

## Chapter 2

# The Relation Between Classical and Quantum Statistics

The definition of thermal average values in the canonical ensemble as a sum over all states with a Boltzmann factor as the weight, given in Eq. (1.68), is rigorous. It is also useful insofar as we can actually calculate the levels and their properties quantum mechanically. This is possible for a number of Hamiltonians but certainly not for all interesting ones. Happily there will often be an alternative in the form of a classical treatment. A classical description of a system requires that quantum numbers are big compared to unity and is useful because one needs not know all details of the system to apply it.

There are two approaches to explain the classical-quantum statistics connection. One may either start from the truth as we have learned it at school, that quantum statistics is fundamental and classical statistics can be derived in the classical limit, the ‘bottom-up’ approach. Alternatively, one can use a more historical approach and start with classical dynamics and postulate certain rules which will turn out to give the right result, the ‘top-down’ approach. We will do both. One advantage of the ‘bottom-up’ approach is that it provides some training in the ensembles that were introduced in Chap. 1. The main but not exclusive virtue of the ‘top-down’ approach is conceptual; you will be wiser after having understood the procedure.

As an essential step towards application of the classical equations of motion and determining the range of validity of the results, we need to establish the rule which relates the classical and the quantum mechanical counting of states. We also need to consider the special quantum mechanical effects of the indistinguishability of particles. We will start with the latter.

Quantum statistical mechanics is influenced in an essential manner by the symmetry of the wave function upon permutation of the particles. It is well known from quantum mechanics that fermions of the same type (half-integer spin particles, electrons being the prime example) are described by a wave function that must be antisymmetric on exchange of any two fermions. This has the consequence that two identical fermions cannot be in the same single particle quantum state. This rule is absolutely essential for the description of the types of matter where bound state electrons are involved, be it in atoms, molecules and solids, and whether these solids are metals or insulators. Basically the Pauli exclusion principle, as the rule is called,

prohibits most of the states one would otherwise include in a counting of states. For identical bosons (integer spin particles) an analogous rule applies, except that the wave function must be symmetric. This means that bosons are social particles and will tend to cluster together. The consequences of this is probably best known for the Bose-Einstein condensates which you can read about in press releases from the Nobel committee. But even everyday objects like lasers(!) work precisely because of this social tendency (photons are bosons).

Quantum mechanically, identical particles are indistinguishable. Even in the classical limit, the partition functions therefore needs to be divided by the number of permutations of the number of particles in the system. For  $N$  identical particles the factor is  $N!$  Hence the canonical partition function of  $N$  indistinguishable particles with the single particle partition function  $z$  is

$$Z_N = \frac{z^N}{N!}, \quad (2.1)$$

which we have already used in the Introduction. The factor of  $N!$  appears only if the particles really *are* indistinguishable, which means that it will be applicable for a gas but not for atoms in a solid, where the atoms can be identified by their position in the lattice. Molecules in a gas will move around freely apart from infrequent collisions with other molecules and possibly the walls of a container, and after some time it becomes impossible to determine the position of a specific molecule, even classically.

As indicated, indistinguishability may be a time dependent question. We can speculate on the time scales. If we perform a Gedanken experiment where we measure the positions of gas molecules at some specific time such that we can tell them apart at the time of measurement, even if they are otherwise indistinguishable, the entropy will be less than before the measurement. For the sake of the argument we assume that the measurement is made such that the wave functions of individual molecules collapse to Gaussian wave packets, and for simplicity consider the subsequent development in one dimension only. The wave packets spread out as

$$(\Delta x)^2 = (\Delta x(0))^2 + \left( \frac{\Delta p}{m} t \right)^2. \quad (2.2)$$

For a Gaussian wave packet,  $\Delta p = \hbar/2\Delta x(0)$  and we can therefore express  $\Delta x$  in terms of  $\Delta x(0)$  and time as

$$(\Delta x)^2 = (\Delta x(0))^2 + \left( \frac{\hbar}{2m\Delta x(0)} t \right)^2. \quad (2.3)$$

We can find the time it takes for two identical molecules to have a quantum mechanical overlap and become indistinguishable. This time depends on  $\Delta x(0)$ . The longest value of this time for two particles a distance  $d$  apart corresponds to  $\Delta x(0) = d/2\sqrt{2}$  and is equal to  $t = md^2/8\hbar \sim m/\hbar\rho^{2/3}$ , where  $m$  is the mass of the particle and  $\rho$  the gas density. For an ideal gas at Standard Pressure and Temperature of  $P = 1 \text{ bar} = 1.013 \times 10^5 \text{ N/m}^2$ ,  $T = 293 \text{ K}$ , the time is  $t \sim (m/1 \text{ u}) \times 2 \cdot 10^{-10} \text{ s}$ . This is a short time but it is not zero.

The example is a little artificial because the width of the wave packet corresponds to a very low kinetic energy. A more realistic estimate is obtained by using the average root-mean-square thermal speed  $\langle p^2 \rangle^{1/2}/m = \sqrt{2T/m}$ . Under the same conditions as before, this gives  $t \sim d\sqrt{m/T} = \sqrt{m/T}\rho^{-1/3} = 2 \cdot 10^{-12}$  s for a 1 u particle (the width of the wave packet can be ignored in this calculation, making it effectively a classical calculation).

In practise, this time dependence causes few problems for gases. For liquids, it may be different because the motion of atoms is constrained, but not completely hindered as in a solid at low temperature. The calculation of the thermal properties including the proper distinguishability factor may then be non-trivial and depend on the specific molecular properties of the liquid state. We will leave this subject for future studies.

