

On deriving the Maxwellian velocity distribution

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NOTES AND DISCUSSIONS

Why is the Legendre transformation its own inverse?

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The Legendre transformation is a mathematical concept of great significance to physics. In mechanics and field theory, it provides the transition between Hamiltonian and Lagrangian descriptions, and in thermodynamics it relates the different thermodynamic potentials. Nevertheless, with very few exceptions (notably Ref. 1), the Legendre transformation is introduced in passing and with little emphasis; this leaves the impression of a sleight-of-hand. The feeling that some essential point might be missing from the standard description provided the motivation for the present considerations. In the following, we state the definition of the Legendre transform $G(y)$ of a function $F(x)$ and provide a simple argument for the symmetry between F and G .

Let us assume that the function $F(x)$ is continuously differentiable, with a derivative

$$f(x) \equiv F'(x), \quad (1)$$

that is strictly monotonically increasing. This condition guarantees that the function $f(x)$ has a unique inverse $g(y)$,

$$y = f(x) \iff x = g(y), \quad (2)$$

and the Legendre transform of $F(x)$ is then defined as

$$G(y) \equiv [xy - F(x)]_{x=g(y)}. \quad (3)$$

If we now perform the same operation on $G(y)$ so that

$$z \equiv G'(y) \quad \text{and} \quad H(z) \equiv [yz - G(y)]_{y=h(z)}, \quad (4)$$

where h is the function inverse to G' , a short calculation reveals that $z = x$, $h = f$, and $H = F$, i.e., one has returned to the original function.

This is, of course, perfectly sufficient as a proof of involutivity, but a physicist would prefer a more intuitive explanation, ideally in terms of geometry. The standard geometric interpretation of the Legendre transform proceeds by considering the graph of the convex function $F(x)$ and its tangents. This is a correct pictorial account of Eq. (3) that can be used to give a geometric proof (see, e.g., Ref. 2), but it does not make the symmetry between F, f , and x and G, g , and y manifest. Let us therefore look at the graph of the monotonic function $f(x)$ instead.

We first assume that x and $f(x)$ are positive (see Fig. 1). The same curve can be interpreted as the graph of $g(y)$ with respect to the y -axis. Expressed in a symmetric manner, the curve shows the locus of all pairs (x, y) with $y = f(x)$ or, equivalently, $x = g(y)$. Now consider the rectangle bounded by the coordinate axes and their parallels through such a

point (x, y) . The area of that rectangle is $A = xy$, and the curve cuts this rectangle into two parts with areas \tilde{F} and \tilde{G} . From Fig. 1, it is clear that

$$\tilde{F} = \int_{x_0}^x f(\hat{x}) d\hat{x}, \quad \tilde{G} = \int_{y_0}^y g(\hat{y}) d\hat{y} \quad (5)$$

and

$$\tilde{F} + \tilde{G} = xy \quad (6)$$

with $x_0 = 0$ if the graph intersects the y -axis at $y_0 \geq 0$, and $y_0 = 0$ if the graph intersects the x -axis at $x_0 \geq 0$. Clearly, \tilde{F} is a function of x with $\tilde{F}'(x) = f(x) = F'(x)$, hence

$$F(x) = \tilde{F}(x) + c, \quad G(y) = \tilde{G}(y) - c, \quad (7)$$

for some real constant c . So F is, up to a constant, the area under the graph of f , and G is, up to minus that constant, the area under the graph of g , and the symmetry is manifest.

What if our assumptions $x \geq 0$ and $y \geq 0$ are not satisfied? For $x \leq 0$ and $y \leq 0$, the argument is essentially unmodified because $(-x)(-y) = xy$. But for $xy < 0$, consider Fig. 2. Here, we have fixed two arbitrary constant values x_0, y_0 in such a way that $x_0 > x > 0$ and $y_0 < y < 0$ for the range of pairs (x, y) we want to consider. Denote by A_0 the area determined by the coordinate axes, the vertical line through x_0 , the horizontal line through y_0 , and the curve. We then have

$$A_0 = -xy + \tilde{F} + \tilde{G}, \quad (8)$$

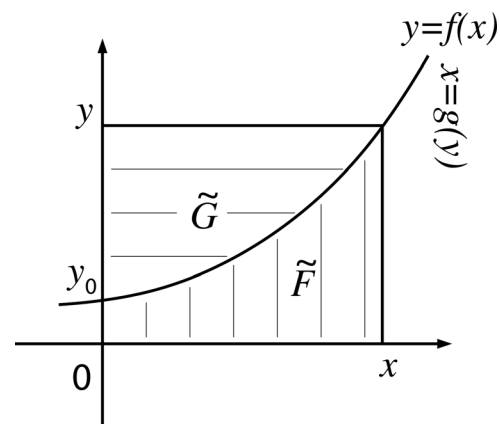


Fig. 1. The graph of $y = f(x)$ for the case $x > 0$ and $y > 0$.

