

## Problem 1. Parametrizing the EOS

The pressure as a function of temperature and 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  $\beta_p$  and  $\kappa_T$ . Consider an ideal gas at temperature  $T$  with  $N$  particles

- (a) Explain the physical meaning of the thermal expansion coefficient  $\beta_p$  and isothermal compressibility  $\kappa_T$ , and compute them for an ideal gas.

The first items only involved the EOS,  $p(T, V)$ . The next items also involve the energetics, so the specific heat and adiabatic index play a role. Assume that  $U = c_0 T$  with  $c_0$  a constant

- (b) Write down  $c_0$  for a mono-atomic ideal gas and a diatomic ideal gas?
- (c) Write down the specific heats  $C_p$  and  $C_v$  for a mono-atomic and diatomic gas and determine the adiabatic index  $\gamma$ .
- (d) In class we said that for a general substance (and not necessarily an ideal gas) the specific heats  $C_p$  and  $C_V$  are related by a formula which we will prove in full generality only later:

$$C_p = C_V + \frac{VT\beta_p^2}{\kappa_T}. \quad (1)$$

For an ideal gas we proved the following special case of this formula:

$$C_p = C_V + Nk_B. \quad (2)$$

Or, for one mole of substance

$$C_p^{1\text{ml}} = C_V^{1\text{ml}} + R. \quad (3)$$

Show that Eq. (3) follows from Eq. (1) together with the results from parts (a).

- (e) The *adiabatic* compressibility  $\kappa_S$  is defined by<sup>1</sup>

$$\kappa_S \equiv \frac{-1}{V} \left( \frac{\partial V}{\partial p} \right)_{\text{adiab}} \quad (5)$$

This “*adiab*” means that as we change the pressure, the volume and temperature change, so that no heat flows,  $dQ = 0$ . Show for an ideal gas that

$$\kappa_S = \frac{\kappa_T}{\gamma} \quad (6)$$

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<sup>1</sup>The suffix  $S$  means adiabatic,  $dQ = 0$ . We will see that  $dQ$  is related to the change in entropy  $S$ ,  $dS = dQ/T$ . So  $S$  suffix means at fixed entropy.

$$\kappa_S \equiv \frac{-1}{V} \left( \frac{\partial V}{\partial p} \right)_S \equiv \frac{-1}{V} \left( \frac{\partial V}{\partial p} \right)_{\text{adiab}} \quad (4)$$

We will show later that this result is not limited to an ideal gas.

*Hint:* You will need to recall that in an adiabatic change of pressure and volume, we have  $pV^\gamma = \text{const}$  for an ideal gas.

- (f) As discussed in class, the speed of sound is related to the compressibility<sup>2</sup>

$$c_s = \sqrt{\frac{B_S}{\rho}} \quad (7)$$

where the bulk modulus

$$B_S \equiv -V \left( \frac{\partial p}{\partial V} \right)_{adiab} \equiv \frac{1}{\kappa_S} \quad (8)$$

serves as a kind of spring constant for the material, and  $\rho$  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  $20^\circ C$  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. You should find favorable agreement.

- (g) The frequency of the tuning note (A440) in the orchestra is 440 Hz. Explain qualitatively why it is the adiabatic compressibility  $\kappa_S$ , and not the isothermal one  $\kappa_T$  which is relevant for the speed of sound, by comparing the time scales of oscillation with a typical time scale for heat conduction. Consider the following questions. When you turn on the heat on a frying pan, how long does it take to get hot? Why are the best frying pans made of cast iron? Is iron a better heat conductor than air?

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<sup>2</sup>I will not derive this. A good derivation at your level is given [here](#). Unfortunately, this derivation uses the symbol  $\kappa$  for  $B_S$ , which for us (and indeed almost everyone) is  $1/\kappa_S$ !

## Problem 2. Energy In Combustion

**Note:** This is one of the few places where one needs to work rather precisely to see the physics point. My rule of thumb is that an Avagadros number times an electron volt is 100 kJ. But, here should use a more accurate evaluation,  $N_A \cdot \text{eV} = 96.5 \text{ eV}$ . In evaluating the numbers below you should keep to an accuracy of one part in a thousand,  $R = 8.314 \text{ J/K}\cdot\text{mol}$ .