A consequence of quantum statistics is that the counting of states is often much more complicated for a system with a fixed number of particles than for a system with a fixed chemical potential. In a grand canonical ensemble, with its fixed chemical potential and fluctuating particle number, the partition function is calculated with a summation over all particle numbers, with the chemical potential as the constant price you pay for the addition of a single particle. In the canonical and microcanonical ensembles you need to restrict the summation to states that have precisely the right number of particles. This restriction of the summation is generally a non-trivial task. This means that the description of fermionic and bosonic systems usually is very cumbersome in the canonical ensemble and is best done with the grand canonical ensemble. There are exceptions. Bosons such as photons and phonons are cases for which the canonical partition functions can often be calculated analytically. The feasibility of summing over states with the correct quantum statistics is the one important property which makes the grand canonical ensemble useful and in practice *the* ensemble of choice, even in cases where particle numbers are conserved. The practical, computational advantages of the ensemble can simply outweigh this inconsistency.

The cases where the grand canonical ensemble is particularly useful are those where the system can be described in the independent particle approximation, *i.e.* where one can write the energies of the system as sums of single particle state energies, and when the system is a strongly degenerate fermionic or a bosonic system. Strongly degenerate means for fermions that the lowest energy single particle states are occupied with a probability which is close to unity, and for bosons that a significant fraction of the particles are in the lowest energy state. For fermions, the energy of the highest occupied level at zero temperature is called the Fermi energy and is on the order of usual molecular electronic energies, *i.e.* several eV. For bosons, the highest occupied level at zero temperature is simply the ground single particle state, which we can assign zero energy. For low enough temperatures we therefore have

$$\mu \approx E_f \quad (\text{fermions}) \quad (2.4)$$

$$\mu \approx 0 \quad (\text{bosons}). \quad (2.5)$$

## 2.1 Fermi and Bose Statistics of Independent Particles

Fermionic and bosonic systems of independent particle states are prototype ‘bottom-up’ situations and are the natural choices to illustrate a concrete application of the grand canonical ensemble and the transition from quantum to classical statistics.

Irrespective of whether a system is strongly degenerate or not, *i.e.* whether or not the occupation number is small compared to unity or not, in the single particle picture the total energy is given by

$$E = \sum_j n_j \varepsilon_j, \quad (2.6)$$

and the number of particles by

$$N = \sum_j n_j, \quad (2.7)$$

where  $n_j$  is the occupation number of state  $j$ , *i.e.* the (integer) number of particles in that single particle state. The canonical partition function is therefore

$$Z_{can}(N, V, T) = \sum_{(n_1, n_2, \dots)} \delta_{N, \sum n_j} e^{-\beta \sum_j n_j \varepsilon_j}, \quad (2.8)$$

where the sum runs over all combinations of the  $n_j$ ’s consistent with the permutation symmetry of the particles. The permutation symmetry requires that

$$\begin{aligned} n_i &= 0, 1 \quad (\text{fermions}) \\ n_i &= 0, 1, \dots, N-1, N \quad (\text{bosons}) \end{aligned} \quad (2.9)$$

The Kronecker delta  $\delta_{n,m}$ , which is one if  $n = m$  and zero otherwise, picks out the configurations with the right total number of particles in Eq. (2.8).

The grand canonical partition function, Eq. (1.73), can therefore be written as

$$Z_{gcan} = \sum_{N=0}^{\infty} \sum_{(n_1, n_2, \dots)} \delta_{N, \sum n_j} e^{-\beta \sum_j n_j \varepsilon_j} e^{\beta \mu N}. \quad (2.10)$$

Summation over all values of  $N$  cancels the Kronecker delta because

$$\sum_m \delta_{n,m} = 1, \quad (2.11)$$

and we can then sum unrestricted over all sets of occupation numbers, apart from the permutational symmetry constraint in Eq. (2.9):

$$Z_{gcan} = \sum_{(n_1, n_2, \dots)} e^{-\beta \sum_j n_j \varepsilon_j + \beta \sum_j n_j \mu}. \quad (2.12)$$

The exponential can be factorized into contributions from each level, and one ends with a product of grand canonical partition functions for individual levels:

$$Z_{gcan} = \prod_j \left( \sum_{n_j} e^{-\beta n_j \varepsilon_j + \beta n_j \mu} \right). \quad (2.13)$$

This is valid for both fermions and bosons. The difference between the two shows up when one calculates the sums, taking the permitted particle numbers into account,

$$Z_{gcan} = \prod_j (1 + e^{-\beta(\varepsilon_j - \mu)}) \quad (\text{fermions, independent particles}), \quad (2.14)$$

and

$$Z_{gcan} = \prod_j (1 - e^{-\beta(\varepsilon_j - \mu)})^{-1} \quad (\text{bosons, independent particles}). \quad (2.15)$$

One may want to think of these two partition functions in a different way. They are formally identical to those of independent excitations with the spectra

$$e_{i,n} = n(\varepsilon_i - \mu), \quad n = 0, 1 \text{ (fermions)}, \quad n = 0, 1, 2, \dots, \infty \text{ (bosons)}, \quad (2.16)$$

and the average occupation number is the thermal average of the excitation energy in units of  $\varepsilon_i - \mu$ .

From the partition functions one finds the populations of the individual quantum states to be

$$p_j = \frac{e^{-\beta(\varepsilon_j - \mu)}}{1 \pm e^{-\beta(\varepsilon_j - \mu)}} \quad (2.17)$$

(+ for fermions, − for bosons). These populations are illustrated in Fig. 2.1 for both types of systems, both with 100 particles and with single particle states that are equidistant in energy,  $\varepsilon_j = j\Delta$ , where  $j$  is a non-negative integer. Also shown are the chemical potentials corresponding to 100 particles on the average, for the range of temperatures  $T = 5$  to 50.

