Problem 1.   Classical distribution of a harmonic oscillator

Consider a classical harmonic oscillator in one dimension interacting with a thermal environment. This could be for example a single atom attached to a large molecule in a gas.

The potential energy is $U = \frac{1}{2}kx^2$. At some point in physics we stop using the spring constant k (for some unknown reason) and start expressing k in terms of the oscillation frequency $\omega_0 = \sqrt{k/m}$. Thus, I will (usually) write the potential as

$$U = \frac{1}{2}m\omega_0^2 x^2 \tag{1}$$

The energy is the kinetic and potential energies and the Hamiltonian[1] is

$$H(x,p) = \frac{p^2}{2m} + \frac{1}{2}m\omega_0^2 x^2 \tag{2}$$

The oscillator is in equilibrium with an environment at temperature T.

(a) What is the normalized probability density $P(x,p)$ to find the harmonic oscillator with position between x and $x+\mathrm{d}x$ and momentum between p and $p+\mathrm{d}p$, i.e. the probability per phase space volume $\mathrm{d}x\,\mathrm{d}p$:

$$\mathrm{d}\mathscr{P} = P(x,p)\,\mathrm{d}x\,\mathrm{d}p \tag{3}$$

Your final result for $P(x,p)$ should be a function of ω_0, p, x, m and $k_B T$. You can check your result by doing part (b). Check that your result for $P(x,p)$ is dimensionally correct.

Hint: Change variables to $u_1 = x/\sigma_x$ and $u_2 = p/\sigma_p$ before doing any integrals. You need to look at the integrand (like the exponent) and decide what the appropriate length scale, σ_x, and momentum scale, σ_p, are.

(b) Compute the $\langle x^2 \rangle$ and $\langle p^2 \rangle$ by integrating over the probability distribution. (Don't do dimensionful integrals.)

You should find $\langle x^2 \rangle = k_B T/m\omega_0^2$ and $\langle p^2 \rangle = mk_B T$.

(c) The equipartition theorem precisely says that, for a classical system, the average of each quadratic form in the Hamiltonian is $\frac{1}{2}k_B T$. The quadratic forms here are the kinetic energy $p^2/2m$, and the potential energy, $m\omega_0^2 x^2/2$. Are your results of the part (b) consistent with the equipartition theorem. What is the average total energy of the oscillator and the number of "degrees of freedom" of the oscillator?

(d) (i) For one mole of an ideal diatomic molecule H_2 (treated in a classical approximation), what are the total number of degrees of freedom (in the sense of the equi-partition theorem), if translations, rotations, *and* now vibrations are included and treated classically? (ii) What is the energy of the gas? Express your result in terms of R and T. (iii) What is C_V/R and C_p/R for this one mole of substance. Is your result consistent with the experimental data shown below? Explain.

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[1] The Hamiltonian is the energy *as a function of* x and p.

c_p/R vs Temperature, K
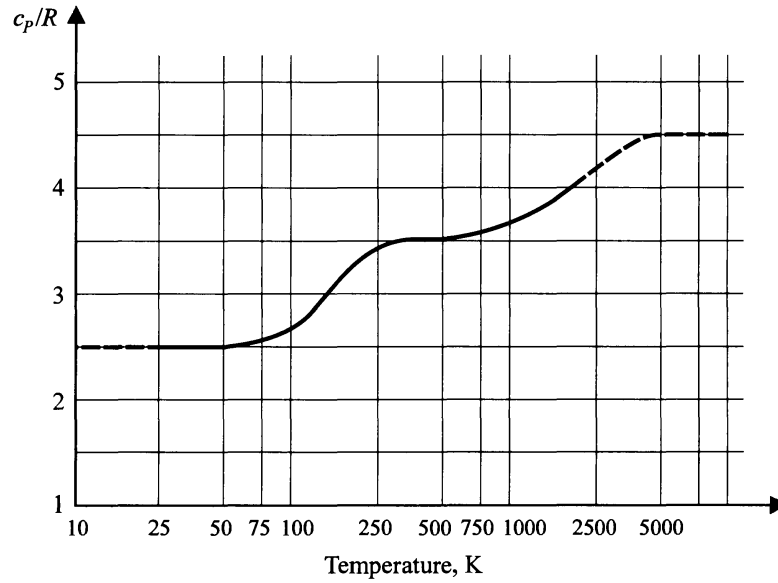
Problem 2.   (Optional) Volume of Phase Space: Part II

The purpose is here to get started, talking about the accessible phase space volume. The phase space volume is a measure of the total number of possible ways for N of particles to *share* (or to partition) the total energy. For instance one particle could have almost all the available energy and the remaining $N-1$ could have very little. Those possible configurations of the particles occupy only a small portion of the available phase space volume.

