histogram. For a large system and for a small system coupled to or embedded into a much larger one, there may still exist extremely tiny regions in phase space that confine trajectories starting there. However, the resulting violations of the fundamental hypothesis will be negligible, i.e., unobservable for all reasonable mesoscopic and macroscopic observables $A(\boldsymbol{\xi})$ in a genuine many-particle system.

Indeed, the consequences derived by assuming this hypothesis to be true agree with experimental and numerical data for observables of many systems. We will therefore elevate the hypothesis to the fundamental principle of statistical physics within this dynamical approach.

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[4] The existence of this limit has been proven rigorously by Birkhoff; see, for example, the presentation in Khinchin (1949).

[5] See, for example, Dumas (2014).

1.2.3 Microcanonical Distribution

By invoking this fundamental principle, a simple prescription for calculating the distribution $p(A|E)$ can be derived as follows:

$$\begin{aligned} p(A|E) &= \int d\boldsymbol{\xi}^0 \delta(H(\boldsymbol{\xi}^0) - E) p_\infty^{\text{the}}(A|\boldsymbol{\xi}^0)/\Omega(E) \\ &= \int d\boldsymbol{\xi}^0 \delta(H(\boldsymbol{\xi}^0) - E) \left[\lim_{T\to\infty} \frac{1}{T} \int_0^T dt \delta(A(\boldsymbol{\xi}^t) - A) \right] /\Omega(E) \\ &= \lim_{T\to\infty} \frac{1}{T} \int_0^T dt \int d\boldsymbol{\xi}^t \delta(H(\boldsymbol{\xi}^t) - E) \delta(A(\boldsymbol{\xi}^t) - A)/\Omega(E). \end{aligned} \tag{1.6}$$

The first equality exploits the assumption that the histogram is the same for any initial point $\boldsymbol{\xi}^0$ on the energy shell. Thus, we can equally well average over this shell, which is achieved by introducing the delta function that characterizes it, and then integrate over the phase space of the many-body system. The size of the energy shell, called the **structure function**,

$$\Omega(E) \equiv \int d\boldsymbol{\xi}^0 \delta(H(\boldsymbol{\xi}^0) - E), \tag{1.7}$$

provides the normalization. In the second line, we have inserted (1.4) with (1.3). In the third line, after exchanging the limit with the integration over the shell, we have exploited that the energy is conserved, $H(\boldsymbol{\xi}^t) = H(\boldsymbol{\xi}^0)$, and that the Jacobian for the transformation from $d\boldsymbol{\xi}^0$ to $d\boldsymbol{\xi}^t$ is unity (due to Liouville's theorem; see Appendix B). The dependence on t thus becomes obsolete and we are left with an integration over the energy shell leading to

$$p(A|E) = \int d\boldsymbol{\xi} \delta(H(\boldsymbol{\xi}) - E) \delta(A(\boldsymbol{\xi}) - A)/\Omega(E). \tag{1.8}$$

As a consequence of the main assumption, codified in the fundamental principle, we have thus found that, in the long-time limit, the histogram resulting from such a trajectory is given by the so-called **microcanonical distribution** for this observable. This result eliminates any need for dealing with the impossible tasks of knowing the initial phase point and of solving the dynamics explicitly. Introducing the microcanonical probability (density) for a microstate $\boldsymbol{\xi}$

$$p(\boldsymbol{\xi}|E) \equiv \delta(H(\boldsymbol{\xi}) - E)/\Omega(E), \tag{1.9}$$

we can write this distribution as

$$p(A|E) = \int d\boldsymbol{\xi} p(\boldsymbol{\xi}|E) \delta(A(\boldsymbol{\xi}) - A). \tag{1.10}$$

The microcanonical average of any such variable becomes

$$\langle A|E \rangle \equiv \langle A(\boldsymbol{\xi})|E \rangle \equiv \int dA A p(A|E) = \int d\boldsymbol{\xi} p(\boldsymbol{\xi}|E) A(\boldsymbol{\xi}). \tag{1.11}$$

As a special case, we will sometimes need the joint distribution for a subset $\boldsymbol{\xi}_1$ of the microscopic degrees of freedom. With $\boldsymbol{\xi} = (\boldsymbol{\xi}_1, \boldsymbol{\xi}_2)$, we get

$$p(\boldsymbol{\xi}_1|E) = \int d\boldsymbol{\xi}_2 \delta(H(\boldsymbol{\xi}_1, \boldsymbol{\xi}_2) - E)/\Omega(E). \tag{1.12}$$

This relation, which results from integrating out the second set of degrees of freedom, holds for any splitting of $\boldsymbol{\xi}$ into two subsets.

It is crucial to prevent a possible misunderstanding of $p(\boldsymbol{\xi}|E)$. For a small element $\Delta_{\boldsymbol{\xi}'}$ on the energy shell around a specific $\boldsymbol{\xi}'$, it would be misleading to consider $p(\boldsymbol{\xi}|E)\Delta_{\boldsymbol{\xi}'}$ as a measurable probability to find the system in this small element. The histogram of the corresponding variable $A(\boldsymbol{\xi})$, with $A(\boldsymbol{\xi}) = 1$ if $\boldsymbol{\xi} \in \Delta_{\boldsymbol{\xi}'}$ and $A(\boldsymbol{\xi}) = 0$ otherwise, will depend on the initial value $\boldsymbol{\xi}^0$ for times far longer than any numerically or experimentally accessible time T. The notation $p(\boldsymbol{\xi}|E)$ and concomitant parlance ("in equilibrium, each microstate occurs over the course of time with equal probability") should be understood as a procedure for how to determine the distribution of more coarse-grained observables $A(\boldsymbol{\xi})$ to which a huge number of microstates contribute. Note that even variables referring to a single degree of freedom like the position of a colloidal particle or its velocity are legitimate observables since many microstates made up by the unobserved particles of the surrounding gas or liquid contribute to their distribution. This property justifies calling such observables mesoscopic rather than microscopic.

The physical justification for focusing on the histogram and on its theoretical counterpart, the microcanonical distribution, lies in the fact that if one performs a measurement of the observable A at an arbitrary (random) time after the system has reached **equilibrium**, i.e., has lost its dependence from the initial phase point $\boldsymbol{\xi}^0$, a result in the interval $[A, A+dA]$ will be measured with probability $p(A|E)dA$.[6] Hence, repeated (uncorrelated) measurements will finally produce the histogram.

For an isolated system, we thus know, in principle, how to calculate the distribution for any observable by using (1.10). This prescription is often called the **microcanonical ensemble**. The notion of an ensemble should not be taken literally. What is typically observed is one system over the course of time rather than an ensemble of weakly interacting copies of the system as sometimes insinuated in the older literature.