The stage is now set to find the classical limit of the thermal properties of the quantum gases. This limit is defined as the situation where the occupation number of each state is much less than unity;

$$p_j = \frac{e^{-\beta(\varepsilon_j - \mu)}}{1 \pm e^{-\beta(\varepsilon_j - \mu)}} \ll 1. \quad (2.18)$$

We can ignore the exponential in the denominator to get

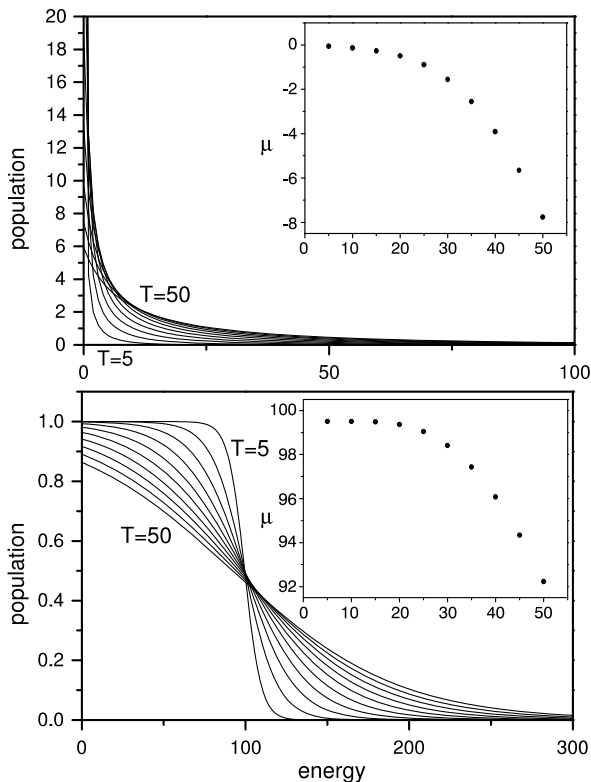
$$\bar{N} = \sum_j e^{-\beta(\varepsilon_j - \mu)} = e^{\beta\mu} \sum_j e^{-\beta\varepsilon_j}. \quad (2.19)$$

The sum is nothing but the canonical partition function for a single particle (identical expressions for a fermion and a boson),  $z_{c,1}$ , and we find that the chemical potential is

$$\mu = -T \ln(z_{c,1}/\bar{N}). \quad (2.20)$$

This chemical potential can be compared with the one calculated for a classical gas of indistinguishable molecules, Eq. (1.79), in Chap. 1. Apart from the replacement of a fixed number  $N$  of atoms with an average number,  $\bar{N}$ , the two expressions are identical. Because the chemical potential is the derivative of the canonical partition function, this also means that the classical limit of the (canonical) partition functions

**Fig. 2.1** The population in single particle states for  $\overline{N} = 100$  bosons (*top frame*) and fermions (*bottom frame*) in the grand canonical ensemble at temperatures 5 to 50, for equidistant single particle spectra. The chemical potentials vs. temperature are shown in the *insets*. All energies and temperatures are in units of the spacing in the single particle spectrum,  $\Delta$



for non-interacting bosons and fermions have the same form as the classical limit written down in Chap. 1, Eq. (1.77). It is noteworthy that the indistinguishability factor  $N!$  appeared automatically here, without any need to introduce it by hand. Historical remark: The factor was postulated by Gibbs before quantum mechanics was even an idea, in order to get the correct additivity of the entropy of a classical gas.

## 2.2 Classical Phase Space

So let's turn to the second point of this chapter, the 'top-down' approach. In a quantum description of matter you have well-defined energy levels which can be numbered and counted. In classical mechanics this is not the case. An instructive example is (again) the harmonic oscillator. Quantum mechanically it has one more state each time the energy is increased by  $\hbar\omega$ . Suppose you had not solved the quantum mechanical problem and still had to decide the number of states of the system at a certain energy. What would you do?

The solution is found when we take a closer look at the classical counterpart of the Hilbert space used in quantum mechanics. It is called phase space and is,

like the Hilbert space, a multi dimensional space. Unlike Hilbert space it is not spanned by square integrable functions, but the coordinates and momenta of all the particles in the system. These coordinates and momenta need not be the usual linear quantities you learn about in the first course on mechanics, but can be generalized coordinates and their conjugate momenta, for example an angle and its associated angular momentum.

A system of  $N$  particles will span a space with  $6N$  dimensions, or more generally  $2dN$  dimensions if the physical space is  $d$ -dimensional. A state of the system is defined as the point in this  $6N$  dimensional space that specifies all the momenta and coordinates. The classical microcanonical partition function is the area of the surface with the prescribed energy, embedded into this space. It does not sound as if it is easy to calculate, and often it isn't. The canonical partition function is easier. It is calculated as the integral over the whole space with the Boltzmann factor as the weight function:

$$Z \propto \int \exp[-\beta E(x_1, x_2, \dots, x_{3N}, p_1, p_2, \dots, p_{3N})] dx_1 dp_1 dx_2 dp_2 \cdots dx_{3N} dp_{3N}. \quad (2.21)$$

As an application of the classical distribution we will calculate a few results for an ideal gas. In an ideal gas the molecules do not interact with each other or anything else and the Hamiltonian is therefore a sum of the kinetic energies of all molecules, which for simplicity will be assumed to have the same mass  $m$ :

$$H = \sum_i \frac{p_i^2}{2m}. \quad (2.22)$$

The Boltzmann factor therefore factorizes, and for every molecule the momentum distribution is

$$P(p_x, p_y, p_z) dp_x dp_y dp_z \propto e^{-\beta \frac{p_x^2 + p_y^2 + p_z^2}{2m}} dp_x dp_y dp_z. \quad (2.23)$$

The distribution is spherically symmetric in momentum space. With  $p^2 \equiv p_x^2 + p_y^2 + p_z^2$  and integrating out the angular dependence, which just gives a multiplicative constant of  $4\pi$ , we have

$$P(p) dp \propto p^2 e^{-\beta \frac{p^2}{2m}} dp \propto v^2 e^{-\beta m v^2 / 2} dv. \quad (2.24)$$

This is the Maxwell-Boltzmann distribution of momenta or speeds of gas molecules in an ideal gas in three dimensions.