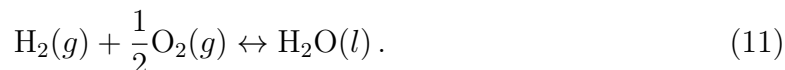
- (a) (Optional) Repeat the argument presented in class for the equation

$$dH = \delta Q_{\text{in}} + V dp \quad (9)$$

where  $H = U + pV$  represents the enthalpy. Enthalpy is particularly useful when the pressure is constant, leading to

$$dH = \delta Q_{\text{in}} \quad (10)$$

- (b) Consider the combustion of Hydrogen gas:



resulting in the formation of liquid water vapor. Tables of enthalpies for reactions are available in many books.

- (i) Look up the enthalpy of the products and reactants at 298 °K and standard pressure<sup>3</sup> in the accompanying data table. Determine the change in enthalpy,  $\Delta H^\circ$ , for each mole of  $\text{H}_2\text{O}$  produced.
  - (ii) Consider the reactants as ideal gasses, and treat the liquid product  $\text{H}_2\text{O}$  as having negligible volume compared to the gasses. Calculate the heat released during the combustion and the change in internal energy,  $\Delta U^\circ = U_{\text{final}} - U_{\text{initial}}$ , per mole. (Ans:  $\Delta U = -282.1 \text{ kJ}$ )
- (c) Consider the reaction at



at NTP, which is accompanied by a large release of heat. Using the enthalpy data tables, determine the energy of a bond between the two atoms in a  $\text{H}_2$  molecule in eV. (Ans:  $\Delta U = -433.5 \text{ kJ}$  and  $\Delta = 4.48 \text{ eV}$ .)

*Hint:* First use the enthalpy data tables to determine the enthalpy change and heat released during the reaction. Use this to find  $\Delta U$  for the reaction, treating all components as ideal gasses. The energy of a single  $\text{H}_2$  molecule is its kinetic energy (translational and rotational) and its potential (or binding) energies:

$$E_{\text{H}_2} = \text{KE} + \text{PE} = \text{KE} - \Delta \quad (13)$$

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<sup>3</sup>This temperature and pressure is the so-called Normal Temperature and Pressure (NTP) and denoted with a circle, i.e.  $T^\circ$ ,  $p^\circ$  and  $H^\circ$  denote the temperature, pressure, and enthalpy at NTP.

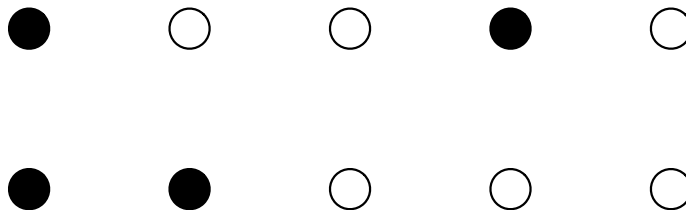
Here  $\text{PE} = -\Delta$  is the binding energy (i.e. the bond energy) of the two atoms. (The negative sign indicates that the energy is lower when the two atoms are bound compared to when they are unbound.  $\Delta$  is a positive value and is what we are trying to find.) The total energy  $U$  is the sum of kinetic and potential energies of the atoms. Use what we know about the kinetic energy of ideal gasses (both the mono-atomic and diatomic cases) to relate  $\Delta U$  for one mol of  $\text{H}_2$  produced to  $\Delta$ .

### Problem 3. Combinatorics and The Stirling Approximation

- (a) Consider a chain of one mole of atoms, laid out in a row. The atoms can be in two states, a ground state, and an excited state.  $1/3$  of them are in the excited states. Using the Stirling approximation, show that the number of configurations with this number of excited states is approximately

$$\Omega = 10^{1.67 \times 10^{23}} \quad (14)$$

For instance, if the number of atoms is five, and the number of excited atoms (shown by the black circles) is 2, then two possible configurations are shown below.



- (b) Now repeat the calculation, but work with symbols rather than numbers. Assume there are  $N$  atoms laid out in a row. Assume that  $N_1$  of them are in the ground state, and  $N_2$  are in the excited state, with  $N_1 + N_2 = N$ . Show that the log of the number of configurations is

$$\ln \Omega = - \sum_{i=1,2} N_i \ln(N_i/N) \quad (15)$$

$$= N \sum_{i=1,2} -P_i \ln P_i \quad (16)$$

In the last step we have recognized that the  $P_1 = N_1/N$  is the probability that an atom will be in the ground state, and  $P_2 = N_2/N$  is the probability that an atom will be in the excited state.