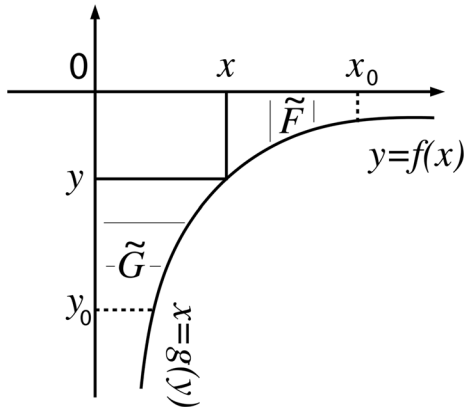


Fig. 2. The graph of $y = f(x)$ for the case $x > 0$ and $y < 0$.

with

$$\tilde{F} = -\int_x^{x_0} f(\hat{x}) d\hat{x}, \quad \tilde{G} = \int_{y_0}^y g(\hat{y}) d\hat{y}. \quad (9)$$

Up to the constant A_0 , which can be absorbed in the redefinitions of \tilde{F} to F and \tilde{G} to G , \tilde{F} and \tilde{G} again add up to xy .

The fact that the present picture requires redefinitions of functions by constants is directly related to the interpretation

of $F(x)$ and $G(y)$ as integrals of $f(x)$ and $g(y)$, respectively. As always, integrals are well-defined only up to equivalences of the type $F \sim \tilde{F}$, with “ \sim ” meaning “equal up to a constant function.” This geometric description fits nicely with our physical interpretation, where the predictions do not change if quantities like the Hamiltonian or thermodynamic potentials are redefined by constants.

I first presented this material in informal talks on March 15, 2012 in Vienna and on June 4, 2012 in Heidelberg. After completion of the present manuscript I became aware of Ref. 3, which is dated June 29, 2012 (submission)/August 22, 2012 (publication), and has some overlap in content. I am grateful to Johanna Knapp for pointing out this reference to me. One of the referees remarked that the present argument was also developed in a lecture available on Youtube.⁴

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On deriving the Maxwellian velocity distribution

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Maxwell’s 1860 derivation of the molecular velocity distribution does not constitute a valid approach for pedagogical use. © 2013 American Association of Physics Teachers.

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In 1860, James Clerk Maxwell published a derivation¹ of what we now call the Maxwellian velocity distribution, the distribution of molecular speeds in an ideal gas in thermal equilibrium. The essential ingredient was an assumption, motivated by symmetry and mathematical considerations, that the velocity-space number density of molecules as a function of speed must factor into separate, identical functions of the Cartesian velocity components. That is, the number of molecules in velocity space volume element $dv_x dv_y dv_z$ must be given by an expression of the form

$$NF(v) dv_x dv_y dv_z = Nf(v_x)f(v_y)f(v_z) dv_x dv_y dv_z, \quad (1)$$

where N is the total number of molecules. This posit of factorability leads directly to the conclusion that the velocity space density function

$$F(v) = f(v_x)f(v_y)f(v_z) \quad (2)$$

is proportional to e^{-Av^2} , where $v = (v_x^2 + v_y^2 + v_z^2)^{1/2}$ is the speed and A is a constant. For, by differentiation of Eq. (2), we have

$$\frac{\partial F}{\partial v_x} = \frac{dF}{dv} \frac{v_x}{v} = \frac{df(v_x)}{dv_x} f(v_y)f(v_z), \quad (3)$$

which, upon dividing by $v_x F(v) = v_x f(v_x)f(v_y)f(v_z)$, gives

$$\begin{aligned} \frac{1}{vF} \frac{dF}{dv} &= \frac{1}{v_x f(v_x)} \frac{df(v_x)}{dv_x} = \frac{1}{v_y f(v_y)} \frac{df(v_y)}{dv_y} \\ &= \frac{1}{v_z f(v_z)} \frac{df(v_z)}{dv_z}, \end{aligned} \quad (4)$$

where the last two equalities follow by symmetry. Given the mathematical independence of the velocity components, each of the equal terms must in fact be constant. Upon integration, one finds

$$F(v) = Ce^{-Av^2}, \quad (5)$$

where A and C are positive constants. (The exponential e^{+Av^2} would also be a solution but it blows up at high speeds.) Integrations over velocity space, together with elementary considerations regarding the pressure of an ideal gas, suffice to determine $A = m/2kT$, with m the molecular mass, k Boltzmann’s constant, and T the absolute temperature. And thus, out pops the Boltzmann factor $e^{-mv^2/2kT}$ as if by magic.

Maxwell later acknowledged² that the reasoning behind this early derivation “may appear precarious.” Writing

several decades later, in a historical note within a treatise on the dynamical theory of gases, Jeans stated³ that “[t]his proof must be admitted to be unsatisfactory” and identified the assumption of independence of the velocity components, that is, the factorability assumption, as the problem. In a subsequent work⁴ Jeans’ disclaimer was slightly different: “This proof ... is now generally agreed to be unsatisfactory.” The implication is that its inadequacy was well-recognized.