The absence of intermolecular interactions is an unnecessary restriction. Any realistic Hamiltonian will contain terms that represent the interaction of the gas molecules with each other or it may even describe a condensed phase where interactions are plentiful. As long as the interaction terms only depend on the positions and not on the momenta/velocities of the molecules, the coordinates can be integrated out independently of the momenta,<sup>1</sup> and consequently the velocity distribution is also given by Eq. (2.24) for these situations.

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<sup>1</sup>In principle. In practise it is not that easy. This is another Gedanken calculation.

The classical partition function in Eq. (2.21) still leaves out the value of the constant of proportionality. A suggestion of what that constant can be is found in the dimensions of  $Z$ . If we want to have any correspondence between the classical and the quantum cases, we must at least demand that the dimensions of the two quantities are identical. The quantum partition function is dimensionless as it is a sum over exponentials. But the integral in  $Z$  in Eq. (2.21) has dimension of coordinate times momentum, all to the power  $3N$ . If you calculate the dimensions of the product of a coordinate and its conjugate momentum you get the dimension of Planck's constant. This is no accident. The normalization constant is  $1/h^{3N}$ . In other words: one state of a system with  $M$  sets of conjugate coordinates and momenta has a volume of  $h^M$  in phase space. We can define a semiclassical canonical partition function as

$$Z_{\text{semiclass}} \equiv \frac{1}{h^{3N}} Z_{\text{class}}. \quad (2.25)$$

It should be clear that this prescription only works for systems that actually have a classical description. This rules out the application of Eq. (2.25) to spins and similar degrees of freedom.

For many purposes the distinction between the semiclassical expression and the truly classical partition functions is no problem because any multiplicative constant drops out when calculating observables with logarithmic derivatives or comparing volumes in phase space (of similar dimensionality). For calculation of entropies, it does count, however.

Equation (2.25) can be derived with a calculation where the partition function is expanded in powers of  $\hbar$ . The calculation will not be reproduced here. Instead, we will show with several examples, at the end of this chapter, that the result holds and then hope that the perfect agreement with our *Ansatz* applied together with exact calculations will convince you that all other (classically meaningful) cases can be treated this way. Before that, we will calculate some general results for the classical limit.

## 2.3 A Few Elementary and Useful Results from Classical Statistical Mechanics

The classical partition function allows a simple estimate of the high energy/temperature limit of the thermal properties of the systems for which the classical limit makes sense (a spin in a magnetic field wouldn't work, for example). A coordinate,  $q_i$  say, may appear in quadratic form uncoupled from other coordinates and momenta in the Hamiltonian,  $H$ :

$$H = \alpha q_i^2 + H'(q', p), \quad (2.26)$$

where  $p$  is the set of all momenta and  $q'$  is the set of all coordinates except  $q_i$ . The contribution to the canonical partition function from  $q_i$  factorizes:



$$\begin{aligned}
Z &= \frac{1}{h^{3N}} \int e^{-\beta H} \prod_j dq_j dp_j = \frac{1}{h^{3N}} \int e^{-\beta(\alpha q_i^2 + H')} dq_i \prod_j' dq_j dp_j \\
&= \int \frac{1}{h} e^{-\beta \alpha q_i^2} dq_i \int \frac{1}{h^{3N-1}} e^{-\beta H'} \prod_j' dq_j dp_j,
\end{aligned} \tag{2.27}$$

where the primed product of differentials is the one where  $dq_i$  is left out. The last integral is denoted  $Z'$  and then

$$Z = Z' \frac{1}{h} \int e^{-\beta \alpha q_i^2} dq_i. \tag{2.28}$$

If  $q_i$  can take all values, the integration over  $q_i$  can be expressed in closed form;

$$Z = \frac{1}{h} \sqrt{\frac{\pi}{\beta \alpha}} Z'. \tag{2.29}$$

It should be clear that this holds for all degrees of freedom that separate the way  $q_i$  did, coordinates and momenta alike. Consequently, the contributions to the partition function from all those degrees of freedom will be proportional to  $\sqrt{1/\beta} = \sqrt{T}$ , taken to a power which is this number of degrees of freedom. It is equally clear that the factorization does not depend on whether or not the Hamiltonian is quadratic in the degree of freedom or has some other functional form, although the value of the specific integral will.

The average thermal energy of the system in the canonical ensemble is

$$\langle E \rangle = -\frac{d \ln(Z)}{d\beta} = -\frac{d \ln(\sqrt{\frac{\pi}{h^2 \beta \alpha}})}{d\beta} - \frac{d \ln(Z')}{d\beta} = \frac{T}{2} + \langle E' \rangle, \tag{2.30}$$

with the above meaning of the primed quantity. Hence the contribution to the thermal energy is  $T/2$  from each degree of freedom that enters into the energy quadratically. With this result, the properties of the Maxwell-Boltzmann distribution can practically be read off the Hamiltonian without any further work. The partition function for an ideal gas of  $N$  particles is

$$Z \propto \beta^{-3N/2} = T^{3N/2}, \tag{2.31}$$

and the average kinetic energy

$$\langle E \rangle = -\frac{\ln(Z)}{\partial \beta} = \frac{3N}{2} T. \tag{2.32}$$

The 3 appears because of the number of independent momenta in space. The heat capacity from these types of degrees of freedom is also easy to find. For one d.o.f. it is simply  $C = 1/2$  ( $= k_B/2$ ), and like the energy it is additive. Note that the value of  $\alpha$  does not appear in either of these quantities.

