E.1 *Phase space* Γ

Statistical mechanics as the theory behind thermodynamics is concerned with systems with many degrees of freedom which follow Hamiltonian, energy-conserving dynamical laws. For linking mechanical microscopic properties of these systems with thermodynamic concepts like entropy and temperature we need to introduce some conceptual ideas.

The ✈ phase space of a Hamiltonian system is made up from all coordinates $\{q_i, p_i\}$. For a system like a collection of point particles interacting with potentials as the microscopic idea behind a real gas, it would be $6n$-dimensional for n particles. As the Lagrange-function $\mathcal{L}(q_i, \dot{q}_i)$ does not explicitly depend on time, the value of the Hamilton-function $\mathcal{H}(q_i, p_i)$ interpreted as the energy of the system is conserved: It is a straightforward visualisation that the system moves on a surface of fixed energy through phase space Γ. If we combine the phase space coordinates into a vector $\boldsymbol{x} = (q_i, p_i)$ the phase space motion proceeds at velocity $\boldsymbol{v}$

$$\boldsymbol{v} = \dot{\boldsymbol{x}} = (\dot{q}_i, \dot{p}_i) = \left(\frac{\partial \mathcal{H}}{\partial p_i}, -\frac{\partial \mathcal{H}}{\partial q_i} \right) \tag{E.154}$$

At the same time, the gradient of the Hamilton-function is given by

$$\nabla \mathcal{H}(q_i, p_i) = \left(\frac{\partial \mathcal{H}}{\partial q_i}, \frac{\partial \mathcal{H}}{\partial p_i} \right) \tag{E.155}$$

such that we can conclude two things:

$$\boldsymbol{v} \cdot \nabla \mathcal{H} = 0 \quad \text{as well as} \quad |\boldsymbol{v}| = |\nabla \mathcal{H}| \tag{E.156}$$

i.e. that the velocity and the gradient are equal in magnitude but perpendicular to each other.

E.2 *Phase space density* ρ

Populating the phase space Γ with an ensemble of physically equivalent systems (with identical Hamilton-functions) leads to a density ρ of encountering systems at a certain phase space coordinate. There should be a continuity equation making sure that in the course of time evolution systems are not spontaneously lost or added to the ensemble,

$$\frac{\partial \rho}{\partial t} + \text{div}(\rho \boldsymbol{v}) = \frac{\partial \rho}{\partial t} + \nabla \rho \cdot \boldsymbol{v} + \rho \, \text{div} \boldsymbol{v} = 0 \tag{E.157}$$

with the application of the Leibnitz-rule to $\text{div}(\rho\boldsymbol{v})$ and the successive definition of the advective derivative: As the density $\rho(t, x^i)$ is a function of both time and the full phase space coordinates bundled in $\boldsymbol{x}$ one gets:

$$\frac{\mathrm{d}}{\mathrm{d}t} \rho(t, x^i) = \frac{\partial \rho}{\partial t} + \dot{x}^i \frac{\partial \rho}{\partial x^i} = \frac{\partial \rho}{\partial t} + v^i \frac{\partial \rho}{\partial x^i} \tag{E.158}$$

The divergence of the velocity v vanishes, as one can quickly see

$$\text{div}\,v = \sum_i \frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i} = \sum_i \frac{\partial}{\partial q_i}\frac{\partial \mathcal{H}}{\partial p_i} - \frac{\partial}{\partial p_i}\frac{\partial \mathcal{H}}{\partial q_i} = 0 \qquad (E.159)$$

through substitution of the Hamilton equations of motion. With the advective derivative,

$$\frac{d\rho}{dt} \equiv \frac{\partial \rho}{\partial t} + v \cdot \nabla \rho \qquad (E.160)$$

in the laboratory frame in which the coordinates are defined, and

$$\frac{\partial \rho}{\partial t} = 0 \qquad (E.161)$$

for a comoving observer that is advected with the flow, as for that observer $v = 0$. But is there something that we can say about $\partial \rho / \partial t$ in the laboratory frame? This is a surprising result, as

$$\text{div}\,(\rho v) = \sum_i \frac{\partial \rho}{\partial p_i}\dot{p}_i + \frac{\partial \rho}{\partial q_i}\dot{q}_i = \sum_i \frac{\partial \rho}{\partial p_i}\frac{\partial \mathcal{H}}{\partial p_i} + \frac{\partial \rho}{\partial q_i}\frac{\partial \mathcal{H}}{\partial q_i} = -[\rho, \mathcal{H}] \qquad (E.162)$$

where the Hamilton equations of motion and then the Poisson-bracket was substituted. For the derivatives of ρ with respect to the phase space coordinates one can do an intermediate step by differentiating with respect to $\mathcal{H}$ first and then continue the differentiation with the chain rule.

$$\text{div}\,(\rho v) = \frac{\partial \rho}{\partial \mathcal{H}}\sum_i \frac{\partial \mathcal{H}}{\partial q_i}\frac{\partial \mathcal{H}}{\partial p_i} - \frac{\partial \mathcal{H}}{\partial q_i}\frac{\partial \mathcal{H}}{\partial p_i} = \frac{\partial \rho}{\partial \mathcal{H}}[\mathcal{H}, \mathcal{H}] = 0 \qquad (E.163)$$

where the Poisson-bracket of the Hamilton-function with itself vanishes, setting the divergence of ρv to zero. That implies in turn that the partial derivative of ρ in the laboratory frame

$$\frac{\partial \rho}{\partial t} = 0 \qquad (E.164)$$

vanishes: The distribution of the systems in phase space is non-evolving, neither for the comoving observer nor for an observer in the laboratory frame. Being advected with the flow, observers would see a constant density around them, and observing the flow at any point from the laboratory frame would always yield the same density, too.