1.3 Total Kinetic Energy and Structure Functions

As a first example, we will calculate the probability distribution of the total kinetic energy of a simple fluid, which will turn out to be an extremely narrow Gaussian. Even though such a quantity cannot be measured experimentally, several important notions and concepts can be introduced with this example. It is therefore worthwhile

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[6] It is highly nontrivial to estimate the time necessary to reach this equilibration for an observable $A(\boldsymbol{\xi})$, given a Hamiltonian $H(\boldsymbol{\xi})$.

to go through this calculation in some detail. Moreover, the distribution of this variable is representative for other macroscopic variables consisting of a sum of single-particle contributions.

1.3.1 Model

We consider a fluid of N spherical particles of mass m confined in a box of volume V. The degrees of freedom, i.e., the momenta and positions, are denoted by $\boldsymbol{\xi} \equiv \{\boldsymbol{\xi}_i\} \equiv \{(\mathbf{p}_i, \mathbf{q}_i)\}$, where $i = 1, \ldots, N$ labels the particles. Equivalently, $\boldsymbol{\xi}$ can be ordered as $\boldsymbol{\xi} \equiv (\mathbf{p}, \mathbf{q})$ with $\mathbf{p} \equiv \{\mathbf{p}_i\}$ and $\mathbf{q} \equiv \{\mathbf{q}_i\}$. The Hamiltonian reads

$$H(\boldsymbol{\xi}) = \sum_{j=1}^{3N} p_j^2/2m + \Phi(\mathbf{q}), \tag{1.13}$$

where the potential energy $\Phi(\mathbf{q})$ includes external fields like gravity, interactions with the confining box, and intermolecular interactions. The index j runs over the $3N$ Cartesian components.

By applying the general expression (1.8), the probability distribution for the kinetic energy,

$$E_{\mathrm{k}}(\boldsymbol{\xi}) \equiv \sum_{j=1}^{3N} p_j^2/2m, \tag{1.14}$$

can be written in the form

$$\begin{aligned} p(E_{\mathrm{k}}|E) &= \int d\boldsymbol{\xi}\ \delta\left(\sum_{j=1}^{3N} p_j^2/2m - E_{\mathrm{k}}\right) \delta(H(\boldsymbol{\xi}) - E)/\Omega(E) \\ &= \int d\mathbf{p}\ \delta\left(\sum_{j=1}^{3N} p_j^2/2m - E_{\mathrm{k}}\right) \int d\mathbf{q}\ \delta(\Phi(\mathbf{q}) - (E - E_{\mathrm{k}}))/\Omega(E) \\ &\equiv \Omega_{\mathrm{k}}(E_{\mathrm{k}})\Omega_{\mathrm{c}}(E - E_{\mathrm{k}})/\Omega(E). \end{aligned} \tag{1.15}$$

The following analysis of this expression will lead to several crucial generic features that will be used later in the further development of the theory.

1.3.2 Kinetic and Configurational Structure Functions

The **kinetic structure function** is

$$\Omega_{\mathrm{k}}(E_{\mathrm{k}}) \equiv \int d\mathbf{p}\ \delta\left(\sum_{j=1}^{3N} p_j^2/2m - E_{\mathrm{k}}\right) = E_{\mathrm{k}}^{3N/2-1} m^{3N/2} C_N. \tag{1.16}$$

The right-hand side follows by first pulling out a factor of E_k from the delta function and then rescaling all $3N$ integration variables. The dimensionless constant C_N is not required explicitly at this stage and is given in Appendix A.5.

It will be relevant to formulate the energy dependence of this integral in a generalizable form as follows. We define a **kinetic beta function**

$$\beta_\mathrm{k}(E_\mathrm{k}) \equiv \partial_{E_\mathrm{k}} \Omega_\mathrm{k}(E_\mathrm{k})/\Omega_\mathrm{k}(E_\mathrm{k}) \tag{1.17}$$

that quantifies how the size of this shell varies with kinetic energy. For large N, we can approximate it with (1.16) as

$$\beta_\mathrm{k}(E_\mathrm{k}) \approx 3N/2E_\mathrm{k}. \tag{1.18}$$

Thus, $\beta_\mathrm{k}(E_\mathrm{k})$ turns out to be one half of the inverse of the kinetic energy per kinetic degree of freedom. We will also need its derivative:

$$\beta'_\mathrm{k}(E_\mathrm{k}) \equiv \partial_{E_\mathrm{k}} \beta_\mathrm{k}(E_\mathrm{k}) \approx -3N/2E_\mathrm{k}^2. \tag{1.19}$$

The energy dependence of the size of this shell around any base value E_k can then be expressed as[7]

$$\begin{aligned}\Omega_\mathrm{k}(E_\mathrm{k} + \Delta E_\mathrm{k}) &= \Omega_\mathrm{k}(E_\mathrm{k}) \exp \int_{E_\mathrm{k}}^{E_\mathrm{k}+\Delta E_\mathrm{k}} dE'_\mathrm{k} \beta_\mathrm{k}(E'_\mathrm{k}) \\ &\approx \Omega_\mathrm{k}(E_\mathrm{k}) \exp \left[\beta_\mathrm{k}(E_\mathrm{k})\Delta E_\mathrm{k} + \beta'_\mathrm{k}(E_\mathrm{k})(\Delta E_\mathrm{k})^2/2\right].\end{aligned} \tag{1.20}$$

Note that with (1.19) the expansion parameter is of order $\Delta E_\mathrm{k}/E_\mathrm{k}$. So whenever the increment ΔE_k is small compared to the base energy E_k, the exponential truncated after the first term is an excellent approximation. The second-order term will be required only if further factors lead to a cancellation of the linear term. If one had expanded $\Omega_\mathrm{k}(E_\mathrm{k} + \Delta E_\mathrm{k})$ naively as $\Omega_\mathrm{k}(E + \Delta E_\mathrm{k}) \approx \Omega_\mathrm{k}(E_\mathrm{k}) + \Delta E_\mathrm{k} \Omega'_\mathrm{k}(E_\mathrm{k})$, truncation of the series would require $\beta_\mathrm{k}(E_\mathrm{k})\Delta E_\mathrm{k} \sim N\Delta E_\mathrm{k}/E_\mathrm{k} \ll 1$, which, for large N, is a tremendously more restrictive condition.