(a) Take two non-interacting particles in three dimensions sharing (or partitioning) the available energy which lies between E and $E + \delta E$

$$E < \frac{p_{x1}^2}{2m} + \frac{p_{y1}^2}{2m} + \frac{p_{z1}^2}{2m} + \frac{p_{x2}^2}{2m} + \frac{p_{y2}^2}{2m} + \frac{p_{z2}^2}{2m} < E + \delta E \tag{4}$$

The two particles can be anywhere in phase space, but the total energy must lie in this range. The coordinates are in a box $0 < x, y, z < L$. Show that the total phase space volume which is available to be shared amongst the six degrees of freedom $p_{x1}, p_{y1}, p_{z1}, p_{x2}, p_{y2}, p_{z2}$ is

$$V_{\text{ps}} = \int_E^{E+\delta E} \mathrm{d}^3\boldsymbol{r}_1 \mathrm{d}^3\boldsymbol{p}_1 \, \mathrm{d}^3\boldsymbol{r}_2 \mathrm{d}^3\boldsymbol{p}_2 = V^2(2mE)^3 \, \pi^3 \frac{\delta E}{2E} \tag{5}$$

It is helpful to realize that the area of a sphere in six dimensions is given by a general formula

$$A_d = \frac{2\pi^{d/2}}{\Gamma(d/2)} r^{d-1} \tag{6}$$

So far we have been talking about phase space volume. Now we show how to translate the phase space volume into "the number of ways to share energy E", or in other words, the number of accessible configurations with energy between E and $E + \delta E$.

Lets go back to one particle in three dimensions which you worked out last week. Consider (again) a single particle in three dimensions in a box

$$0 < x, y, z < L \tag{7}$$

The three momenta components are sharing (or partitioning) the total energy which lies between E and $E + \delta E$, i.e.

$$E < \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m} < E + \delta E \,, \tag{8}$$

The particle is free to move around in phase space but the energy must lie in this range. To count the number of configurations, divide up the phase space volume into cells of (arbitrary) small size $h_0 = \Delta x \Delta p_x$, or in three dimensions cells of size[2]

$$h_0^3 = (\Delta x \Delta y \Delta z)(\Delta p_x \Delta p_y \Delta p_z) \tag{9}$$

The "number of ways" for p_x, p_y, p_z and to share (or partition) the available energy is denoted by $\Omega(E)$ and it is phase space volume divided by the cell size

$$\Omega(E) = \frac{1}{h_0^3} \int_E^{E+\delta E} \mathrm{d}^3\boldsymbol{r} \mathrm{d}^3\boldsymbol{p} \tag{10}$$

$$= V \left(\frac{2mE}{h_0^2}\right)^{3/2} 4\pi \frac{\delta E}{2E} \tag{11}$$

$\Omega(E)$ is the number of accessible configurations for a single particle with energy between E and $E + \delta E$. The

The number of accessible configurations for two particles sharing energy between E and $E + \delta E$ is

$$\Omega(E) = \frac{1}{2!} \int_E^{E+\delta E} \frac{\mathrm{d}^3\boldsymbol{r}_1 \mathrm{d}^3\boldsymbol{p}_1}{h_0^3} \frac{\mathrm{d}^3\boldsymbol{r}_2 \mathrm{d}^3\boldsymbol{p}_2}{h_0^3} \tag{12}$$

$$= V^2 \left(\frac{2\pi E}{h_0^2}\right)^3 \pi^3 \frac{\delta E}{4E} \tag{13}$$

The 2! is inserted because if I simply exchange what I call particle 1 and particle 2, that is not to be considered a new configuration.

(b) For two particles in one dimension what is the total number of accessible configurations $\Omega(E)$ with energy in range $[E, E + \delta E]$? This is visualized in Fig. 1.