E.3 *Phase space volume: surface and volume*

The volume of the phase space Γ as bounded by a surface of constant energy $\mathcal{H} \leq E$ would be

$$\phi^*(E) = \int_{\mathcal{H}\leq E} \prod_i d^3q_i d^3p_i \qquad (E.165)$$

where we have introduced the asterisk for the time being as it needs to be corrected by the Gibbs factor. Adding or removing energy from the system leads to a change

in volume, as the surface of constant energy will move to a different location and enclose a different amount of volume in Γ: The rate of change of the volume with energy is simply the derivative of $\phi^*(E)$,

$$\omega^*(E) = \frac{d}{dE}\phi^*(E) = \frac{d}{dE}\int_{\mathcal{H}\leq E}\prod_i d^3q_i d^3p_i \tag{E.166}$$

Quite commonly one deals with kinetic systems: Particles are trapped in a box of volume V and their energy only depends on their momentum; in essence there is no potential energy and only the notion of kinetic energy. In these cases, the configuration space integral over dq only yields the volume of the box, and the momentum integral over dp is the only relevant quantity. Quite often, it is advantageous to reformulate that integral in terms of energy (because the Boltzmann-factor only cares about energy) and introduce a quantity called the density of states $g(E)$: In n dimensions and assuming spherical symmetry this would be

$$d^np = S_n p^{n-1} dp = \underbrace{S_n p^{n-1}\frac{dp}{dE}}_{=g(E)}dE = g(E)dE \tag{E.167}$$

effectively through an integration by substitution replacing dp by dE. The volume V_n and surface S_n of an n-dimensional unit sphere is given by

$$V_n = \frac{\pi^{n/2}}{\Gamma(n/2+1)} \quad \text{and} \quad S_n = \frac{2\pi^{n/2}}{\Gamma(n/2)}, \tag{E.168}$$

where $\Gamma(n) = (n-1)!$ is the Γ-function (the derivation is shown in Section X.2).

For computing the density of states on needs to make an assumption about the dispersion relation of the particles, which could be relativistic or classical,

$$E = \frac{p^2}{2m} \quad \text{or} \quad E = \sqrt{(cp)^2 + (mc^2)^2} - mc^2 \tag{E.169}$$

where it is necessary to subtract the energy associated to rest mass as we only account for kinetic energy. The result for $g(E)$ is shown in Fig. 10 setting $m = 1$ and $c = 1$ for simplicity, for $n = 3, 4, 5$.

E.4 *Microcanonical ensemble*

With these ideas it is possible to define the ◄ microcanonical ensemble: One populates the phase space Γ with a large number of physically equivalent systems with the same Hamilton-function $\mathcal{H}$ on the surface of constant energy E. In doing that, one needs to make an assumption how this ensemble of systems will be distributed on the hypersurface at constant E. For continuing, one can adopt now the fundamental postulate of statistical physics and require axiomatically that this distribution ρ is constant in thermodynamic equilibrium, or, perhaps a bit more insightful, we ask what distribution ρ would maximise the information entropy as an expression about the largest possible amount of randomness, which we would suspect to be present in thermodynamic equilibrium. A constant distribution would in fact extremise Shannon's entropy (if there are no boundary conditions to be fulfilled), so we will work
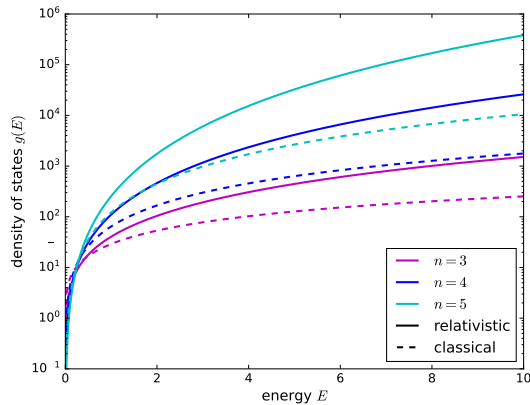
Figure 10: Density of states $g(E)$ for classical and relativistic dispersion relations.

with that! The previous section showed that for a conservative Hamiltonian system this density ρ, once initialised, is stationary $\partial\rho/\partial t = 0$ but that does not mean that there is no dynamics going on. The every system in the ensemble is pursuing its path in phase space Γ, but it is the case that the number of systems that evolve away from a certain volume in phase space are replaced by new systems moving into that volume, keeping the density constant.

Therefore, the distribution of systems on the surface of constant energy (or to be more exact, in an infinitesimally thin shell between energies E and E + δE, for mathematical convenience) is chosen to be constant, because that imposes the least assumption on the phase space density.

$$\rho(E) = \begin{cases} 1, & \text{if } E \leq \mathcal{H} \leq E + \delta E \\ 0, & \text{elsewhere} \end{cases} \tag{E.170}$$

such that the number n of systems becomes proportional to the volume between E and E + dE,

$$n = \rho\omega^*(E)dE = \omega^*(E)dE \tag{E.171}$$

using the phase space volume element defined above.

E.5 *Equipartition theorem*

Suppose one would like to determine the average $\langle A \rangle$ of a function $A(p_i, q_i, t)$ that can depend on the coordinates (q_i, p_i) and possibly on time t. The average should be characterised by a predefined energy E (which the Hamiltonian system conserves). There are fundamentally two ways of computing the average, first summing over the ensemble,

$$\langle A \rangle = \frac{\displaystyle\int_{E \leq \mathcal{H} \leq E+\delta E} \prod_i \mathrm{d}^3 q_i \mathrm{d}^3 p_i \, A(p_i, q_i, t)}{\displaystyle\int_{E \leq \mathcal{H} \leq E+\delta E} \prod_i \mathrm{d}^3 q_i \mathrm{d}^3 p_i} = \frac{\dfrac{\mathrm{d}}{\mathrm{d}E} \displaystyle\int_0^E \prod_i \mathrm{d}^3 q_i \mathrm{d}^3 p_i \, A(p_i, q_i, t)}{\dfrac{\mathrm{d}}{\mathrm{d}E} \displaystyle\int_0^E \prod_i \mathrm{d}^3 q_i \mathrm{d}^3 p_i} \qquad (E.172)$$

where the averages are normalised by the volume. The idea in this equation is that the ensemble of statistically equivalent systems is distributed evenly over the allowed phase space volume at coordinates (q_i, p_i). Every system of the ensemble contributes to this average with a specific value for $A(p_i, q_i, t)$. The denominator in the ensemble average is just $\omega^*(E)$.