These rules, known as equipartition, can be very useful because they quickly give a value for the classical thermal energy and heat capacity. One use is to judge, from experimental data, whether certain d.o.f.'s are classical or not. Historically, equipartition was a problem for statistical mechanics because the heat capacity of

electrons in metals was observed not to obey this simple law. Not knowing the Pauli principle it was very difficult to explain the anomalously low heat capacity of these components of matter.

Another simple observation can be very useful. If the level density can be written as a power of the excitation energy, the partition function is easily calculated to be:

$$Z \propto \int_0^\infty E^{s-1} e^{-\beta E} dE \propto \beta^{-s} = T^s. \quad (2.33)$$

The converse also holds; a partition function of the latter form will only arise from a powerlaw level density with the powers of the two related as  $s$  and  $s - 1$ .

## 2.4 Quantum Corrections to Interatomic Potentials

Above we discussed how to convert the classical canonical partition function to the semiclassical by division with a factor  $2\pi\hbar$  to an appropriate power, and to account for the indistinguishability with the factor  $1/N!$  In this section we will go a step closer to the quantum limit and calculate quantum corrections to the equations of motion for two particles interacting with a two-body potential.

The classical motion of a particle represents it as a point moving on a trajectory. The correction we will calculate here amounts to treating it as a propagating wave packet. The simplest of these are Gaussian. In  $\bar{x}$ -space;

$$\phi \propto e^{\alpha(\bar{x}-\bar{x}_0)^2/2}. \quad (2.34)$$

The probability distribution  $|\phi|^2$  for this wave function has the width

$$\langle \Delta \bar{x}^2 \rangle = \frac{1}{2\alpha}. \quad (2.35)$$

For the momentum the width is equal to the thermal width:

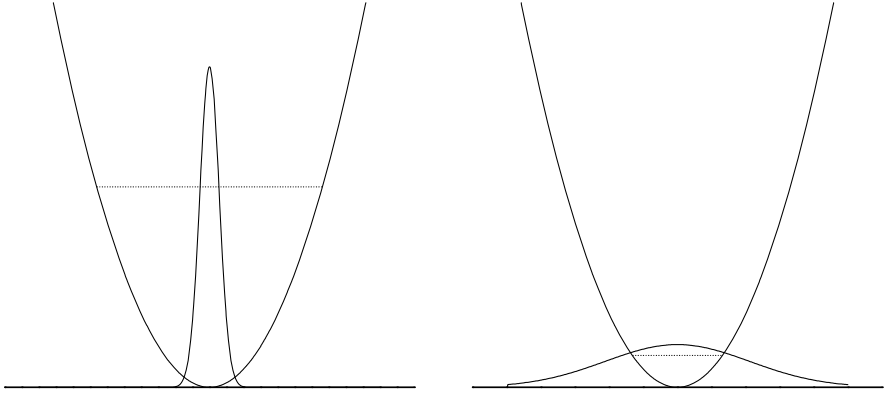
$$\langle \Delta \bar{p}^2 \rangle = \langle 2m E_k \rangle = 3mT. \quad (2.36)$$

This relation expresses that the particle is not in a pure momentum or kinetic energy eigenstate, but rather in a superposition of kinetic energy eigenstates that has a width determined by the temperature. Next we use the Heisenberg indeterminacy relations, better known under the slightly more convenient names Heisenberg uncertainty relations, or uncertainty principle, to relate the width of the wave packet to the temperature;

$$\Delta p \Delta x = \frac{\hbar}{2}. \quad (2.37)$$

(The equality holds for a Gaussian wave packet.) This gives the shape parameter,  $\alpha$ , of the wave packet in terms of the temperature:

$$\alpha = \frac{6mT}{\hbar^2}. \quad (2.38)$$



**Fig. 2.2** Two situations where the wave packet dynamics can (*left*) and cannot (*right*) be used. The potentials are quadratic and the wave packets are Gaussians. The energies corresponding to the widths of the wave packets are given as *dotted lines*

Because we are dealing with two-body interatomic potentials, we will replace the mass  $m$  with the reduced mass of the two identical mass particles,  $\mu \equiv (m^{-1} + m^{-1})^{-1} = m/2$ , in the following.

The next step is to place the wave packet on a potential energy surface, because this is what we are interested in. This introduces other length scales in the problem that may not be compatible with the one determined by  $T$ . Specifically, if the temperature is low, the wave packet in Eq. (2.34) will be very broad and reach into regions of very high energy. When the presumed wave packet spreads into regions with potential energies that are much higher than  $\Delta p^2/2\mu$ , it is a sign that the *Ansatz* Gaussian wave function is a poor description of the physical situation. For a quantitative calculation of where this limitation sets in we use the example of a one-dimensional harmonic oscillator. We have the criterion:

$$\frac{1}{2}\mu\omega^2\Delta x^2 = \frac{1}{2}\mu\omega^2\left(\frac{\hbar}{2\Delta p}\right)^2 \lesssim \frac{\Delta p^2}{2\mu}. \quad (2.39)$$

This requirement means that the potential energy associated with the width of the wave packet is less than the kinetic energy of the same. Using that the kinetic energy is half the total energy for a harmonic oscillator,  $\Delta p^2/2\mu = E/2$ , we get the condition

$$E \gtrsim \frac{1}{2}\hbar\omega, \quad (2.40)$$

which looks like a reasonable condition. It tells us that we are dealing with a high temperature approximation of the quantum contribution to the equations of motion. The condition is illustrated in Fig. 2.2.