**Discussion:** The log of the number of configurations  $\ln \Omega$  is known as the entropy of the system<sup>4</sup>. Then entropy per site, i.e.  $\ln \Omega/N$ , is given by

$$\frac{\ln \Omega}{N} = \sum_i -P_i \ln P_i \quad (17)$$

which is known as the Shannon formula for the entropy of a probability distribution. The importance of these things will become clearer as the course progresses.

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<sup>4</sup>Actually  $\ln \Omega$  is the entropy up to a conventional constant. For historical reasons the entropy is defined as  $k_B \ln \Omega$ , with  $k_B$  the Boltzmann constant. Similarly the entropy per site is defined only up to a conventional constant and later in the course we will respect tradition and take  $-k_B \sum_i P_i \ln P_i$  as the entropy per site.

## Problem 4. Central Limit Theorem and Random Walk

In a random walk, a collegiate drunkard starts at the origin and takes a step of size  $a$ , to the right with probability  $p$  and to the left with probability  $1 - p$ .

- Take  $p = 1/2$ , i.e. equal probability of right and left steps. Determine the probability of the drunkard having position  $X$ , i.e.  $P(X)$ , after three steps. Plot  $P(X)$  where  $X$  can be one of  $X/a = 0, \pm 1, \pm 2, \pm 3$ . Note how your graph begins to approach a Gaussian after just three steps<sup>5</sup>
- Now keep  $p$  general. What is the mean and variance variance in the drunkard's position  $X$  after one step, and after two steps? You can check your reasoning by doing the next part.
- After  $n$  steps (with  $n \gg 1$ ) find his mean position  $\langle X \rangle$ , and the std. deviation in his position  $\sigma_X = \sqrt{\langle \delta X^2 \rangle}$ . Check your result by comparing with the figure below

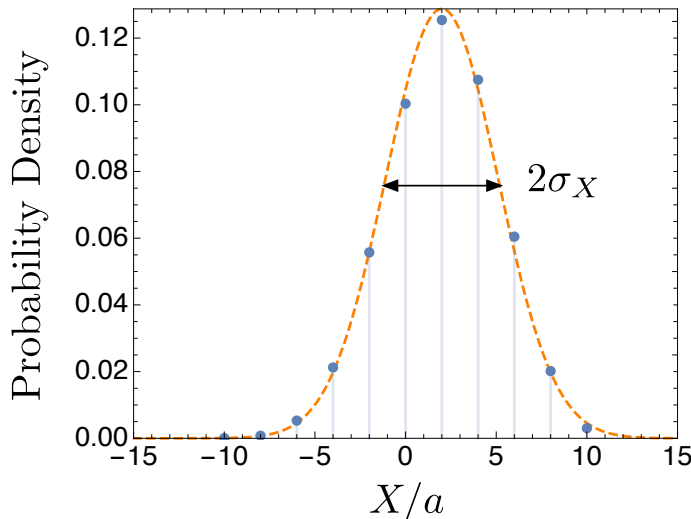


Figure 1: Probability of our drunkard having position  $X$  after  $n = 10$  steps (the blue points). Of course after 10 steps the drunkard will be between  $-10 \dots 10$ , and it is easy to show that he will be only at the even sites, i.e.  $-10, -8, -6, \dots 10$ . For  $p = 0.6$ , I find  $\langle X \rangle = 2.0$ . Twice the std deviation,  $2\sigma_X$ , is shown in the figure and is about six in this case. The orange curve is a gaussian (a.k.a the “bell-shaped” curve) approximation discussed in class and approximately agrees with the points – this is the central limit theorem. Recall that the central limit theorem says that if the number of steps  $n$  is large, the probability of  $X$  (a sum of  $n$  independent events) is approximately  $P(x) dX \propto \exp(-(X - \langle X \rangle)^2 / 2\sigma_X^2)$ . Evidently the gaussian approximation works well already for  $n = 10$ .

Hint:  $X$  is a sum  $N$  independent events  $x_i$  where  $x_i = \pm a$ . Use results from class on the probability distribution of a *sum* of independent events.