Secondly, if the system is ergodic, the ensemble average is equal to the average of a single system in its time evolution,

$$\langle A \rangle = \lim_{\Delta t \to \infty} \frac{1}{\Delta t} \int_0^{\Delta t} \mathrm{d}t \, (p_i(t), q_i(t), t); \qquad (E.173)$$

the idea being that a single system in its time evolution comes by every point of the allowed phase space volume the exactly the same even measure.

For a specific choice of the phase space function $A = p_1 \partial \mathcal{H}/\partial p_1$ one can compute the expectation value of the phase space average by an integration by parts,

$$\int \mathrm{d}^3 p_1 \, p_1 \frac{\partial \mathcal{H}}{\partial p_1} = \int \mathrm{d}^3 p_1 \frac{\partial}{\partial p_1}(p_1 \mathcal{H}) - \int \mathrm{d}^3 p_1 \, \mathcal{H} \qquad (E.174)$$

because obviously $\partial p_1/\partial p_1 = 1$, and the first term will simply be the evaluation of the integrand at the boundaries, where $\mathcal{H} = E$.

Applying this simplification to the entire integrand,

$$\int_0^E \prod_i \mathrm{d}^3 p_i \mathrm{d}^3 q_i \, p_1 \frac{\partial \mathcal{H}}{\partial p_1} = E \cdot (p_{1,\max} - p_{1,\min}) \int_0^E \prod_{i \geq 2} \mathrm{d}^3 p_i \mathrm{d}^3 q_i - \int_0^E \prod_i \mathrm{d}^3 p_i \mathrm{d}^3 q_i \mathcal{H}$$
$$(E.175)$$

such that a differentiation with respect to the energy E would yield

$$\frac{\mathrm{d}}{\mathrm{d}E} \int_0^E \prod_i \mathrm{d}^3 p_i \mathrm{d}^3 q_i \mathcal{H} = \frac{1}{\delta E} \int_E^{E+\delta E} \prod_i \mathrm{d}^3 p_i \mathrm{d}^3 q_i \mathcal{H} = E \frac{1}{\delta E} \prod_i \mathrm{d}^3 p_i \mathrm{d}^3 q_i = E \omega^*(E)$$
$$(E.176)$$

In summary, this leads to the expectation values

$$\frac{\mathrm{d}}{\mathrm{dE}} \int_0^E \prod_i \mathrm{d}^3 p_i \mathrm{d}^3 q_i p_1 \frac{\partial \mathcal{H}}{\partial p_1} = \phi^*(E) \tag{E.177}$$

so that one obtains for the virial expression

$$\left\langle p_i \frac{\partial \mathcal{H}}{\partial p_i} \right\rangle = \left\langle q_i \frac{\partial \mathcal{H}}{\partial q_i} \right\rangle = \frac{\phi^*}{\omega^*} = \frac{1}{\frac{\mathrm{d}\ln\phi^*}{\mathrm{dE}}} \tag{E.178}$$

The ✈ equipartition theorem then follows from these considerations: If

$$\frac{\mathrm{d}\ln\phi^*}{\mathrm{dE}} = \frac{1}{k_B T} \tag{E.179}$$

then the average kinetic energy for a non-relativistic system follows from

$$\left\langle p_i \frac{\partial \mathcal{H}}{\partial p_i} \right\rangle = 2\langle T \rangle \sim k_B T \tag{E.180}$$

As a consequence of the virial theorem,

$$\left\langle q_i \frac{\partial \mathcal{H}}{\partial q_i} \right\rangle \sim \left\langle p_i \frac{\partial \mathcal{H}}{\partial p_i} \right\rangle \sim k_B T \tag{E.181}$$

as well: This is a far-reaching result, and shows that every degree of freedom carries on average a typical amount of $k_B T$ of the total thermal energy of the system.

E.6   *Entropy for Hamiltonian systems*

Let's introduce a parameter a in the Hamilton-function $\mathcal{H}$

$$\mathcal{H} = \mathcal{H}(p_i, q_i, a) \tag{E.182}$$

which can be controlled from the outside and changes the mechanics of the system: For instance, it could be the length of a pendulum or the distance between the capacitor plates in an LC-circuit or in fact the volume of a gas in a container. If changes in a have an influence on the Hamilton-function, energy can be added to or removed from the system:

$$\frac{\mathrm{d}\mathcal{H}}{\mathrm{d}t} = \dot{a}\frac{\partial \mathcal{H}}{\partial a} \quad \rightarrow \quad \mathrm{d}\mathcal{H} = \frac{\partial \mathcal{H}}{\partial a}\mathrm{d}a \tag{E.183}$$

which leads to an energy gain

$$\mathrm{dE} = \lim_{\Delta t \to \infty} \int_t^{t+\Delta t} \mathrm{d}t \frac{\partial \mathcal{H}}{\partial a}\dot{a} \tag{E.184}$$

over the interval Δt. For an entire ensemble of systems one would write for the average gain in energy

$$\mathrm{dE} = \left\langle \frac{\partial \mathcal{H}}{\partial a} \right\rangle \mathrm{d}a \tag{E.185}$$

where the quantity $\langle \partial \mathcal{H}/\partial a \rangle$ could be interpreted in an ensemble-average sense, or if ergodicity is given, as a time average

$$\left\langle \frac{\partial \mathcal{H}}{\partial a} \right\rangle = \lim_{\Delta t \to \infty} \frac{1}{\Delta t} \int_{t}^{t+\Delta t} \mathrm{d}t \, \frac{\partial \mathcal{H}}{\partial a} \tag{E.186}$$

For the particular case of a being the volume V of a container filled with gas, the change in energy would be

$$\left\langle \frac{\partial \mathcal{H}}{\partial V} \right\rangle = -p \tag{E.187}$$

and correspond to the pressure, such that one can write $\mathrm{dE} = -p\mathrm{dV}$ with $\mathrm{dE} = \langle \partial \mathcal{H}/\partial V \rangle \mathrm{dV}$, identical to $\mathrm{dU} = -p\mathrm{dV}$! Relations like this one start to bridge the gap between ensembles of Hamiltonian systems with many degrees of freedom at thermodynamic quantities. Surely, the next building block of the theory that we need to understand is the relation between a term like $\mathrm{dU} = \mathrm{TdS}$ with the underlying Hamiltonian dynamics.