Likewise, the size of the energy shell associated with the configurational degrees of freedom, i.e., the **configurational structure function**, is defined as

$$\Omega_\mathrm{c}(E_\mathrm{c}) \equiv \int d\mathbf{q}\, \delta(E_\mathrm{c} - \Phi(\mathbf{q})). \tag{1.21}$$

In contrast to the kinetic one, it cannot be evaluated explicitly for any realistic interacting system. For an ideal gas, i.e., for point-like particles confined to a volume

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[7] In this and similar expressions in the math that follows, one should not confuse the prime at the beta function, which indicates a derivative with respect to the energy argument, with the prime at the dummy variable indicating the energy integration.

V and $\Phi(\mathbf{q}) = 0$ in (1.13), it is formally given by $V^N \delta(E_c)$. For the general case, we define a **configurational beta function**

$$\beta_{\rm c}(E_{\rm c}) \equiv \partial_{E_{\rm c}} \Omega_{\rm c}(E_{\rm c}) / \Omega_{\rm c}(E_{\rm c}) \tag{1.22}$$

leading to the exponential approximation

$$\Omega_{\rm c}(E_{\rm c} + \Delta E_{\rm c}) \approx \Omega_{\rm c}(E_{\rm c}) \exp\left[\beta_{\rm c}(E_{\rm c})\Delta E_{\rm c} + \beta_{\rm c}'(E_{\rm c})(\Delta E_{\rm c})^2/2\right]. \tag{1.23}$$

1.3.3 Gaussian Approximation and Its Justification

The probability $p(E_{\rm k}|E)$ (1.15) peaks at a value $\hat{E}_{\rm k}$ that, using (1.17) and (1.22), is determined by

$$\beta_{\rm k}(\hat{E}_{\rm k}) = \beta_{\rm c}(E - \hat{E}_{\rm k}), \tag{1.24}$$

which will make this most likely value a function of the total energy, i.e., $\hat{E}_{\rm k} = \hat{E}_{\rm k}(E)$. Inserting this relation and the exponential expansions (1.20) and (1.23) around $\hat{E}_{\rm k}$ into (1.15) leads to a Gaussian distribution for the kinetic energy

$$p(E_{\rm k}|E) \approx (2\pi\sigma_{E_{\rm k}}^2)^{-1/2} \exp\left[-(E_{\rm k} - \hat{E}_{\rm k})^2/2\sigma_{E_{\rm k}}^2\right] \tag{1.25}$$

with the variance

$$\sigma_{E_{\rm k}}^2 \equiv \int dE_{\rm k} (E_{\rm k} - \hat{E}_{\rm k})^2 p(E_{\rm k}|E) = -[\beta_{\rm c}'(E - \hat{E}_{\rm k}) + \beta_{\rm k}'(\hat{E}_{\rm k})]^{-1} \tag{1.26}$$

that determines the posterior normalization.

This Gaussian approximation to the full distribution is a sensible one, provided we can show that it is indeed sharply peaked, i.e., that its variance is small compared to $\hat{E}_{\rm k}^2$. By applying a derivative with respect to E to (1.24), we get a relation between the slopes of the two beta functions as follows:

$$\beta_{\rm c}'(E - \hat{E}_{\rm k}) = \beta_{\rm k}'(\hat{E}_{\rm k}) \frac{\partial_E \hat{E}_{\rm k}}{1 - \partial_E \hat{E}_{\rm k}}. \tag{1.27}$$

Inserting this into (1.26) and using (1.19) for the derivative of the kinetic beta function, we get

$$\sigma_{E_{\rm k}}^2 / \hat{E}_{\rm k}^2 = (1/N)\{2[1 - \partial_E \hat{E}_{\rm k}(E)]/3\}. \tag{1.28}$$

For a large system, we have thus derived that the relative fluctuations of the kinetic energy, $(\sigma_{E_{\rm k}}^2/\hat{E}_{\rm k}^2)^{1/2}$, are of the order $1/\sqrt{N}$.[8] The scaling $\sim 1/\sqrt{N}$ is indeed typical for the relative fluctuations of any observable that is the sum of one-particle observables in a macroscopic system.[9]

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[8] A trivial exception from this scaling occurs for the ideal gas for which this distribution is singular with $p(E_k|E) = \delta(E_k - E)$, i.e., $\hat{E}_{\rm k} = E$ and hence $\partial_E \hat{E}_{\rm k}(E) = 1$.

[9] This fact is usually argued to follow from the central limit theorem, which, however, cannot naively be applied in the presence of a constraint, such as here given by the conserved total energy.

1.3.4 Structure Function Revisited

In a Gaussian approximation, the structure function (1.7) can be evaluated as

$$\Omega(E) = \int_0^E dE_\mathrm{k}\Omega_\mathrm{k}(E_\mathrm{k})\Omega_\mathrm{c}(E - E_\mathrm{k}) \approx \Omega_\mathrm{k}(\hat{E}_\mathrm{k})\Omega_\mathrm{c}(E - \hat{E}_\mathrm{k})(2\pi\sigma^2_{E_\mathrm{k}})^{1/2} \tag{1.29}$$

where we use (1.20) and (1.23) with $E_\mathrm{k} = \hat{E}_\mathrm{k}$ and $E_\mathrm{c} = E - \hat{E}_\mathrm{k}$, respectively. Its logarithmic derivative[10] becomes

$$\begin{aligned}\bar{\beta}(E) &\equiv \partial_E\Omega(E)/\Omega(E)\\ &\approx \beta_\mathrm{k}(\hat{E}_\mathrm{k}(E))\partial_E\hat{E}_\mathrm{k}(E) + \beta_\mathrm{c}(E - \hat{E}_\mathrm{k}(E))[1 - \partial_E\hat{E}_\mathrm{k}(E)]\\ &= \beta_\mathrm{c}(E - \hat{E}_\mathrm{k}(E)) = \beta_\mathrm{k}(\hat{E}_\mathrm{k}(E)).\end{aligned} \tag{1.30}$$

The first approximation arises from ignoring the E-dependence of $\sigma^2_{E_\mathrm{k}}$ in leading order in N. The third line follows with (1.24). This relation shows that for large systems the values of the three β-functions at the corresponding arguments become the same. Consequently, with (1.18) and (1.30), the important and far-reaching physical interpretation of $\bar{\beta}(E)$ is that this quantity corresponds to one-half of the inverse of the mean kinetic energy per degree of freedom for an isolated system with total energy E.[11] In the next chapter, we will see that this quantity is the only relevant property of a heat bath to which a system of interest is weakly coupled to or embedded in.

For later reference, we state the exponential representation for the structure function as

$$\Omega(E + \Delta E) = \Omega(E)\exp\int_E^{E+\Delta E} dE'\bar{\beta}(E') \approx \Omega(E)\exp[\bar{\beta}(E)\Delta E + \bar{\beta}'(E)(\Delta E)^2/2], \tag{1.31}$$

similar to (1.20) and (1.23).