After having established the limit of the approximation, we proceed with the calculation of the average potential. It is the average over the wave packet:

$$V_{qc}(r) = \int V(|\vec{r} + \vec{R}|) |\phi|^2 d\vec{R}, \quad (2.41)$$

where  $V$  is the classical potential. The integrand is a function of the distance between the two atoms, although the integration is over a three dimensional space. We perform the integral with an expansion to second order in the distance. First  $\bar{R}$  is expressed in polar coordinates with the  $z$ -axis along the line connecting the atoms,

$$|\bar{r} + \bar{R}| = (R^2 \sin^2 \theta + (r + R \cos \theta)^2)^{1/2} \approx r + \frac{R^2}{2r} + R \cos \theta - \frac{R^2}{r} \cos^2 \theta, \quad (2.42)$$

where  $r = |\bar{r}|$  and similar for  $R$ , and terms to second order in  $R$  have been retained. We therefore have the expansion of the potential along the interatomic axis, retaining terms to the same order;

$$V = V(r) + V'(r) \left( \frac{R^2}{2r} + R \cos \theta - \frac{R^2}{r} \cos^2 \theta \right) + \frac{1}{2} V'' R^2 \cos^2 \theta + \dots \quad (2.43)$$

This gives the effective (quadratic Feynman-Hibbs) potential

$$\begin{aligned} V_{QFH}(r) \approx & \left( \frac{6\mu}{\pi\beta\hbar^2} \right)^{3/2} \int d\phi d\theta \sin \theta d\bar{R} R^2 e^{-\frac{6\mu}{\beta\hbar^2} R^2} \\ & \times \left[ V(r) + V'(r) \left( \frac{R^2}{2r} + R \cos \theta - \frac{R^2}{r} \cos^2 \theta \right) + \frac{1}{2} V'' R^2 \cos^2 \theta \right]. \end{aligned} \quad (2.44)$$

The integrals are standard. We get

$$V_{QFH}(r) = V(r) + \frac{\hbar^2}{24\mu T} \left( V'' + \frac{2V'}{r} \right). \quad (2.45)$$

This is the effective two-body potential in the high energy limit for the classical potential  $V$ .

## 2.5 Example 1: The Harmonic Oscillator

We will now give a few examples of the classical limit of thermal properties of single particle systems with known or traceable quantum mechanical properties. First the harmonic oscillator. The canonical partition function for a quantum harmonic oscillator is one of the simplest to calculate. It is

$$Z_{qm} = \sum_{n=0}^{\infty} e^{-\beta n \hbar \omega} = \frac{1}{1 - e^{-\beta \hbar \omega}}. \quad (2.46)$$

At high temperatures,  $T \gg \hbar \omega$ , the average quantum number is big and one reaches the classical limit:

$$\begin{aligned} Z_{qm} &= \frac{1}{1 - (1 - \beta \hbar \omega + \frac{(\beta \hbar \omega)^2}{2} + \dots)} = \frac{1}{\beta \hbar \omega (1 - \frac{\beta \hbar \omega}{2} + \dots)} \\ &\approx \frac{T}{\hbar \omega} \left( 1 + \frac{\hbar \omega}{2T} \right) = \frac{T}{\hbar \omega} + \frac{1}{2}. \end{aligned} \quad (2.47)$$

The next-to-leading term of  $1/2$  is the same  $1/2$  which appeared in the improved formula for the level density, Eq. (1.28).

Let's now calculate the classical partition function. The energy is

$$E = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2. \quad (2.48)$$

Inserting this into Eq. (2.21) we have:

$$Z_{class} = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dp e^{-\beta(\frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2)}. \quad (2.49)$$

The exponential factorizes into two parts which depend on  $x$  and  $p$  alone. We therefore end up with two Gaussian integrals that can be done:<sup>2</sup>

$$\begin{aligned} Z_{class} &= \int_{-\infty}^{\infty} e^{-\beta \frac{1}{2}m\omega^2 x^2} dx \int_{-\infty}^{\infty} e^{-\beta \frac{p^2}{2m}} dp \\ &= \left[ \sqrt{\frac{2}{\beta m}} \frac{1}{\omega} \int_{-\infty}^{\infty} e^{-x'^2} dx' \right] \left[ \sqrt{\frac{2m}{\beta}} \int_{-\infty}^{\infty} e^{-p'^2} dp' \right] = \frac{2\pi T}{\omega}. \end{aligned} \quad (2.50)$$

If you compare this with the leading order in  $Z_{qm}$  from Eq. (2.47) you see that the missing constant of proportionality is  $h$ :

$$Z_{qm} = \frac{1}{h} Z_{class}. \quad (2.51)$$

At least our rule in Eq. (2.25) holds for the harmonic oscillator.

We can use semiclassical quantum physics to understand the origin of this rule. Semiclassical quantization uses classical equations of motion but accept only solutions where the trajectories obey a certain quantization condition. According to this theory, the energy of a harmonic oscillator is quantized as

$$E = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 = n\hbar\omega, \quad (2.52)$$

where  $n$  is a non-negative integer. This equation defines a curve in phase space which is an ellipse and on which the semiclassical harmonic oscillator moves. The length of the two axis are determined by solving Eq. (2.52) with  $p = 0$  and  $x = 0$  for the biggest values of the coordinate  $x$  and the momentum  $p$  with the result

$$x_{max} = \left( n\hbar\omega \frac{2}{m\omega^2} \right)^{1/2}, \quad p_{max} = (n\hbar\omega 2m)^{1/2}. \quad (2.53)$$

We can find the volume in phase space,  $V_n$ , of the lowest  $n + 1$  states that have the quantum numbers from 0 to  $n$ , as the area of the ellipse:

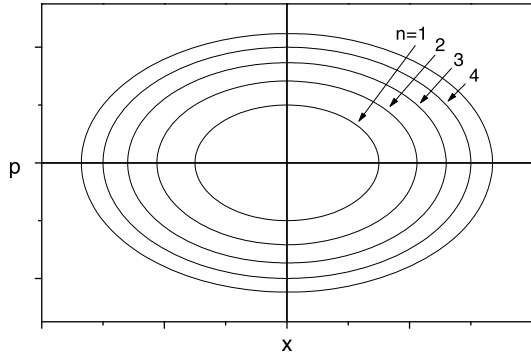
$$V_n = \pi x_{max} p_{max} = \pi 2n\hbar\omega = nh. \quad (2.54)$$

The volume in phase space of state  $n$  is then  $nh - (n - 1)h = h$ . It is illustrated in Fig. 2.3.