E.7 *Adiabatic invariance of entropy*

The phase space volume $\phi^*(\mathcal{H}, a)$ and its differential change $\omega^*(\mathcal{H}, a)$ are defined as

$$\phi^*(\mathcal{H}, a) = \int_{\mathcal{H} \leq \mathrm{E}} \prod_i \mathrm{d}^3 p_i \mathrm{d}^3 q_i \quad \text{and} \quad \omega^*(\mathcal{H}, a) = \frac{\mathrm{d}}{\mathrm{dE}} \phi^*(\mathrm{E}, a) \tag{E.188}$$

where both quantities depend through the Hamilton-function $\mathcal{H}$ on the control parameter a, which in fact can change the energy and therefore the accessible phase space volume of the system:

$$\frac{\partial \phi^*}{\partial a} \mathrm{d}a = \phi^*(\mathrm{E}, a + \delta a) - \phi(\mathrm{E}, a) \tag{E.189}$$

This quantity exactly corresponds to the volume contained between

$$\mathcal{H}(p, q, a) = \mathrm{E} \quad \text{and} \quad \mathcal{H}(p, q, a + \delta a) = \mathrm{E} - \frac{\partial \mathcal{H}}{\partial a} \delta a \tag{E.190}$$

with the idea that $\partial \mathrm{H}/\partial a$ points into the direction of smaller energies, but in the formula we need the inverse gradient, pointing towards higher energies.

The change of the accessible phase space volume is given by

$$\frac{\partial \phi^*}{\partial a} \delta a = \int \delta s \mathrm{d}O \tag{E.191}$$

δs is parallel to $\nabla \mathcal{H}$

$$\mathrm{d}\mathcal{H} = \frac{\partial \mathcal{H}}{\partial S} \delta S \tag{E.192}$$

and consequently,

$$|\nabla \mathcal{H}| \delta s = -\frac{\partial \mathcal{H}}{\partial a} \delta a \quad \rightarrow \quad \frac{\partial \phi^*}{\partial a} \mathrm{d}a = \int \frac{\partial \mathcal{H}}{\partial a} \frac{\mathrm{d}O}{|\nabla \mathcal{H}|} \delta a \tag{E.193}$$

In the average defined by the microcanonical ensemble one obtains for the average change in energy

$$\left\langle \frac{\partial \mathcal{H}}{\partial a} \right\rangle = \frac{1}{\omega^*(E)} \int \frac{\partial \mathcal{H}}{\partial a} \frac{\mathrm{d}O}{|\nabla \mathcal{H}|} \quad \rightarrow \quad \frac{\partial \phi^*}{\partial a} = -\omega^*(E) \left\langle \frac{\partial \mathcal{H}}{\partial a} \right\rangle \tag{E.194}$$

Therefore, for an arbitrary change in $\phi^*(E, a)$ by $\mathrm{d}a$ one would obtain

$$\mathrm{d}\phi^* = \omega^* \left[\mathrm{d}E - \left\langle \frac{\partial \mathcal{H}}{\partial a} \right\rangle \mathrm{d}a \right] \tag{E.195}$$

Both changes ($\mathrm{d}E$ and $\mathrm{d}a$) affect the phase space volume and therefore the entropy

$$\mathrm{d}E = \frac{1}{\omega^*} \mathrm{d}\phi^* + \left\langle \frac{\partial \mathcal{H}}{\partial a} \right\rangle \mathrm{d}a \tag{E.196}$$

which is a formula reminiscent of the first law of thermodynamics,

$$\mathrm{d}U = \delta Q + \delta W \tag{E.197}$$

Should we continue by analogy? If this is the case, one would identify the thermal energy with $\delta Q = \frac{1}{\omega^*} \mathrm{d}\phi^*$, and consequently the entropy with $S = k_B \phi^*$:

$$\frac{k_B}{\phi^*} \frac{\mathrm{d}\phi^*}{\omega^*} = \frac{k_B}{\phi^*} \left[\mathrm{d}E - \left\langle \frac{\partial \mathcal{H}}{\partial a} \right\rangle \mathrm{d}a \right] \tag{E.198}$$

Using logarithmic derivatives this can be rewritten as

$$k_B \mathrm{d} \ln \phi^* = k_B \frac{\omega^*}{\phi^*} = k_B \frac{1}{\phi^*} \frac{\mathrm{d}\phi^*}{\mathrm{d}E} \left[\mathrm{d}E - \left\langle \frac{\partial \mathcal{H}}{\partial a} \right\rangle \mathrm{d}a \right] = k_B \frac{\mathrm{d} \ln \phi^*}{\mathrm{d}E} \left[\mathrm{d}E - \left\langle \frac{\partial \mathcal{H}}{\partial a} \right\rangle \mathrm{d}a \right] \tag{E.199}$$

Comparison with the second law of thermodynamics, $dS = \frac{1}{T}[dE - \delta W]$, would imply that the change dS in entropy

$$dS = k_B d \ln \phi^*$$
(E.200)

is just given by the change in logarithmic phase space volume, with k_B as a prefactor fixing the units. Then, comparing with the definition of temperature as $1/(k_B T) = \partial S/\partial E$, consistency implies that

$$\frac{1}{k_B T} = \frac{\partial \ln \phi^*}{\partial E}$$
(E.201)

The phase space volume of a system and how that volume changes with changing energy determine entropy and temperature. Fig. 11 summarises these concepts with the numerical example of a harmonic oscillator with parametric changes to its frequency ω, as well as an external driving with a resonant harmonic oscillation.