<sup>5</sup>The graph should be symmetric. You should find  $P_0 = 0$ ,  $P_{\pm 1} = \frac{3}{8}$ ,  $P_{\pm 2} = 0$ ,  $P_{\pm 3} = \frac{1}{8}$ . Your graph should look something like the figure below but symmetric around the origin.

## Problem 5. A reminder on Jacobians

Recall that if I have a probability distribution

$$d\mathcal{P}_x = P(x)dx, \quad (18)$$

and I want to change variables to a new variable  $u(x)$ , then the probability distribution for  $u$  is

$$d\mathcal{P}_u = P(x(u)) \left| \frac{dx}{du} \right| du. \quad (19)$$

So the probability densities are related by

$$P(u) = P(x(u)) \left| \frac{dx}{du} \right|. \quad (20)$$

We will have many physical examples of this in homework, e.g. the probability of a particle having a given velocity vs. the probability of a particle having a given energy.

The change of variables generalizes to two and higher dimensions. Suppose we have a probability density in  $x, y$  describing a particle's position:

$$d\mathcal{P}_{x,y} = P(x, y) dx dy. \quad (21)$$

For definiteness consider the gaussian

$$d\mathcal{P}_{x,y} = \frac{1}{2\pi\sigma^2} \exp\left(-\frac{x^2}{2\sigma^2} - \frac{y^2}{2\sigma^2}\right) dx dy, \quad (22)$$

shown in Fig. 2. It seems more natural here to use polar coordinates, defining  $x = r \cos \theta$  and  $y = r \sin \theta$  with  $r \in [0, \infty]$  and  $\theta \in [0, 2\pi]$  shown in the figure.

In analogy with the 1D case, for a change of variables  $x(r, \theta)$  and  $y(r, \theta)$ , the probability of finding a particle with radius between  $r$  and  $r + dr$  and angle  $\theta$  between  $\theta$  and  $\theta + d\theta$  is

$$d\mathcal{P}_{r,\theta} = P(x(r, \theta), y(r, \theta)) \left\| \frac{\partial(x, y)}{\partial(r, \theta)} \right\| dr d\theta. \quad (23)$$

The double bars mean determinant and then absolute value of the Jacobian matrix, which is defined as a matrix with all the possible derivatives of the map  $(r, \theta) \rightarrow (x, y)$ :<sup>6</sup>

$$\frac{\partial(x, y)}{\partial(r, \theta)} \equiv \begin{pmatrix} \frac{\partial x}{\partial r} & \frac{\partial x}{\partial \theta} \\ \frac{\partial y}{\partial r} & \frac{\partial y}{\partial \theta} \end{pmatrix}. \quad (24)$$

So the densities are related by

$$P(r, \theta) = P(x, y) \left\| \frac{\partial(x, y)}{\partial(r, \theta)} \right\|, \quad (25)$$

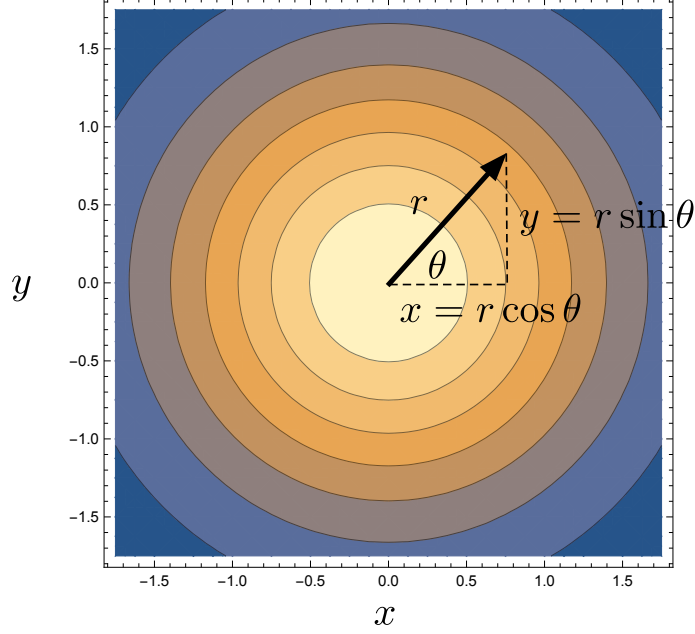


Figure 2: A probability distribution which has no dependence on  $\theta$ .

where it is understood that  $x = r \cos \theta$  and  $y = r \sin \theta$ .