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<sup>2</sup>If we are average physicists, that is. As Predrag Cvitanovic remarked, a Gaussian integral is the only integral an average physicist can do (Classics Illustrated: Field Theory, NORDITA Lecture notes, 1983).

**Fig. 2.3** The phase space of a single harmonic oscillator. The states permitted according to semiclassical quantization are drawn as *lines*. The area between each line is constant and equal to  $h$



As the alert reader will have noticed, the ground state is not represented correctly this way. This is a general problem, both with semiclassical quantization and with the classical partition function. At energies comparable to or below the lowest excitation energy, the classical partition function should not be used.

## 2.6 Example 2: A Free Particle

The free particle is particularly important because it is frequently encountered. There are no discrete quantum numbers associated with the translational motion, and we need a trick to calculate the level density. The trick is to regularize the calculation by using the particle in a box solutions for the energy eigenstates, and then let the size of the box go to infinity.

The energy of a particle in a box is given by

$$E = \frac{\hbar^2 \pi^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2), \quad (2.55)$$

where  $L$  is the length of the box and  $(n_x, n_y, n_z)$  is a set of positive integers. The equation for the energy looks like the equation for a sphere in the three dimensional space spanned by  $n_x, n_y$  and  $n_z$ , with radius

$$r = \frac{\sqrt{E2mL}}{\hbar\pi} = \sqrt{n_x^2 + n_y^2 + n_z^2}. \quad (2.56)$$

The radius and volume of the sphere are dimensionless. To count the number of states with energy up to  $E$ , we should count the number of lattice points inside the volume defined by this radius. This is difficult to do exactly and we will use the volume instead, corresponding to a high energy approximation. The relative error of the result will approach zero when the energy goes to infinity. More correctly stated, we will use the part of the volume where all coordinates are positive. Negative quantum numbers do not give rise to new states, just a phase factor on the ones represented by the positive quantum number states. To avoid double counting we therefore need to

divide the whole volume of the sphere by  $2^3 = 8$ . Hence the total number of states below  $E$  is

$$N_t(E) = \frac{1}{8} V \left( r = \frac{\sqrt{E2mL}}{\hbar\pi} \right) = \frac{1}{8} \frac{4\pi}{3} \left( \frac{\sqrt{E2mL}}{\hbar\pi} \right)^3. \quad (2.57)$$

The level density for the whole physical volume of  $L^3$  is therefore

$$\rho_{qm}(E) = \frac{dN_t(E)}{dE} = \frac{1}{h^3} m^{3/2} 4\pi E^{1/2} \sqrt{2} L^3. \quad (2.58)$$

Let's now calculate the analogous level density according to the classical-to-quantum recipe. The volume element in phase space is<sup>3</sup>

$$dV_f = d\vec{x} d\vec{p}, \quad (2.59)$$

and the total volume up to energy  $E$  is

$$V_f(E) = \int_{V=L^3} d\vec{x} \int_{p^2/2m \leq E} d\vec{p} = L^3 \int_0^{(2mE)^{1/2}} 4\pi p^2 dp = L^3 4\pi \frac{(2mE)^{3/2}}{3}. \quad (2.60)$$

The density of classical phase space at energy  $E$  is then:

$$\rho_{class}(E) \equiv \frac{V_f(E)}{dE} = L^3 4\sqrt{2}\pi m^{3/2} E^{1/2}. \quad (2.61)$$

We see that for a free particle the quantum mechanical translational level density is the volume in phase space divided by  $h^3$

$$\rho_{qm}(E) = \frac{1}{h^3} \rho_{class}(E). \quad (2.62)$$

Another way of stating this result is to write the density of translational states for a free particle as

$$dn = \frac{1}{h^3} d\vec{x} d\vec{p}. \quad (2.63)$$

In this example we have calculated the level density and not the partition function as in the first example. This makes no difference concerning the conclusions about the factor  $h$ . A constant multiplied on the level density will give the same constant multiplied on the partition function, and *vice versa*.

## 2.7 Example 3: A Particle in the Gravitational Field

The third example is the case of a particle in a constant gravitational field close to earth,

$$\begin{aligned} V(x) &= mgx, & x > 0, \\ V(x) &= \infty, & x \leq 0. \end{aligned} \quad (2.64)$$

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<sup>3</sup>A *quantity* is a vector in this section, not an average.