E.7.1   Example: adiabatic invariance in a string pendulum

Adiabatic invariance of the phase space volume ϕ^* when changing a control parameter is an incredibly abstract and interesting concept as it defines entropy and what exactly corresponds to adiabatic changes of state in the underlying mechanics of a system. We should consolidate this idea by considering a mechanical string pendulum of length $l = a$ which serves as the control parameter. It performs oscillations in angle φ with time t according to the differential equation $\ddot{\varphi} + \omega^2 \varphi = 0$ with $\omega^2 = g/l$, which follow from variation of the Lagrange-function,

$$\mathcal{L} = \frac{m}{2}(l\dot{\varphi})^2 + mgl \cos \varphi \simeq \frac{m}{2}(l\dot{\varphi})^2 + mgl\left(1 - \frac{\varphi^2}{2}\right)$$
(E.202)

The canonical momentum p_φ is just the angular momentum L,

$$p_\varphi = \frac{\partial \mathcal{L}}{\partial \dot{\varphi}} = ml^2 \dot{\varphi} = L$$
(E.203)

so that the Legendre-transform replacing $\dot{\varphi}$ with L yields the Hamilton-function

$$\mathcal{H}(\varphi, L, l) = \frac{L^2}{2ml^2} + \frac{mgl}{2}\varphi^2 - mgl = E$$
(E.204)

where we keep the explicit dependence of $\mathcal{H}$ on the control parameter l. The phase space volume ϕ^* is given as the integral

$$\phi^* = \int\limits_{\mathcal{H} \leq E} d\varphi dL$$
(E.205)

which in the case of the harmonic oscillator is just and ellipse bounded by the surface of constant energy, specifically by the semi axes in L

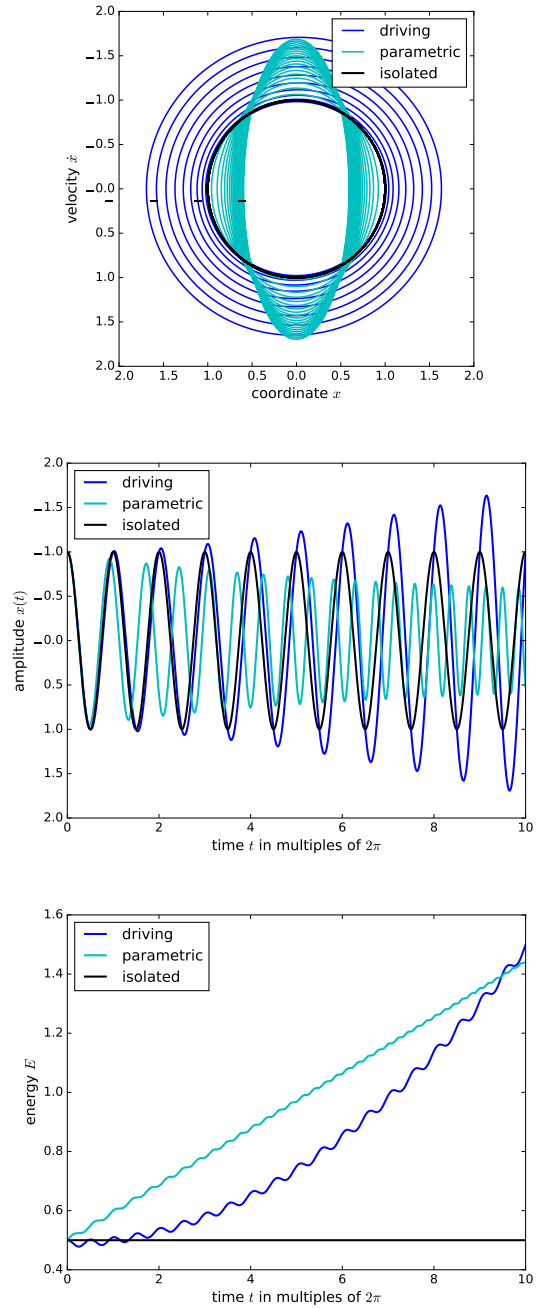$$a^2 = l^2 2m(E + mgl) \quad \text{and} \quad b^2 = \frac{2E + mgl}{mgl}$$
(E.206)

Figure 11: Phase plot (top panel), amplitude evolution (centre panel) and energy increase (bottom panel) of the driven and of the parametric oscillator.

in φ, such that the volume (which is really the area of a 2-dimensional ellipse, therefore the factor 2π) becomes

$$\phi^*(E, l) = 2\pi\sqrt{\frac{l}{g}}(E + mgl) \qquad (E.207)$$

The corresponding rate of change of this volume

$$d\phi^*(E, l) = 2\pi\sqrt{\frac{l}{g}}\left[dE + \left(\frac{E + 3mgl}{2l}\right)dl\right] \qquad (E.208)$$

implying that one can operate on $d\phi^*$ both by adding energy dE or by changing the control parameter dl.