We say that the “volume elements” are related by the Jacobian determinant:

$$dx dy = \left\| \frac{\partial(x, y)}{\partial(r, \theta)} \right\| dr d\theta = r dr d\theta, \quad (26)$$

where it is understood that these expressions are meant to be integrated over.

- (a) Compute the Jacobian matrix and find its determinant. Explicitly determine  $d\mathcal{P}_{r,\theta} = P(r, \theta) dr d\theta$  for the probability distribution in Eq. (22). By marginalizing over (aka integrating over) the unobserved coordinate, determine  $d\mathcal{P}_r = P(r) dr$  and  $d\mathcal{P}_\theta = P(\theta) d\theta$ , that is to say the probability distribution for  $r$  (without regards to  $\theta$ ) and the probability distribution for  $\theta$  (without regards to  $r$ ) ?
- (b) Let’s understand the Jacobian. The columns of the Jacobian form vectors

$$\mathbf{e}_r \equiv \frac{\partial x}{\partial r} \hat{\mathbf{i}} + \frac{\partial y}{\partial r} \hat{\mathbf{j}} = \frac{\partial \mathbf{R}}{\partial r}, \quad (27)$$

$$\mathbf{e}_\theta \equiv \frac{\partial x}{\partial \theta} \hat{\mathbf{i}} + \frac{\partial y}{\partial \theta} \hat{\mathbf{j}} = \frac{\partial \mathbf{R}}{\partial \theta}, \quad (28)$$

where  $\mathbf{R} = x\hat{\mathbf{i}} + y\hat{\mathbf{j}}$  is the position vector of the particle. The determinant of two vectors is the area of the parallelogram spanned by the two vectors<sup>7</sup>. Compute the

<sup>6</sup>Sometimes people use  $\partial(x, y)/\partial(v, \theta)$  to mean the determinant of the Jacobian matrix, rather than just the matrix itself. Our book uses this notation, as is described in appendix C.

<sup>7</sup>See for instance [The Kahn video](#).



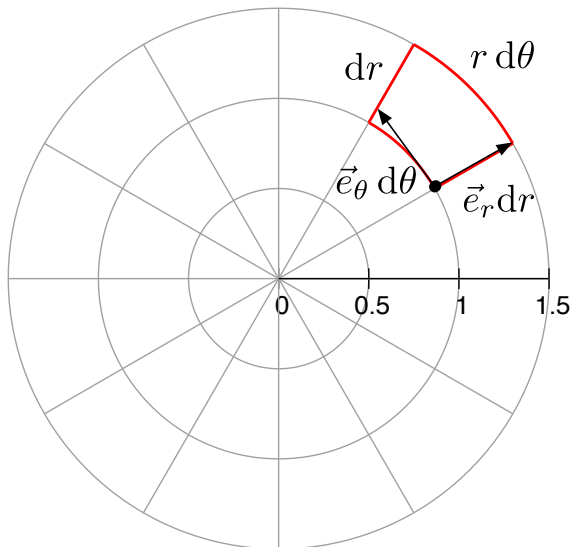


Figure 3: Cylindrical coordinates in two dimensions.

vectors<sup>8</sup>  $\mathbf{e}_r dr$  and  $\mathbf{e}_\theta d\theta$ , and the norms of these vectors  $|\mathbf{e}_r dr|$  and  $|\mathbf{e}_\theta d\theta|$  and show that the vectors are orthogonal in this case. In a sentence or two, use the word “displacement” to explain the physical meaning of the vectors  $\mathbf{e}_r dr$  and  $\mathbf{e}_\theta d\theta$  and their lengths by referring to Fig. 3. Note that the volume element is  $|\mathbf{e}_r dr| |\mathbf{e}_\theta d\theta|$  since the vectors are orthogonal.

Consider the probability distribution

$$d\mathcal{P}_{x,y} = \frac{1}{6\pi} e^{(-5x^2 + 2xy - 2y^2)/18} dx dy \quad (29)$$

A contour plot of this probability distribution is shown in Fig. 4(a). Consider the change of variables

$$x = (u + v) \quad (30)$$

$$y = (-u + 2v) \quad (31)$$

The  $u, v$  coordinates are better adapted to the probability distribution and are shown in Fig. 4(a).