The potential in the two other dimensions is constant, and since these solutions are the well-known plane waves, we can concentrate on the vertical direction. The semiclassical partition function for this d.o.f. is

$$Z = \frac{1}{h} \int_0^\infty dx \int_{-\infty}^\infty e^{-\beta(\frac{p^2}{2m} + mgx)} dp. \quad (2.65)$$

Both integrals in this expression can be done easily, and the result is

$$Z = \frac{1}{h} \sqrt{\frac{2m\pi}{\beta}} \frac{1}{\beta gm}. \quad (2.66)$$

$Z$  is proportional to a power of the temperature and we can therefore apply the results from Sect. 2.3 on the functional form of the level density. Explicitly, if we calculate the partition function as

$$Z = \int_0^\infty \rho(E) e^{-\beta E} dE, \quad (2.67)$$

we can set  $\rho(E) = cE^{1/2}$ , which gives us

$$Z = c \int_0^\infty E^{1/2} e^{-\beta E} dE = c\beta^{-3/2} \int_0^\infty x^{1/2} e^{-x} dx. \quad (2.68)$$

With the substitution  $u = x^{1/2}$  one gets

$$Z = c\beta^{-3/2} 2 \int_0^\infty u^2 e^{-u^2} du. \quad (2.69)$$

The integral can be done easily if we know one trick and how to do a Gaussian integral.<sup>4</sup> The trick will occasionally be useful so here it is:

$$\int_0^\infty x^2 e^{-x^2} dx = -\frac{d}{d\alpha} \int_0^\infty e^{-\alpha x^2} dx \Big|_{\alpha=1} = -\frac{d}{d\alpha} \frac{1}{\sqrt{\alpha}} \frac{\sqrt{\pi}}{2} \Big|_{\alpha=1} = \frac{\sqrt{\pi}}{4}. \quad (2.70)$$

This gives

$$Z = c\beta^{-3/2} \frac{\sqrt{\pi}}{2}. \quad (2.71)$$

We can now identify the two different expressions for  $Z$  in Eqs. (2.66, 2.71) and find that they agree provided

$$c = \frac{2^{3/2}}{hgm^{1/2}}. \quad (2.72)$$

By expressing the partition function in two equivalent ways, we have derived the level density for a particle in a constant gravitational field, complete with numerical constants. This level density is the reciprocal of the average of the spacing between two neighboring quantum mechanical levels (see Eq. (1.19)), and the calculation therefore implies a constraint on the quantum energies of the system. This may

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<sup>4</sup>Predrag Cvitanovic has remarked...



seem a little surprising at first sight. It should not be, though, because that is what we learn from Niels Bohr's Correspondence Principle. For large quantum numbers the quantum mechanical solution must have observables which approach those of the analogous classical problem.

To show explicitly that this is indeed correct in our case and that the introduction of  $1/h$  into Eq. (2.65) is justified, we find the quantum eigenstates for the problem by solving the Schrödinger equation. For the gravitational potential it reads

$$-\frac{\hbar^2}{2m}\nabla^2\psi + gmx\psi = E\psi, \quad (2.73)$$

with  $\psi(x) = 0$  for  $x \leq 0$ . Expressing the height in scaled dimensionless units as

$$u = x\left(\frac{2m^2g}{\hbar^2}\right)^{1/3}, \quad (2.74)$$

one gets the equation

$$\frac{d^2\psi}{du^2} - u\psi = \varepsilon\psi, \quad -\varepsilon \equiv E \frac{2m}{\hbar^2} \left(\frac{\hbar^2}{2m^2g}\right)^{2/3}. \quad (2.75)$$

We have used the same symbol for the wave function although it is a different function of  $u$  than of  $x$ . The quantization is imposed by the boundary condition  $\psi(0) = 0$ . Note that the scaled energy is dimensionless like the scaled coordinate. If the zero of the scaled coordinate  $u$  is shifted by  $\varepsilon$ ,  $v \equiv u - \varepsilon$ , the equation reads

$$\frac{d^2\psi}{dv^2} - v\psi = 0, \quad (2.76)$$

with the condition that  $\psi(-\varepsilon) = 0$ . The differential equation is second order and thus has two solutions. These are known as the Airy functions  $Ai$  and  $Bi$ . Only  $Ai$  has relevant solutions here (decreasing for sufficiently large positive values of  $v$ ). The zeroes are given asymptotically by  $(3\pi(4n-1)/8)^{2/3} \approx (3\pi/2)^{2/3}n^{2/3}$ , with corrections on the order  $1/n$ . The energies for large quantum numbers are then

$$E_n = \varepsilon \frac{\hbar^2}{2m} \left(\frac{2m^2g}{\hbar^2}\right)^{2/3} \approx \left(\frac{3\pi}{2}\right)^{2/3} n^{2/3} \frac{\hbar^2}{2m} \left(\frac{2m^2g}{\hbar^2}\right)^{2/3}. \quad (2.77)$$

With the shorthand  $E_n = c'n^{2/3}$  the level density is

$$\rho(E) = \frac{1}{\frac{dE_n}{dn}} = \frac{3n^{1/3}}{2c'} = \frac{3}{2}c'^{-3/2}E^{1/2}. \quad (2.78)$$

Reintroducing  $c'$  gives

$$\rho(E) = \frac{(8E)^{1/2}}{ghm^{1/2}}, \quad (2.79)$$

*i.e.* identical to the above result.

## 2.8 Exercises

**2.1** Calculate and plot the thermal excitation energy for a harmonic oscillator in the high temperature limit. Use the Euler-Maclaurin formula given in Appendix C to calculate the four highest powers of  $T$  in the expansion. Compare with the exact solution.

**2.2** Consider the phase space of an  $N$  atom particle of which all vibrational degrees of freedom are excited with quantum numbers so that they can be considered classical. An isolated particle will not sample the whole phase space, because conservation laws restrict the motion. What is the dimension of the subspace on which the particle moves, when all these conservation laws are taken into account?

**2.3** Find the scaling that leads from Eq. (2.73) to Eq. (2.75). It is not enough to verify that the solution give is correct.

**2.4** Which way does the oscillator move in Fig. 2.3.

**2.5** Calculate the volume of phase space in units of  $h$  of a gold atom in a  $1\text{ cm}^3$  container with kinetic energy between 0.1 and 1 eV.

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