Changing l very slowly in comparison to the typical time scale of the system would require a force F, as the weight needs to be lifted against the centrifugal force as well as the outside gravity,

$$F = -\frac{\partial\mathcal{H}}{\partial l} = \frac{L^2}{ml^3} - \frac{mg\varphi^2}{2} + mg \qquad (E.209)$$

The change to the system is required to be slow such that the ensemble is not disrupted: One needs to maintain an even distribution of the members of the ensemble over phase space, and a sudden change in the control parameter could potentially mess up the distribution. On the side of time averages it is imperative that the virial theorem is not affected, which relates the average kinetic and potential energies: Any rapid change in the control parameter would affect the ratio between the two energy forms. Specifically for a harmonic oscillator one gets $\langle T \rangle = \langle \phi \rangle$ and therefore

$$\frac{\langle L^2 \rangle}{2ml^2} = \frac{mgl}{2}\langle \varphi^2 \rangle = \frac{1}{2}(E + mgl) \qquad (E.210)$$

and therefore for the average force

$$\langle F \rangle = -\left\langle \frac{\partial\mathcal{H}}{\partial l} \right\rangle = -\frac{1}{2l}(E + 3mgl) \qquad (E.211)$$

with $\langle L^2 \rangle$ and $\langle \varphi^2 \rangle$ re-expressed with the energy E. Changes dE in energy then take place in performing work by changing the control parameter against this force,

$$dE = -\langle F \rangle dl = -\frac{E + 3mgl}{2l}dl \qquad (E.212)$$

Comparison with eqn. (E.208) then implies directly that the change in phase space volume is in fact vanishing, $d\phi^* = 0$ and, using the results of the previous chapter, that the corresponding energy is unchanged, $dS = d\ln(k_B\phi^*) = 0$. With this, we have gained a mechanical intuition about adiabatic changes and the invariance of the phase space volume.

E.8 *Entropy as phase space volume at fixed energy*

Up to this point, the idea of phase space volume was driven by the geometry of the boundary surface defined by energy. For continuing one needs to get a bit more specific, for instance with the example of an ideal gas, consisting of N point particles with no mutual interaction following a classical dispersion relation

$$\mathcal{H} = \sum_i \frac{\boldsymbol{p}_i^2}{2m} \tag{E.213}$$

The corresponding phase space volume ϕ^* bounded by $\mathcal{H}$ is given by

$$\phi^* = \int_{\mathcal{H} \leq E} \prod_i \mathrm{d}^3 p_i \mathrm{d}^3 q_i \tag{E.214}$$

While the spatial part of the integration is easy,

$$\int \prod_i \mathrm{d}^3 q_i = \prod_i \int \mathrm{d}^3 q_i = \prod_i V = V^N \tag{E.215}$$

and yields just the total physical volume of the system, taken to the Nth power, the integral over momentum space is bounded,

$$\sum_i \frac{\boldsymbol{p}_i^2}{2m} \leq E, \quad \text{or} \quad \sum_i \boldsymbol{p}_i^2 \leq 2mE \tag{E.216}$$

Effectively, this is the volume $C(3N)r^{3N}$ of a 3N-dimensional sphere of radius $r = \sqrt{2mE}$.

$$\phi^* = C(3N) \cdot (2mE)^{\frac{3N}{2}} \cdot V^N = \left(\frac{4\pi}{3} \cdot \frac{mE}{N} \exp 1 \right)^{\frac{3N}{2}} \cdot V^N \tag{E.217}$$

Moving towards the entropy requires the logarithm of the phase space volume,

$$k_B \ln \phi^* = \frac{3N}{2} k_B \ln E + N k_B \ln V + \frac{3N}{2} k_B \ln(2m) \tag{E.218}$$

with the last two terms being constant. If the relationship between entropy and phase space volume would be given by $S = k_B \ln \phi^*$, the definition of temperature would be sensible,

$$\frac{\partial S}{\partial E} = \frac{\frac{3}{2} N k_B}{E} = \frac{1}{T} \tag{E.219}$$

as it corresponds to what we expect from equipartition, $E = 3/2\, N k_B T$, as well as the change of entropy with volume,

$$\frac{\partial S}{\partial V} = \frac{N k_B}{V} = \frac{p}{T} \tag{E.220}$$

as it corresponds to the ideal gas law, $pV = Nk_BT$. But what about the scaling of the entropy S with particle number?

E.9 *Gibbs-paradox*

The ✈ Gibbs paradox is a thought experiment that shows that eqn. (E.218) with terms that are all proportional to the particle number N is incompatible with the idea that entropy should be additive. Writing

$$S = \frac{3}{2}Nk_B \ln T + Nk_B \ln V - Nk_B \ln N + N\sigma_0 = \frac{3}{2}Nk_B \ln T + Nk_B \ln\left(\frac{V}{N}\right) + N\sigma_0 \quad (E.221)$$

with an additional factor $\propto N \ln N$ would remedy this: Imagine a system with $N = N_1 + N_2$ particles in the total volume $V = V_1 + V_2$, which can be separated by inserting a wall, such that two partial systems with N_1 and N_2 particles in volumes V_1 and V_2 exist. In doing that, the density N/V is equal to N_1/V_1 and to N_2/V_2.

Before the barrier is removed, the entropies read

$$S_1 = \frac{3}{2}N_1 k_B \ln T + N_1 k_B \ln \frac{V_1}{N_1} + N_1 \sigma_0 \quad (E.222)$$

$$S_2 = \frac{3}{2}N_2 k_B \ln T + N_2 k_B \ln \frac{V_2}{N_2} + N_2 \sigma_0 \quad (E.223)$$

and after removing the barrier, the two entropies need to be combined in an additive way: $S_1 + S_2 = S$. Separating or combining the volumes can be done without any physical change to the system, neither thermal energy nor mechanical work is needed to insert the separating wall.