1.4 Thermodynamic Limit

Characteristic for most systems described in statistical mechanics is the fact that their properties become, in a well-defined sense, independent of the size of the system if the latter becomes big. For a one-component system, this **thermodynamic limit** is defined as $N \to \infty$, with the energy and volume per particle,

$$\epsilon \equiv E/N \quad \text{and} \quad v \equiv V/N, \tag{1.32}$$

respectively, kept fixed. We distinguish two classes of quantities depending on their scaling with N in this thermodynamic limit.

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[10] Since $\Omega(E)$ is not dimensionless, writing $\bar{\beta}(E) \equiv \partial_E \ln\Omega(E)$ would be somewhat sloppy, even though a constant with physical dimension would not affect a derivative.

[11] The reason for introducing a bar in $\bar{\beta}(E)$ will become clear in the next chapter.

The mean of an **extensive macroscopic variables** $A(\boldsymbol{\xi})$ scales as

$$\langle A|E,V,N\rangle \approx Na(\epsilon,v), \tag{1.33}$$

with $a(\epsilon,v)=\mathcal{O}(1)$ in this thermodynamic limit.[12] Examples of extensive macroscopic variables are the mean total kinetic energy as discussed in the previous section or the mean number of particles in the left half of a container. The quantity $a(\epsilon,v)$, which characterizes a property per particle, thus becomes an **intensive variable** that depends only on the energy and volume per particle.

Mesoscopic observables lead to a second class of variables, which are necessarily intensive. These variables, denoted here as $B(\boldsymbol{\xi})$, include the momentum of a fluid particle or of a colloidal one, the number of fluid particles in a fixed neighborhood of the center of a colloidal particle, and, for short-range interactions, the total interaction energy between fluid and an individual colloidal particle. In these cases, only a bounded number of the degrees of freedom of the fluid, i.e., of the embedding macroscopic system, contributes to such a variable at any given time. Since this number does not scale with an increasing system size, we can expect that the mean of such variables becomes independent of system size, i.e.,

$$\langle B|E,V,N\rangle \approx b(\epsilon,v), \tag{1.34}$$

with $b(\epsilon,v)=\mathcal{O}(1)$.

Finally, we anticipate that there is a further class of intensive variables, like temperature and pressure, that characterize macroscopic systems. These variables, denoted for the moment generically as $c(\epsilon,v)$, also depend on these two parameters.

As a consequence of these assumptions, the derivatives of extensive and intensive variables with respect to the macroscopic parameters E,V, and N show a characteristic scaling that we will often exploit in the following. Specifically,

$$\partial_E\langle A|E,V,N\rangle_{|V,N} \approx \partial_\epsilon a(\epsilon,v)_{|v}=\mathcal{O}(1) \tag{1.35}$$

and, for intensive variables,

$$\partial_E\{a,b,c\}_{|V,N}=(1/N)\partial_\epsilon\{a,b,c\}_{|v}=\mathcal{O}(1/N). \tag{1.36}$$

For derivatives with respect to V and N analogous relations hold true with the same scaling in N. In particular, a derivative of an intensive variable with respect to either E,V, or N, with the other two fixed, vanishes in the thermodynamic limit.

The existence of these scalings in the thermodynamic limit can be proven rigorously for Hamiltonians with short-ranged interactions.[13]

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[12] We use this $\mathcal{O}$-notation to indicate the dependence on N even if a quantity like $a(\epsilon,v)$ still carries a physical dimension. Here, we also make the dependence of the averages on V and N explicit that we have so far notationally suppressed, as we will often do so later on.

[13] See,for example, Mazur and Van der Linden (1963) and the advanced monograph Ruelle (2007).

1.5 Pressure and Temperature and Their Microscopic Identification

1.5.1 A Technical Master Relation

We first need a technical master relation that will be used repeatedly in this and the next chapter. For a mesoscopic variable $h(\boldsymbol{\xi})$, we have

$$\begin{aligned}\int d\boldsymbol{\xi}\delta(H(\boldsymbol{\xi})+h(\boldsymbol{\xi})-E) &= \sum_{n=0}^{\infty}\frac{(-1)^n}{n!}\partial_E^n\int d\boldsymbol{\xi}h^n(\boldsymbol{\xi})\delta(H(\boldsymbol{\xi})-E)\\ &= \sum_{n=0}^{\infty}\frac{(-1)^n}{n!}\partial_E^n\langle h^n(\boldsymbol{\xi})|E\rangle\Omega(E), \qquad (1.37)\end{aligned}$$

based on a formal Taylor expansion of the delta function. Since, for all n, the power $h^n(\boldsymbol{\xi})$ is still a mesoscopic variable, the derivative of its mean vanishes in the thermodynamic limit as do derivatives of the intensive variable $\bar{\beta}(E)$, recall (1.36). Hence each derivative in the series (1.37) generates a factor of $\bar{\beta}(E)$,

$$\partial_E^n h^n(\boldsymbol{\xi})|E\rangle\Omega(E) \approx \langle h^n(\boldsymbol{\xi})|E\rangle[\bar{\beta}(E)]^n\Omega(E) = \langle[h(\boldsymbol{\xi})\bar{\beta}(E)]^n|E\rangle\Omega(E). \qquad (1.38)$$

Inserting this expression into (1.37) and then summing the series leads to an exponential, and, hence,

$$\int d\boldsymbol{\xi}\delta(H(\boldsymbol{\xi})+h(\boldsymbol{\xi})-E) \approx \langle\exp[-\bar{\beta}(E)h(\boldsymbol{\xi})]|E\rangle\Omega(E). \qquad (1.39)$$

In the trivial case of a constant h, this result corresponds to (1.31) truncated to the first term in the exponent.