(c) Show that the total number of ways for N particles to share the energy E (i.e. total number of accessible configurations with energy E and $E + \delta E$) is

$$\Omega(E) = \frac{1}{N!} \int \frac{\mathrm{d}^3\boldsymbol{r}_1 \mathrm{d}^3\boldsymbol{p}_1}{h_0^3} \cdots \frac{\mathrm{d}^3\boldsymbol{r}_N \mathrm{d}^3\boldsymbol{p}_N}{h_0^3} = \frac{1}{N!} V^N \left(\frac{2\pi mE}{h_0^2}\right)^{3N/2} \frac{1}{\Gamma(3N/2)} \frac{\delta E}{E} \tag{14}$$

N here is like Avogadro's number large. (Just try and imagine how it depends on energy, e.g. what does the graph of x^{10} look like. Now what does $x^{10^{23}}$ look like.)

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[2]Classically this cell size was arbitrary. With the advent of quantum mechanics, it was realized that a natural choice for the cell size is the Plank constant h. But here lets understand it from a classical perspective first, choosing the cell size to be h_0. We will drop the "0" eventually.
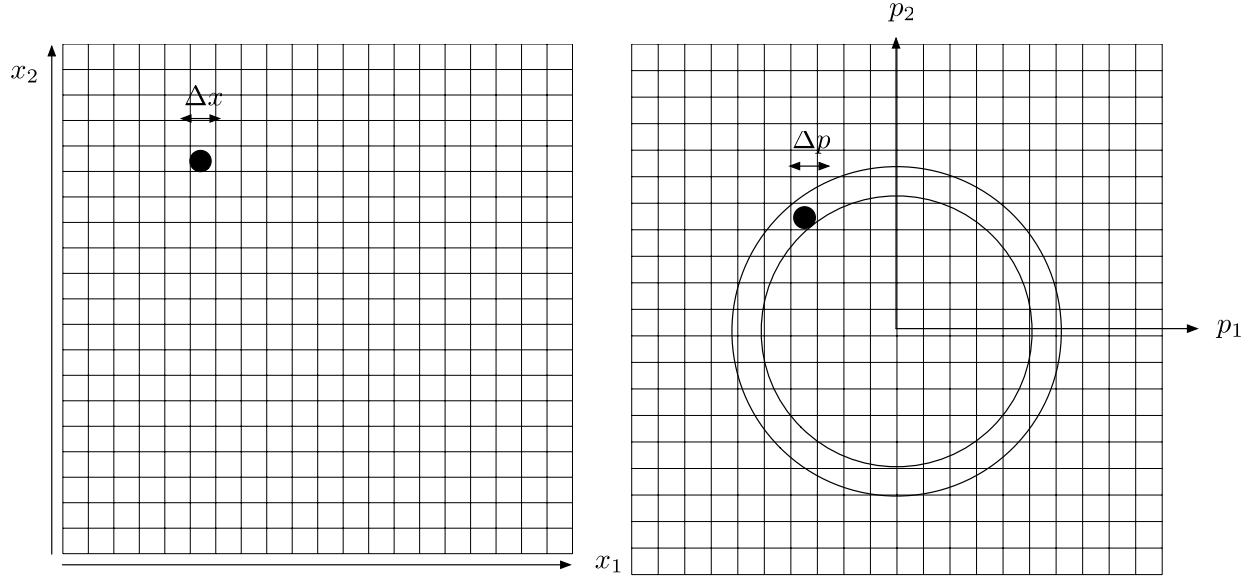
Figure 1: The available phase space for two particles in one dimension. The black points shows one possible configuration for (x_1, p_1, x_2, p_2). The accessible phase space lies in a four dimensional space. One black point can be placed anywhere in the x_1, x_2 plane, and one black point can be placed in the grid somewhere in the shell in the p_1, p_2 plane, so that $2mE < p_1^2 + p_2^2 < 2m(E + \delta E)$. The cell size is $h_0 = \Delta x \Delta p$. The number of possible configurations is $\frac{1}{2! h_0^2} \int dx_1 dp_1 dx_2 dp_2$. For an Avogadro's number of particles in three dimensions, the space of accessible configurations is a $6N_A$ dimensional space.