Let's inspect the terms one by one. The last term is clearly additive, $N_1\sigma_0 + N_2\sigma_0 = (N_1 + N_2)\sigma_0$, and so is the first term, $\frac{3}{2}N_1 k_B \ln T + \frac{3}{2}N_2 k_B \ln T = \frac{3}{2}(N_1 + N_2)k_B \ln T$. The second term is slightly more complicated:

$$N_1 k_B \ln \frac{V_1}{N_1} + N_2 k_B \ln \frac{V_2}{N_2} = k_B \ln\left[\left(\frac{V_1}{N_1}\right)^{N_1}\left(\frac{V_2}{N_2}\right)^{N_2}\right] \quad (E.224)$$

but the density $V/N = V_1/N_1 = V_2/N_2$ is unchanged:

$$\ldots = k_B \ln\left[\left(\frac{V}{N}\right)^{N_1}\left(\frac{V}{N}\right)^{N_2}\right] = k_B \ln\left[\left(\frac{V}{N}\right)^{N_1+N_2}\right] \quad (E.225)$$

The required additional term $-Nk_B \ln N$ can be generated by changing the definition of entropy,

$$S = k_B \ln \frac{\phi^*}{N!} \simeq k_B \ln \phi^* - k_B N \ln N \quad (E.226)$$

with the approximative ✈ Stirling-formula:

$$\ln N! \simeq N \ln N. \quad (E.227)$$

The physical origin of the Gibbs-factor is the following: When removing the barrier, each of the N_1 particles in the volume V_1 can change place with each of the N_2 particles in the volume V_2, for which there are $N!/N_1!/N_2!$ possibilities. Just by

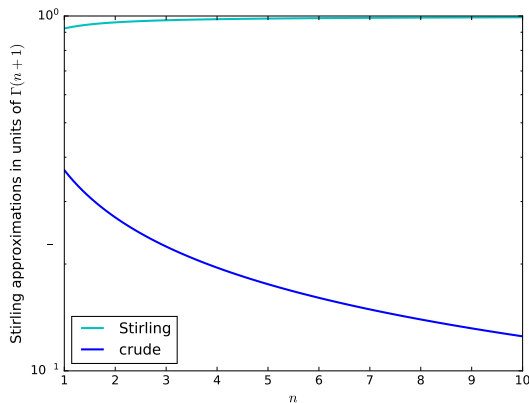Figure 12: Ratio of the Stirling approximation $\sqrt{2\pi n} \times (n/\exp(1))^n$ and the cruder $n \ln n - n$ to the exact value $n! = \Gamma(n+1)$.

removing the barrier the phase space volume ϕ^* would get enlarged by this factor. This is unphysical, just exchanging the particles would not have any influence on the physical properties of the system. If one distributes N particles onto N placeholders, there would be a total of N! possibilities. So one should counteract the increase in phase space volume by setting

$$S = k_B \ln \frac{\phi^*}{N!} \tag{E.228}$$

and by the rules of the logarithms, this becomes $S/k_B = \ln \phi^* - \ln N! = \ln \phi^* - N \ln N$ using Stirling's approximation. The inclusion of this so-called Gibbs-factor provides exactly the right correction to the entropy. Fig. 12 illustrates the validity of the Stirling-approximation

The phase space volume ϕ^* bounded by the energy was defined to be

$$\phi^* \equiv \int\limits_{\mathcal{H} \leq E} \prod_i^N d^3 p_i d^3 q_i \tag{E.229}$$

and has units of an action^{3N}, but should really be dimensionless. Without any particular deeper meaning in classical mechanics we can choose any scale h with units of an action to make the phase space volume dimensionless, although it will become apparent in quantum statistics that this is exactly the right thing to do. Choosing specifically the Planck-constant h and including the 1/N!-factor already in the definition of the phase space volume then yields

$$\phi = \frac{1}{h^{3N} N!} \int\limits_{\mathcal{H} \leq E} \prod_i^N d^3 p_i d^3 q_i \tag{E.230}$$
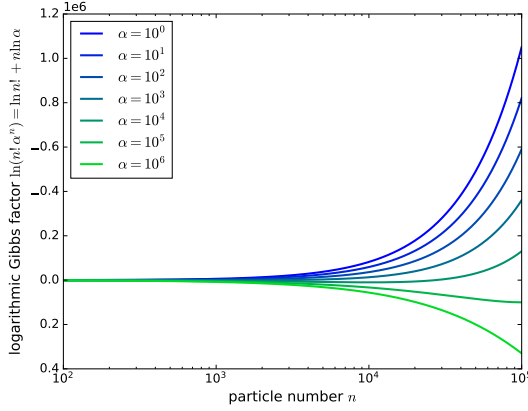
Figure 13: Gibbs-factor $n!\alpha^n$ (with $\alpha = h^3$), as a function of particle number n.

Then, for the ideal gas one would obtain the result

$$\phi = \frac{1}{h^{3N}} \left(\frac{4\pi}{3} \frac{mE}{N} \right)^{\frac{3N}{2}} \left(\frac{V}{N} \right)^{N} \exp\left(\frac{5N}{2} \right) \tag{E.231}$$

In summary, there are two places where quantum mechanics showed up: The proper de-dimensionalisation of the phase space volume and the Gibbs-factor due to the indistinguishability of the particles! One might wonder what the numerical value of $n!h^{3n}$ is, i.e. whether the rapidly growing $n!$ dominates over h^{3n} with a very small value of h. Taking the logarithm shows that $\ln(n!\alpha^n) = \ln n! + n \ln \alpha \simeq n \ln n + n \ln \alpha = n \ln(n\alpha)$ with $\alpha = h^3 \ll 1$. Fig. 13: The logarithm determines with its sign whether the Gibbs-factor is larger or smaller than 1, and this reflects whether α or n is larger. With typical $n \simeq 10^{23}$ but $\alpha \simeq 10^{-100}$ Js, the factor is tiny in this choice of units.