(c) Compute the Jacobian of the map and compute the probability distribution

$$d\mathcal{P}_{u,v} = P(u, v) du dv \quad (32)$$

Your result should be qualitatively consistent with the contour plot of the result shown in Fig. 4(b).

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<sup>8</sup>I am asking for the vector  $\mathbf{e}_r$  times an (arbitrary) small increment in radial coordinate  $dr$ . Weighting  $\mathbf{e}_r$  and  $\mathbf{e}_\theta$  by the corresponding coordinate increments  $dr$  and  $d\theta$  gives these vectors a simple geometric meaning in terms of displacements, which I hope you will begin to understand.

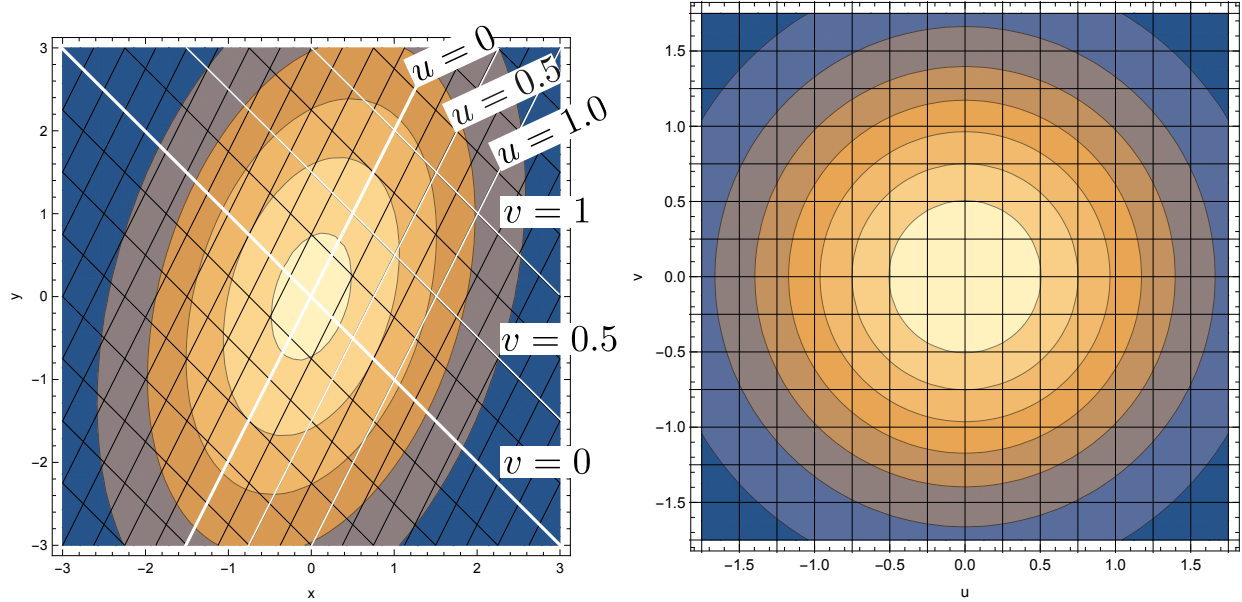


Figure 4: (a) A contour plot of the probability distribution  $P(x, y)$  with lines of constant  $u$  and  $v$  indicated. Specific lines of constant  $u$  and  $v$  are indicated by the white lines. (b) a contour plot  $P(u, v)$  with corresponding lines of constant  $u$  and  $v$ . The distribution becomes circular for this change of variables.

Show that the probability of finding  $u$  in an interval between  $u$  and  $u + du$  is

$$d\mathcal{P}_u = P(u)du \quad \text{with} \quad P(u) = \frac{1}{\sqrt{2\pi}} e^{-\frac{1}{2}u^2}. \quad (33)$$

- (d) Write down the column vectors,  $\mathbf{e}_u$  and  $\mathbf{e}_v$ , of the Jacobian of the map  $(u, v) \mapsto (x, y)$ .

Now interpret these vectors: Sketch a unit coordinate displacement,  $du = 1$  and  $dv = 1$  at the origin of Fig. 4(b) and sketch the displacement vectors  $\mathbf{e}_u du$  for  $du = 1$  and  $\mathbf{e}_v dv$  for  $dv = 1$  at the origin of Fig. 4(a).