1.5.2 Pressure from a Generic Model

We consider a system under the constant pressure exerted by a piston with mass M applied on a cross section A under gravity as shown in Figure 1.3 in Section 1.1.3. The dynamical degrees of freedom will be denoted by $\boldsymbol{\xi} \equiv (\boldsymbol{\xi}_f, P, Z)$, where $\boldsymbol{\xi}_f$ denotes all degrees of freedom of the fluid (gas or liquid). The piston with mass M has momentum P and a position Z in the gravitational field with strength g. At a fixed position of the piston, the fluid has the structure function

$$\Omega_f(E,V,N) \equiv \int d\boldsymbol{\xi}_f\delta(H_f(\boldsymbol{\xi}_f|Z)-E) \qquad (1.40)$$

with the available volume[14]

$$V = AZ. \qquad (1.41)$$

The Hamiltonian of the fluid $H_f(\boldsymbol{\xi}_f|Z)$ includes the kinetic energy of the fluid particles, their potential energy due to gravity, their mutual interaction, and their

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[14] Since the dependence on V and N will become crucial, we now promote these variables to explicit arguments in the structure function of the fluid.

interaction with the piston. The latter leads to the Z-, i.e., volume dependence of H_f. The Hamiltonian for the isolated total system reads

$$H_{\text{tot}}(\boldsymbol{\xi}_f, Z, P) = H_f(\boldsymbol{\xi}_f|Z) + P^2/2M + MgZ. \tag{1.42}$$

From the microcanonical distribution in the form (1.12) with $\boldsymbol{\xi}_1 = Z$ and $\boldsymbol{\xi}_2 = (P, \boldsymbol{\xi}_f)$ applied to the total system with energy E_{tot}, we obtain for the probability of observing the height Z in equilibrium

$$\begin{aligned} p(Z|E_{\text{tot}}) &= \int d\boldsymbol{\xi}_f \int dP \delta(H_{\text{tot}}(\boldsymbol{\xi}) - E_{\text{tot}})/\Omega_{\text{tot}}(E_{\text{tot}}) \\ &= \int dP \Omega_f(E_{\text{tot}} - P^2/2M - MgZ, AZ, N)/\Omega_{\text{tot}}(E_{\text{tot}}) \\ &\approx \int dP \exp[-\bar{\beta}_f P^2/2M] \Omega_f(E_{\text{tot}} - MgZ, AZ, N)/\Omega_{\text{tot}}(E_{\text{tot}}) \\ &= [2\pi M/\bar{\beta}_f]^{1/2} \Omega_f(E_{\text{tot}} - MgZ, AZ, N)/\Omega_{\text{tot}}(E_{\text{tot}}). \end{aligned} \tag{1.43}$$

For the second line, we have integrated out the degrees of freedom of the fluid at fixed P, Z. For the third line, we have used the exponential expansion (1.31) for Ω_f with $\Delta E = -P^2/2M$ and $\bar{\beta}_f \equiv \bar{\beta}_f(E_{\text{tot}} - MgZ, AZ)$. The final Gaussian integration over P is trivial.

The most likely value $\hat{Z}$ for the position of the piston follows from maximizing this distribution with respect to Z, or, equivalently, with respect to the volume at fixed A, by solving

$$\left[-\frac{d\bar{\beta}_f/dV}{2\bar{\beta}_f} - \frac{Mg\bar{\beta}_f}{A} + \frac{\partial_V \Omega_f(E_{\text{tot}} - MgZ, V, N)}{\Omega_f(E_{\text{tot}} - MgZ, V, N)} \right]_{Z=\hat{Z}} = 0. \tag{1.44}$$

The first term in the square bracket can be ignored since, as a derivative of an intensive variable with respect to a macroscopic one, it vanishes in the thermodynamic limit.

We identify the **thermodynamic pressure** $\bar{\mathcal{P}}$ of the fluid by equating it with the external one induced by the weight, which is Mg/A. Solving (1.44) for Mg/A thus leads to the identification

$$\bar{\mathcal{P}}(E, V, N) = \frac{\partial_V \Omega(E, V, N)}{\bar{\beta}(E, V, N)\Omega(E, V, N)}. \tag{1.45}$$

Since this result holds for any macroscopic system, we have dropped the index$_f$.[15] Thus knowledge of $\Omega(E, V, N)$ allows one to calculate the thermodynamic pressure of a macroscopic system in equilibrium.

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[15] Moreover, we identify the energy of the fluid with $E = E_{\text{tot}} - Mg\hat{Z}$, which seems to miss the (mean) kinetic energy of the piston. We will find in the next chapter that the latter is of order $1/\bar{\beta}_f$ and thus negligible on the scale of E_{tot} and $Mg\hat{Z}$, which both are macroscopic, i.e., of order N.

1.5.3 Ideal Gas and Relation to Temperature

At this point, it is instructive to specialize the fluid to an ideal gas.[16] Modeling the piston as a hard wall, we can neglect the interaction potential between piston and gas particles.

For an ideal gas, there is no configurational energy. With (1.16), the structure function becomes

$$\Omega(E,V,N) = \Omega_{\mathrm{k}}(E,V,N)V^N = E^{3N/2-1}m^{3N/2}C_N V^N. \tag{1.46}$$

Inserted into (1.45), we get for the pressure

$$\bar{\mathcal{P}}(E,V,N) = N/\bar{\beta}(E,V,N)V. \tag{1.47}$$

Comparing with the conventional **ideal gas law**

$$\bar{\mathcal{P}}V = N\mathsf{k_B}\mathsf{T}, \tag{1.48}$$

with the **Boltzmann constant** $\mathsf{k_B}$, we get the crucial relation

$$\bar{\beta} = 1/\mathsf{k_B}\mathsf{T} \tag{1.49}$$

between $\bar{\beta}(E,V,N)$ and the **temperature** T. We will show next that this identification holds for any macroscopic system. In the remainder of this book, we will set $\mathsf{k_B} = 1$. Consequently, temperature T has the dimension of an energy.

1.5.4 Two Large Systems in Contact

For two large systems in contact, the Hamiltonian becomes

$$H_{\mathrm{tot}}(\boldsymbol{\xi}_1,\boldsymbol{\xi}_2) = H_1(\boldsymbol{\xi}_1) + H_2(\boldsymbol{\xi}_2) + H_{\mathrm{int}}(\boldsymbol{\xi}_1,\boldsymbol{\xi}_2). \tag{1.50}$$

For a clean derivation, the last term describing the interaction is assumed to be localized, i.e., $H_{\mathrm{int}}(\boldsymbol{\xi}_1,\boldsymbol{\xi}_2)$ is a mesoscopic variable.[17] The total system is isolated, which implies that the total energy E_{tot} is conserved. The (unnormalized) probability distribution for system 1 to have an energy E_1, i.e., more precisely, the probability for $H_1(\boldsymbol{\xi}_1)$ to have the value E_1, follows from (1.10) as

$$\begin{aligned} p(E_1|E_{\mathrm{tot}}) &\propto \int d\boldsymbol{\xi}_1 \int d\boldsymbol{\xi}_2 \delta(H_1(\boldsymbol{\xi}_1) - E_1)\delta(H_2(\boldsymbol{\xi}_2) + H_{\mathrm{int}}(\boldsymbol{\xi}_1,\boldsymbol{\xi}_2) - (E_{\mathrm{tot}} - E_1)) \\ &\approx \int d\boldsymbol{\xi}_1 \delta(H_1(\boldsymbol{\xi}_1) - E_1)\langle \exp[-\bar{\beta}_2(E_2)H_{\mathrm{int}}(\boldsymbol{\xi}_1,\boldsymbol{\xi}_2)]|E_2\rangle\Omega_2(E_2) \\ &= \big\langle\langle \exp[-\bar{\beta}_2(E_2)H_{\mathrm{int}}(\boldsymbol{\xi}_1,\boldsymbol{\xi}_2)]|E_2\rangle|E_1\big\rangle\,\Omega_1(E_1)\Omega_2(E_2), \end{aligned} \tag{1.51}$$

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[16] Strictly speaking, an ideal gas in a box with hard walls does not fulfill the fundamental principle from Section 1.2.2 since the initial kinetic energy of each particle is conserved. One should therefore introduce a tiny interaction between the particles and then consider the limit in which this interaction vanishes.