E.10 *Thermal wavelength* λ_{th}

We already made use of the Planck-constant h to make the phase space volume ϕ dimensionless, up to this point it appears naturally in many quantities without any particular reference to quantum mechanics, where the de Broglie-wavelength of a wave packet with momentum p is given by h/λ. Therefore, the classical dispersion relation suggests that we can assign a length scale λ_{th} to any temperature T,

$$E = \frac{p^2}{2m} = \frac{1}{2m} \left(\frac{h}{\lambda_{\text{th}}} \right)^2 = k_B T \quad \rightarrow \quad \lambda_{\text{th}} = \frac{h}{\sqrt{2mk_B T}} \tag{E.232}$$

assuming equipartition of the thermal energy $k_B T$. By convention, one usually absorbs additional factors of π into the definition $\lambda_{\text{th}} = h/\sqrt{2\pi m k_B T}$ for the ✈ thermal wavelength.
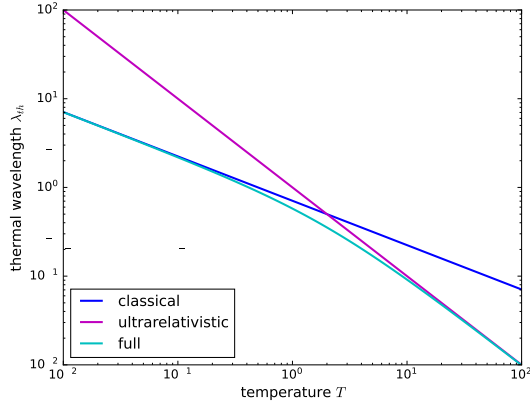
Figure 14: Thermal wavelength as a function of temperature, for the full dispersion relation and its classical and ultrarelativistic approximations.

The situation is slightly diffent if the particles are relativistic, because then a linear dispersion relation holds, $E = cp$, resulting in a direct inverse relation between thermal wavelength and temperature,

$$E = cp = \frac{ch}{\lambda_{th}} = k_B T \quad \rightarrow \quad \lambda_{th} = \frac{ch}{k_B T}. \tag{E.233}$$

Apart from these two limiting cases, the true dispersion relation

$$E^2 = (cp)^2 + (mc^2)^2 \tag{E.234}$$

leads to a biquadratic equation whose solution is given by Fig. 14. It illustrates the thermal wavelength for a classical dispersion and an ultrarelativistic dispersion, in comparison to the full dispersion relation.

With λ_{th} one can write for the phase space volume of an ideal classical gas,

$$\phi = \left(\frac{V}{\lambda_{th}^3} \exp(5/2) \right)^N \tag{E.235}$$

such that the entropy S becomes

$$S = k_B \ln \phi = k_B N \left(\ln \frac{V}{\lambda_{th}^3} + \frac{5}{2} \right) \tag{E.236}$$

It increases with particle number N because it is an extensive quantity, and compares the total available volume V with the fundamental size λ_{th}^3 of the wave packets representing the particles, alluding at the number of possibilities to distribute the wave packets in the volume.

The ensemble average of the phase space function $A(p_i, q_i)$ would be given by

$$\langle A \rangle = \int\limits_{E \leq \mathcal{H} \leq E+\delta E} \frac{1}{N! h^{3N}} \prod_i d^3 p_i d^3 q_i \; A(p_i, q_i) \rho(p_i, q_i) \qquad \text{(E.237)}$$

for an arbitrary density $\rho(p_i, q_i)$, where the fundamental postulate stipulates that this density is constant. If, specifically, it is set to $\rho(p_i, q_i) = 1/\omega(E)$ the average becomes compatible with

$$\langle A \rangle = \frac{\int\limits_{E \leq \mathcal{H} \leq E+\delta E} \frac{1}{N! h^{3N}} \prod_i d^3 p_i d^3 q_i \; A(p_i, q_i)}{\int\limits_{E \leq \mathcal{H} \leq E+\delta E} \frac{1}{N! h^{3N}} \prod_i d^3 p_i d^3 q_i} = \frac{\frac{d}{dE} \int_0^E \frac{1}{N! h^{3N}} \prod_i d^3 p_i d^3 q_i \; A(p_i, q_i)}{\frac{d}{dE} \int_0^E \frac{1}{N! h^{3N}} \prod_i d^3 p_i d^3 q_i}$$

$$\text{(E.238)}$$

where the denominator is by definition the differential phase space density $\omega(E)$

$$\omega(E) = \frac{d}{dE} \int_0^E \frac{1}{N! h^{3N}} \prod_i d^3 p_i d^3 q_i \qquad \text{(E.239)}$$

There is no contradiction between eqn. (E.237) and eqn. (E.238) with $\rho(p_i, q_i) = 1/(\omega(E)\delta E)$. At the same time, the entropy S is given by the logarithmic phase space volume

$$S = k_B \ln \phi \qquad \text{(E.240)}$$

so would it be possible to write S as a phase space average as well? And if yes, of what function? Let's try out the logarithmic phase space density $-\ln \rho$, with a prefactor of k_B to fix the units:

$$S = \int\limits_{E \leq \mathcal{H} \leq E+\delta E} \frac{1}{N! h^{3N}} \prod_i d^3 p_i d^3 q_i \; \rho(-k_B \ln \rho) =$$

$$\int \frac{1}{N! h^{3N}} \prod_i d^3 p_i d^3 q_i \; \frac{1}{\omega \delta E} \left(-k_B \ln \frac{1}{\omega \delta E} \right) \quad \text{(E.241)}$$

with the inverse differential volume $\rho = \frac{1}{\omega(E)}$ and the corresponding logarithm $\ln \omega(E) = -\ln \rho$ the entropy becomes

$$S = \frac{1}{\omega \delta E} k_B \ln(\omega \delta E) \int\limits_{E \leq \mathcal{H} \leq E+\delta E} \frac{1}{N! h^{3N}} \prod_i d^3 p_i d^3 q_i \qquad \text{(E.242)}$$

where the integral is just $\omega \delta E$, canceling with the prefactor. In general, entropy is the ensemble average of the logarithmic phase space density

$$S = -k_B \langle \ln \rho \rangle \qquad \text{(E.243)}$$

obtained by resubstitution of ρ, which is exactly Boltzmann's iconic finding. At the

same time, this formula is very reminiscent of Shannon's entropy for any distribution, and again there is a deep relationship between statistics and thermodynamics.