(d) Use the Stirling approximation to show that

$$\Omega(E) = e^{5N/2} \left(\frac{V}{N}\right)^N \left(\frac{4\pi m}{3h_0^2}\frac{E}{N}\right)^{3N/2} \frac{\delta E}{E} \propto V^N E^{3N/2} \tag{15}$$

The thing to appreciate is how rapidly this function depends on V and E.

Hint: for large n

$$\Gamma(n) \equiv (n-1)! \simeq n! \tag{16}$$

Note the Stirling approximation works for n not integer, if $n!$ is understood as $\Gamma(n+1)$.

Problem 3. Partition function of two state system

Consider a quantum mechanical system with energy levels E_n with $n = 1, 2, \ldots n$. Recall the definition of the partition function from last weeks homework

$$Z = \sum_n e^{-\beta E_n}$$

Z is a the normalization constant so that

$$P_n = \frac{1}{Z} e^{-\beta E_n} \tag{17}$$

is normalized

$$\sum_n P_n = 1 \tag{18}$$

(a) Show that the mean energy can be easily found if you know $Z(\beta)$ via the formula:

$$\langle E \rangle = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{\partial}{\partial \beta}\log Z(\beta) \tag{19}$$

(b) Consider the two state system discussed two homeworks ago – Homework 3 problem 1. Compute the partition function, and then compute the mean energy using the formula from (a). Check that your result agrees with Homework 3's result.

Problem 4. (Optional) Derivatives and Chain Rule

Manipulating derivatives is an unfortunate fact of life.

(a) Let $w = xy$ and $x = yz$. Compute

$$\left(\frac{\partial w}{\partial x}\right)_y \quad \text{and} \quad \left(\frac{\partial w}{\partial x}\right)_z \tag{20}$$

They are not equal.

(b) (Optional) Read and understand appendix C.6 in the book. We parametrized the equation of state by the volume as a function of temperature and pressure, $V = V(T, p)$

$$\mathrm{d}V = \left(\frac{\partial V}{\partial T}\right)_p \mathrm{d}T + \left(\frac{\partial V}{\partial p}\right)_T \mathrm{d}p \tag{21}$$

or with the definitions of β_p and κ_T given in class

$$\mathrm{d}V = V \ (\beta_p \mathrm{d}T - \kappa_T \mathrm{d}p) \tag{22}$$

We could have, equivalently, parametrized the equation of state by the pressure as a function of temperature and volume, $p = p(T, V)$

$$\mathrm{d}p = \left(\frac{\partial p}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial p}{\partial V}\right)_T \mathrm{d}V \tag{23}$$

Show that

$$\mathrm{d}p = \frac{\beta}{\kappa} dT - \frac{1}{\kappa} dV \tag{24}$$

This amounts to showing that[3]

$$\left(\frac{\partial p}{\partial V}\right)_T = \frac{1}{\left(\frac{\partial V}{\partial p}\right)_T} \tag{25}$$

$$\left(\frac{\partial p}{\partial T}\right)_V = -\frac{\left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial V}{\partial p}\right)_T} \tag{26}$$

Problem 5.   Parametrizing the EOS

The pressure as a function of temperature an volume, $p(T, V)$, or equivalently the volume as a function of temperature and pressure $V(T, p)$, is an important physical observable. Recall that its changes are parameterized by the measurables β_p and κ_T

(a) (Optional) The expansion coefficient of mercury is $\beta_p = 1.81 \times 10^{-4} K^{-1}$. Get a mercury thermometer, estimate the size of the bulb at the bottom, and then estimate what the inside diameter of the tube has to be in order for the thermometer to work as required. Assume that the thermal expansion of the glass is negligible.

Take an ideal gas

(b) Compute the expansion coefficient β_p.

(c) Compute the isothermal compressibility κ_T

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[3]Show means show. It is not enough to quote the answer from appendix C. You can translate the proof from appendix C to the current context.

(d) The first items only involved the EOS, $p(T, V)$. The next item also involves the energetics, so the specific heat and adiabatic index play a role. Take a constant specific heat C_V and adiabatic index γ, so $U = C_V T$. The *adiabatic* compressibility κ_S is the defined by[4]

$$\kappa_S \equiv \frac{-1}{V}\left(\frac{\partial V}{\partial p}\right)_{adiab} \tag{28}$$

This "*adiab*" means that as we change pressure by dP, the temperature also changes, so that no heat flows, $đQ = 0$. Show that

$$\kappa_S = \frac{\kappa_T}{\gamma} \tag{29}$$

Hint: You will need to relate dT and dp using the fact that $đQ = 0$.