[17] In fact, it is sufficient to assume that $H_{\mathrm{int}}(\boldsymbol{\xi}_1,\boldsymbol{\xi}_2)$ scales less than linearly with the energy of the total system.

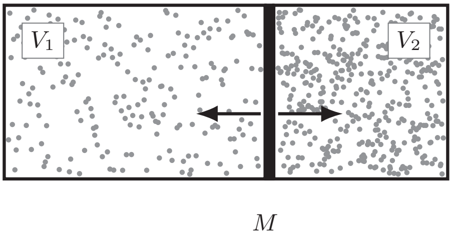

Figure 1.4 Two systems that can exchange volume through the motion of a separating piston with mass M.

with $E_2 = E_{\text{tot}} - E_1$. For the first approximation, we have used (1.39) for system 2 with $h(\boldsymbol{\xi}_2) = H_{\text{int}}(\boldsymbol{\xi}_1, \boldsymbol{\xi}_2)$, where $\boldsymbol{\xi}_1$ can be treated as a fixed parameter. In the final equality, the outer average is the microcanonical one for system 1 at energy E_1. If the E_1-dependence of this term could be ignored, the probability $p(E_1|E_{\text{tot}})$ would be sharply peaked at $\hat{E}_1$ given by

$$\bar{\beta}_1(\hat{E}_1) = \bar{\beta}_2(\hat{E}_2)_{|\hat{E}_2 = E_{\text{tot}} - \hat{E}_1}. \tag{1.52}$$

In fact, for localized interactions between the two systems, the term in angular brackets is a mesoscopic variable that leads to a relative shift in the peak position of $\mathcal{O}(1)$ in N that indeed can be ignored on the scale of $\hat{E}_1$; see Appendix A.3. Still, a small but finite coupling is necessary since without any coupling the two systems could not exchange energy. The combined system with its two conserved quantities E_1 and E_2 would thus violate the fundamental principle. As an aside, note that, conceptually, the relation (1.52) is similar to what we have encountered in the balance between kinetic and configurational energy within one system in (1.30).

Thus, for two macroscopic systems in thermal contact, the two $\bar{\beta}$-functions assume the same value after equilibration, i.e., the mean kinetic energy per particle becomes the same in both systems. We now invoke the naive concept that two systems in thermal contact ultimately should reach the same temperature T. By choosing one of these systems as an ideal gas for which we have established the relation between $\bar{\beta}$ and T in (1.49), it is clear that the equality of the beta functions in (1.52) implies that this relation holds for any macroscopic system.

For two large systems that can exchange not only energy but also volume (subject to the constraint $V_1 + V_2 = V$ with constant V) a Hamiltonian model system with a movable piston with mass M is sketched in Figure 1.4. A calculation similar to the preceding ones will show that the most likely values for individual energy and volume fulfill the conditions $\bar{\beta}_1(\hat{E}_1, \hat{V}_1) = \bar{\beta}_2(\hat{E}_2, \hat{V}_2)$ and $\bar{\mathcal{P}}_1(\hat{E}_1, \hat{V}_1) = \bar{\mathcal{P}}_2(\hat{E}_2, \hat{V}_2)$, respectively.[18] Hence, inverse temperature and pressure equalize for macroscopic systems that can exchange energy and volume.

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[18] Exercise

1.6 Particle Exchange and Chemical Potential

So far, we have considered isolated systems for which the number of particles is constant. In this section, we allow for exchange of particles between subsystems. We will find that two important amendments should be made to the structure function. As a motivation and preparation, consider Figure 1.5 showing particles confined in a container with two parts that are connected by a narrow constriction. The energy of the whole system can be written in the form

$$H(\boldsymbol{\xi}) = H_1(\boldsymbol{\xi}) + H_2(\boldsymbol{\xi}) \tag{1.53}$$

where $H_1(\boldsymbol{\xi})$ contains kinetic, potential, and interaction energies of the particles in the left part and $H_2(\boldsymbol{\xi})$ the energy of those in the right part. For simplicity, we assume that there is no interaction among particles in different parts. Still, the two parts interact because particles can cross the constriction, in which case they switch from being included in $H_1(\boldsymbol{\xi})$ to being included in $H_2(\boldsymbol{\xi})$ and vice versa. At any time t, there is a fluctuating number $N_1(\boldsymbol{\xi}^t)$ of particles in the left part and $N_2(\boldsymbol{\xi}^t) = N - N_1(\boldsymbol{\xi}^t)$ of them in the right part. Total energy E and particle number N are conserved.

The joint probability distribution for the observables N_1 and E_1 follows with the trivial generalization of (1.10) to two observables as

$$\begin{aligned} p(N_1, E_1|E, V, N) &= \int d\boldsymbol{\xi}\,\delta(H_1(\boldsymbol{\xi}) - E_1)\delta_{N_1(\boldsymbol{\xi})N_1}\delta(H_2(\boldsymbol{\xi}) - (E - E_1))/\Omega(E, V, N) \\ &= \frac{N!}{N_1!(N - N_1)!}\frac{\Omega_1(E_1, V_1, N_1)\Omega_2(E - E_1, V_2, N - N_1)}{\Omega(E, V, N)}. \end{aligned} \tag{1.54}$$

The integration runs over the phase space of N particles. The combinatorial factor counts in how many different ways the N_1 particles can be selected from the total pool of N particles. Each specific selection, which will occur repeatedly along a long trajectory, contributes similarly to this probability. Once a set of N_1 particles is selected, the integral over the respective phase space of the two subsystems yields the corresponding structure functions. For macroscopic systems, this probability will peak at the most likely values $\hat{E}_1$ and $\hat{N}_1$, with $\hat{E}_1$ following from $\bar{\beta}_1 = \bar{\beta}_2$ as previously.