Nevertheless, one finds little by way of cogent refutation of Maxwell’s method in the historical literature. Garber *et al.*⁵ refer without elaboration to “the problems that now seem so obvious in his first derivation of the distribution function ...” Brush⁶ states that “Maxwell later realized that the validity of the second [i.e., factorability] assumption was not obvious.” In a later work Brush⁷ says, “Maxwell’s first proof ... was not persuasive to other physicists,” that he “simply asserted that the distribution function must satisfy certain abstract mathematical properties, such as spatial isotropy.” Cropper⁸ writes that Maxwell’s “reasoning was severely abstract and puzzling to his contemporaries, who were looking for more-mechanical details.” Such mild disclaimers leave open the possibility that Maxwell’s original derivation possessed sufficient validity for pedagogical purposes; because the method is so simple, the temptation is great.

In fact, the derivation is simply not valid and obtaining the correct result can only be regarded as a fluke. Otherwise, once one understands the nature and significance of the Boltzmann factor $e^{-E/kT}$, with the energy E appearing in the exponent, it would be necessary to believe that Maxwell had derived, from the most general considerations only tenuously related to dynamics, that kinetic energy is proportional to velocity squared. That is too good to be true, and indeed it is not true relativistically.

Furthermore, precisely analogous considerations would lead us to conclude falsely that the only possible *potential* energy function must be simple harmonic. In Maxwell’s own words, “Now the existence of the velocity x [i.e., v_x] does not in any way affect that of the velocities [v_y] or [v_z], since these are all at right angles to each other and independent.” One might just as well claim that the coordinate x does not affect the coordinates y or z , for the same reasons. Then by the same argument, one infers that the number of molecules in volume element $dx dy dz$ is given by an expression of the form

$$NF(r) dx dy dz = Nf(x)f(y)f(z) dx dy dz, \quad (6)$$

where $r = (x^2 + y^2 + z^2)^{1/2}$ is the radial coordinate. This posit of factorability leads to the conclusion that the spatial density function $F(r)$ is proportional to e^{-Br^2} with B a positive constant. The upshot, considering that e^{-Br^2} must be the Boltzmann factor $e^{-U(r)/kT}$, with $U(r)$ the potential energy function, is that $U(r)$ must be proportional to r^2 . But there is no reason in reality why potential energy might not be some other function of r .

If a vector can take on a continuous range of magnitudes and point in any direction in three-dimensional space, then of course its Cartesian components are “independent” in the sense that they cannot be related by an equation with constant coefficients. But the sense of independence that Maxwell required was something quite different, namely, that the relative probability of different values of one component is not affected by the values of the other components. It so happens that the velocity components in a non-relativistic ideal gas *do*, statistically, possess this latter sense of inde-

pendence, but it is *from* our prior development and understanding of the Boltzmann factor that we learn this. In the Boltzmann factor, what is divided by kT is the energy. The kinetic energy is the sum of separate functions of v_x , v_y , and v_z . Therefore, the Boltzmann factor itself factors into separate functions of v_x , v_y , and v_z . For particles constrained to move in one dimension, the Boltzmann factor would still lead us to the correct speed distribution, but Maxwell’s derivation could not even get off the ground as it requires more than one independent velocity component.

In a relativistic gas, the kinetic energy does not decompose into a sum of independent functions of the Cartesian velocity components, and the relative probability of different values of one component does depend on the values of the others. This latter statement is demonstrated by the fact that while any one of the velocity components might, with equal probability, exceed $c/\sqrt{2}$ (c being the speed of light), all three cannot do so together. If v_x exceeds $c/\sqrt{2}$, the probability of either v_y or v_z doing so is reduced to zero. It is worth emphasizing that the problem is not that Maxwell’s original derivation is non-relativistic. There is no dynamics in it, relativistic or otherwise. The relativistic case represents a disproving counter-example, not merely a limitation in scope.

Unfortunately, Maxwell’s original derivation has been enlisted frequently in the pedagogical literature, usually with attribution to Maxwell, sometimes not. Sometimes, it is accompanied by a vague or mild disclaimer of the sort mentioned already in the historical literature; other times, no indication is given that it might be problematic. It has appeared in textbooks and books aimed at students,^{9–20} in this journal,²¹ in an encyclopedia of physics,²² and on numerous web sites. Among the authors who have deployed this derivation, Richlet¹⁵ correctly notes that Maxwell’s “reasoning was in fact incomplete because the assumed isotropy of the gas does not necessarily imply the statistical independence of the variables along different directions of space.” But he does not elaborate.

Writing three decades ago in the *Journal of Chemical Education*, Dunbar²³ cogently criticizes the use of this derivation. He questions whether it is obvious that the probability distribution for, say, v_y must be independent of whether v_x is high or low, and he points out that the assumption is not true relativistically. Dunbar’s paper thus partially anticipates the arguments presented in this one. Dunbar in turn refers to an older text by Chapman and Cowling,²⁴ who also questioned the independence/factorability assumption. Nevertheless, the continued use of this unsound method of derivation indicates that the message has not been widely enough received. Perhaps the more thorough refutation presented here will help.

The author is indebted to Balázs Gyenis for sharing an unpublished manuscript, “Maxwell and the Normal Distribution,” which helpfully placed Maxwell’s original derivation in a historical context and identified salient literature references.

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