(e) As discussed in class, the speed of sound is related to the compressibility[5]

$$c_s^2 = \sqrt{\frac{B_S}{\rho}} \tag{30}$$

where the bulk modulus

$$B_S \equiv -V\left(\frac{\partial p}{\partial V}\right)_{adiab} \equiv \frac{1}{\kappa_S} \tag{31}$$

serves as a kind of spring constant for the material, and ρ is the mass per volume. Air is made of diatomic molecules, primarily (78%) diatomic nitrogen N_2. Determine the speed of sound of N_2 gas at $20^o C$ treating using only the ideal gas constant R and the fact that a nitrogen atom consists of 7 protons and 7 neutrons. Compare with the nominal value for the speed of sound in air of $330\,\mathrm{m/s}$.

(f) The frequency of the tuning note ($A440$) in the orchestra is 440 Hz. Explain qualitatively why it is the adiabatic compressibility κ_S, and not the isothermal one κ_T which is relevant for the speed of sound, by comparing the time scales of oscillation with a typical time scale for heat conduction.

Problem 6.   Otto Cycle

The Otto cycle is shown in Fig. 2 and was discussed in class.

(a) Show that the efficiency of the Otto cycle is $1 - 1/r^{\gamma-1}$ where $r = V_1/V_2$ is the compression ratio.

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[4]The suffix S means adiabatic, $đQ = 0$. We will see that $đQ$ is related to the change in entropy S, $dS = đQ/T$. So S suffix means at fixed entropy.

$$\kappa_S \equiv \frac{-1}{V}\left(\frac{\partial V}{\partial p}\right)_S \equiv \frac{-1}{V}\left(\frac{\partial V}{\partial p}\right)_{adiab} \tag{27}$$

[5]I will not derive this. A good derivation at your level is given here. Unfortunately, this derivation uses the symbol κ for B_S, which for us (and indeed almost everyone) is $1/\kappa_S$!
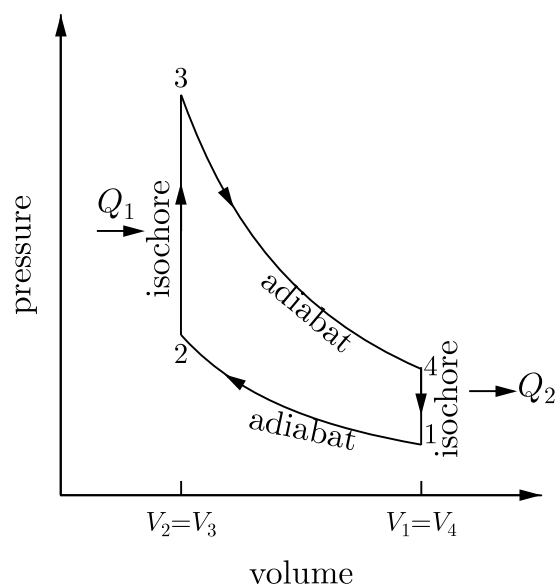
Fig. 13.12 The Otto cycle. (An isochore is a line of constant volume.)

Figure 2: Otto cycle

(b) For definiteness take a volume of $2.5\,\mathrm{L}$ for the volume of the four cylinders. The gas is air which is sucked in at position one, at room temperature 300^oK and standard pressure of 1 bar. Determine the number of moles of air in the cylinders .

(c) For definiteness take a diatomic gas, and a compression ration of 8. The heat injected by burning gasoline during the ignition is $22000\,\mathrm{J}$ per mole of air. Find the temperature and pressure at points 1,2,3,4.

	T	P (in bar)
1	300 K	1 bar
2		
3		
4		

(d) For each of the four stages, 12, 23, 34, 41, find the W, Q, ΔU

	W	Q	U
12			
23			
34			
41			

8

(e) If the car operates at a maximum of 6000 rpm, what is the maximum horsepower of the engine? Note it takes two turns to complete the cycle. I find that the result of this idealized computation is low compared to a nominal engine power of $\sim 200\,\mathrm{hp}$.