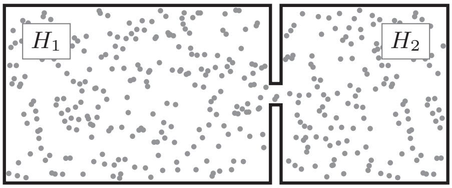

Figure 1.5 Two overall isolated systems characterized by Hamiltonians H_1 and H_2 that can exchange particles through a narrow constriction

The attempt to calculate the most probable splitting of the total number of particles into the two subsystems faces the problem that N_1 is a discrete variable. Treating N_1 as a continuous variable, the most likely value $\hat{N}_1$ follows from

$$\frac{d}{dN_1}\left[\frac{\Omega_1(\hat{E}_1, V_1, N_1)}{N_1!}\frac{\Omega_2(E-\hat{E}_1, V_2, N-N_1)}{(N-N_1)!}\right]_{N_1=\hat{N}_1} = 0. \qquad (1.55)$$

Applying the product rule for the derivative is problematic, since each Ω_i $(i=1,2)$ carries a dimension $(\mathrm{Js})^{3N_i}/\mathrm{J}$, which depends on N_i. Consequently, a derivative with respect to N_i generates a factor $\propto \ln(\mathrm{Js})$ that is, strictly speaking, ill-defined. The arguably cleanest way out of this dilemma is to divide each structure function by a quantity with the dimension of $(\mathrm{Js})^{3N_i}$. We use h^{3N_i}, where h is an arbitrary quantity (independent of E_i, V_i, and N_i) with the dimension of an action. For classical systems, physical observables must not (and will not) depend on the specific value chosen for h.

Finally, the crucial appearance of the factorials in (1.54) and (1.55) suggests including a factor $N!$ in the structure function, leading to the definition

$$\tilde{\Omega}(E, V, N) \equiv \frac{\Omega(E, V, N)}{h^{3N}N!} = \int \frac{d\boldsymbol{\xi}}{h^{3N}N!}\delta(H(\boldsymbol{\xi})-E). \qquad (1.56)$$

This scaling affects neither the value of the (inverse) temperature (1.30) nor that of the pressure (1.44) if both are evaluated by using $\tilde{\Omega}$ rather than Ω since logarithmic derivatives with respect to E and V are the same for both variants. The most likely distribution of particles then follows from

$$\frac{\partial_{N_1}\tilde{\Omega}_1(\hat{E}_1, V_1, N_1)}{\tilde{\Omega}_1(\hat{E}_1, V_1, N_1)}_{|N_1=\hat{N}_1} = \frac{\partial_{N_2}\tilde{\Omega}_2(\hat{E}_2, V_2, N_2)}{\tilde{\Omega}_2(\hat{E}_2, V_2, N_2)}_{|N_2=\hat{N}_2=N-\hat{N}_1}. \qquad (1.57)$$

In analogy with (inverse) temperature and pressure, this equality motivates the definition of a quantity called **chemical potential** as

$$\bar{\mu}(E, V, N) \equiv -\frac{\partial_N\tilde{\Omega}(E, V, N)}{\bar{\beta}(E, V, N)\tilde{\Omega}(E, V, N)}, \qquad (1.58)$$

which acquires the same value in two (weakly) interacting systems that can exchange energy and particles. Including the $\bar{\beta}$-factor in the definition analogously to the identification of pressure in (1.45) makes the dimension of the chemical potential an energy. The minus sign ensures that a larger chemical potential corresponds to a larger energy, as we will see. The thus defined chemical potential is an intensive quantity. This can be checked explicitly for the ideal gas where

$$\bar{\mu}(E, V, N) = -[1/\bar{\beta}(E, V, N)]\ln\{(E^{3/2}V/N^{5/2})(4\pi m/3h^2)^{3/2}]\} \qquad (1.59)$$

as derived in Appendix A.5.

The two amendments to the structure function made in this section arise for different reasons. First, the factorials occur in (1.54) as an inevitable consequence of the dynamical approach in conjunction with the fundamental principle from Section 1.2.2 without the need to invoke a (quantum-mechanical) indistinguishability of identical particles. Their subsequent inclusion in (1.56) allows us to determine the most likely splitting of energy and particle numbers in two interacting systems coherently through equalizing a corresponding intensive quantity.

Second, if the aim was just to get a criterion for equilibration with respect to energy and particle exchange of two large systems, one could get away without explicit factors of h by arguing that in (1.55) the ln(Js) terms would ultimately cancel. However, such an argument would only postpone this issue, since, as we will see in Section 2.8 where we will derive the grand-canonical distribution, we will need to expand the N-dependence of the structure function in an exponential fashion as we did in (1.31) with the energy dependence. Indeed, with (1.58) we get

$$\tilde{\Omega}(E, V, N + \Delta N) \approx \exp[-\bar{\beta}(E, V, N)\bar{\mu}(E, V, N)\Delta N)]\tilde{\Omega}(E, V, N). \tag{1.60}$$

Such an expansion becomes possible only after eliminating the N-dependent dimension in Ω by introducing an h.

The significance of the elementary phase space volume h is often argued to arise from quantum mechanics. Indeed, if the preceding formalism is applied to genuine quantum systems, h should be chosen as Planck's constant. However, classical statistical physics is entirely consistent without introducing explicitly discrete states, i.e., without a specific choice of h.

1.7 Entropy: A First Encounter

1.7.1 Entropy Postulate in Classical Thermodynamics

At this point, we can make contact with phenomenological thermodynamics. In its axiomatic formulation, the existence of an extensive, monotonically increasing, and concave **entropy function** $\mathcal{S}(\mathcal{U}, V, N)$, where $\mathcal{U}$ is the **internal energy**, is postulated. Moreover, for a collection of subsystems, the total entropy

$$\mathcal{S}(\mathcal{U}, V, N) = \sum_i \mathcal{S}_i(\mathcal{U}_i, V_i, N_i) \tag{1.61}$$

is postulated to be additive in the subsystems labeled by the index i.

If, upon contact, previously separated subsystems can exchange energy, with the total energy being conserved, the final equilibrium state is postulated to maximize the total entropy. This condition implies that

$$\beta_i \equiv \partial_{\mathcal{U}_i}\mathcal{S}_i \tag{1.62}$$

acquires the same value in each subsystem.

Likewise, if the systems are allowed to exchange energy and volume, additionally the pressure

$$\mathcal{P}_i \equiv (1/\beta_i)\partial_{V_i}\mathcal{S}_i \tag{1.63}$$

becomes the same in each of them. Finally, if energy and particles can be exchanged (keeping the subvolumes fixed), the chemical potentials

$$\mu_i \equiv -(1/\beta_i)\partial_{N_i}\mathcal{S}_i \tag{1.64}$$

acquire the same values.

These partial derivatives enter the **Gibbs fundamental form**,[19]

$$d\mathcal{S} = \beta d\mathcal{U} + \beta\mathcal{P}dV - \beta\mu dN. \tag{1.65}$$

1.7.2 Microcanonical Entropy and Gibbs Volume Entropy

In our dynamical approach, there has been no need to postulate the existence of an entropy function with the properties just stated. A posteriori, however, there is a natural candidate for such an identification, since, obviously, the derivatives $\partial_X\tilde{\Omega}/\tilde{\Omega}$ fulfill the same requirements as $\partial_X\mathcal{S}$ $(X = E, V, N)$, with $\mathcal{U} = E$, if they are evaluated at the most likely values. If $\tilde{\Omega}$ was dimensionless, we could identify $\mathcal{S}$ with $\ln\tilde{\Omega}$. However, $\tilde{\Omega}$ still carries a dimension of 1/J. There are several ways of rendering $\tilde{\Omega}$ dimensionless while keeping all crucial relations. The two most prominent ones are as follows.

First, by introducing a no further specified "thickness" of the energy shell δE, assumed to be independent of E, V, N, one can introduce a **microcanonical entropy**

$$\bar{S}(E,V,N) \equiv \ln[\tilde{\Omega}(E,V,N)\delta E]. \tag{1.66}$$

Its partial derivatives obviously yield inverse temperature (1.30), pressure (1.44), and chemical potential (1.58) (with the bars). These quantities then obey the barred version of the Gibbs fundamental form (1.65) with $\mathcal{U}$ replaced by E,

$$d\bar{S} = \bar{\beta}dE + \bar{\beta}\bar{\mathcal{P}}dV - \bar{\beta}\bar{\mu}dN. \tag{1.67}$$

A second option is to consider the phase space volume bounded by the energy shell

$$\begin{aligned}\tilde{\Omega}_G(E) &\equiv \int \frac{d\boldsymbol{\xi}}{h^{3N}N!}\theta(E - H(\boldsymbol{\xi}))\\ &= \int_{E_{\min}}^{E} \tilde{\Omega}(E')dE' = \tilde{\Omega}(E)\int_{E_{\min}}^{E} dE' \exp\left[-\int_{E'}^{E} dE''\bar{\beta}(E'')\right],\end{aligned} \tag{1.68}$$

where $E_{\min}$ is the minimal possible energy of the system. By expanding the last exponent to second order as in (1.31), we get

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[19] In fact, in classical thermodynamics, the Gibbs form is written as $d\mathcal{S} = (1/\mathsf{T})d\mathcal{U} + (\mathcal{P}/\mathsf{T})dV - (\mu/\mathsf{T})dN$ with an entropy that has the physical dimensions of $\mathsf{k_B}$. Recall that throughout the book we set $\mathsf{k_B} = 1$, which makes entropy dimensionless (and temperature an energy).

$$\begin{aligned}\tilde{\Omega}_G(E) &\approx \tilde{\Omega}(E)\int_{E_{\min}}^{E} dE' \exp\{-\bar{\beta}(E)[E-E'] + \bar{\beta}'(E)(E-E')^2/2\} \\ &= [\tilde{\Omega}(E)/\bar{\beta}(E)]\int_0^{\bar{\beta}(E)[E-E_{\min}]} du \exp[-u - |\bar{\beta}'(E)|u^2/2\bar{\beta}(E)^2] \\ &\approx \tilde{\Omega}(E)/\bar{\beta}(E). \end{aligned} \tag{1.69}$$

For the last approximation, we use that for $E - E_{\min} \gg 1/\bar{\beta}(E)$ the integral becomes 1 up to a correction that is of relative order $1/N$. In leading order, all the volume underneath the energy shell is thus concentrated in a thin layer of width $1/\bar{\beta}(E)$.

The **Gibbs volume entropy** is identified with

$$\bar{S}_G(E,V,N) \equiv \ln \tilde{\Omega}_G(E,V,N) = \bar{S}(E,V,N) - \ln[\bar{\beta}(E,V,N)\delta E] + \mathcal{O}(1/N). \tag{1.70}$$

If δE is chosen of the order of $1/\bar{\beta}$ then the microcanonical entropy and the Gibbs volume entropy differ only by a term of order 1. Likewise, since $\partial_{E,V,N}\bar{\beta} \sim 1/N$, the corresponding inverse temperature, pressure, and chemical potential $(\bar{\beta}_G, \bar{\mathcal{P}}_G, \bar{\mu}_G)$, obtained through the logarithmic derivatives of $\tilde{\Omega}_G$, differ by only $\mathcal{O}(1/N)$ from their counterparts without subscript$_G$.[20]

Our dynamical approach together with the fundamental principle introduced in Section 1.2.2 has thus led to a quantity (or, rather, two of them) with the properties of the entropy of classical thermodynamics without the necessity of ever postulating the existence of an entropy. Obviously, the microscopic identification of the entropy of classical thermodynamics is not unique, since at least two, and, in fact, several functions fulfill the defining properties, with, however, different finite-N corrections. A definite choice between $\bar{S}$ and $\bar{S}_G$ would require an additional principle, which, at this point, arguably would look somewhat contrived.[21]

Often, the thickness of the energy shell is introduced with the argument that energies can be measured only up to a certain precision δE. While this is true, it cannot be the relevant issue since one should distinguish, at least in classical physics, objective reality from subjective knowledge or capabilities of an observer or experimentalist.

1.8 Notes

The statistical physics of equilibrium systems, and, in particular, the microcanonical and the canonical distribution (see the following chapter), is more comprehensively discussed in any textbook on statistical physics. Excellent classic and modern ones include Reif (1985), Ma (1985), Peliti (2011), and Kardar (2007a,b), respectively. Classical thermodynamics is systematically presented in Callen (1985). Textbooks interweaving thermodynamics and statistical physics include

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[20] Exercise

[21] Merits and shortcomings of different versions of entropy for an isolated system are discussed in Hilbert et al. (2014).

Baierlein (1999), Schroeder (2000), and, more advanced, Gould and Tobochnik (2010) and Swendsen (2012).

While all approaches lead to the same essential definitions and relations, the motivation and justification of the basic principles as well as the order of presentation can differ significantly. The dynamical approach that we have emphasized here is less common. Even though the fundamental hypothesis in Section 1.2.2 becomes technically equivalent to postulating the equality of time averages with ensemble averages, our approach arguably is conceptually somewhat different since it does not require the notion of an ensemble as a crucial input for formulating the fundamental principle.

The foundations of statistical mechanics are discussed further inter alia in the monographs Khinchin (1949), Gallavotti (1999), and Castiglione et al. (2008).