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On the Representation of the Physical Properties of Substances by means of Surfaces.

By W. Peddie.

If the physical state of a substance is completely defined when the simultaneous values of three of its properties are given, then, by measuring off along three rectangular axes, from any point chosen as origin, lengths proportional to these values, we determine a point which represents completely the physical state of the substance. And, evidently, each point lies on a surface, the equation to which is determined by the three co-ordinate properties. If, in the equation to the surface, we give one of the variables a definite value, we get the equation to a contour-line of the surface which represents the necessary relation subsisting between the remaining two properties when the other is constant.

The nature of any quantity is completely known when it is understood *what* units are involved in its measurement and *how* they are involved. Thus a speed involves the unit of length directly, and the unit of time inversely; an acceleration involves a length directly, and the square of a time inversely. When we are dealing with space, however, the unit of length alone is involved. We say that the space considered has one, two, or three, &c., *dimensions*, according as the unit is involved to the first, second, or third, &c., power. A line has only one dimension. Given a certain point on the line as origin, only one number, with the proper sign attached, is required to completely specify the relative position of any other point on the line. A surface has two dimensions. Two directed lengths are necessary to define the position of a point on it with reference to any other point taken as origin. Thus we speak of the position of a point on the earth's surface as being so much north or south of a certain line, and so much east or west of another. In the threedimensioned space to which we are accustomed, three such lengths are required. Thus we speak of the length, breadth, and thickness of a solid.

The intersection of any surface which has a constant characteristic with the surface of a solid of three dimensions is a contour-line. The analogue in two dimensions of a contour-line is what may be termed contour-points, that is, the points in which a line, along which some quantity is constant, cuts the boundary of a surface. The boundary of a surface is a line and exists in two-dimensional space; so that, in two-dimensional space, contours have no dimensions. Similarly, in three-dimensional space, contours are of one dimension. The properties of four-dimensional space, or even n-dimensional space, can be treated mathematically; but, from want of experience, it is impossible to imagine the nature of such space. Contours in it would be surfaces,—the surfaces of intersection of solids, throughout which some quantity was constant, with solids existing in four-dimensional space.

The contour-lines most widely known are those formed by the intersection of level surfaces with the surface of the earth. The line of sea-board is one such contour-line. The essential feature of these lines is that by means of them a third dimension is represented upon a surface. An ordinary map with numbers marked upon it indicating the heights of various places, represents roughly the third dimension. So also does a chart with numbers corresponding to the various depths of the sea. A line drawn free-hand through the points of equal height or depth would approximately coincide with a contour-line. We may obtain any number of contour-lines by supposing the sea-level to rise or fall as necessary. It must be specially observed that the surfaces intersecting the earth's surface are *level*. From this it follows that, since the earth is not spherical in shape, contour-lines are not lines of constant height above, say, ordinary sea-level taken as a standard. The assumption that they are lines of constant height will not introduce appreciable error, however, if the value of gravity is not sensibly different at different parts of the same line. The quantity which is constant over a level surface is the work required to be done in order to raise a given mass to it against gravity from any station on the standard level. This is, therefore, the quantity which is constant along the contour-line. Since the work so done is equal to the kinetic energy (the product of the mass into half the square of the velocity acquired) which would be gained by the mass if allowed to slide from the upper to the lower level by any path, we may define the constant quantity, independently of the mass, as half the square of the velocity acquired by a body falling, by any path, from the upper level to the standard point on the lower level.

To determine the nature of the surface as indicated by peculiarities in the form of the contour-lines, let us suppose the earth to be entirely submerged so that we have only one region, and that a region of depression. If now we suppose the water to be slowly absorbed by the solid matter of the earth, regions of elevation will be formed gradually until, finally, we shall have only one region, and that a region of elevation. Before a region of elevation is formed we have a *summit* appearing above the water-level; and, when the water subsides out of a region of depression, we have a lowest-point, or *immit*, appearing. The number of regions of elevation and depression may vary in two ways. We may have two regions of elevation running into each other as the water sinks. The point where they first meet is termed a *pass*, (see Fig. 24; p_1, p_2, &c.). Again, a region of elevation may throw out arms which run into each other and so cut off a region of depression. The point where they first meet is termed a *bar*, (Fig. 24; b_1, b_2, &c.). The contour-line for a level immediately underneath that corresponding to the bar has a closed branch within the region of depression cut off. Thus the closed curve at I_4, Fig. 24, is part of the contour-line *ux*. If a chart of an insular high-land be constructed as above indicated, a pass occurs at the node (see Fig. 24) of a figure-of-eight curve, (or *out-loop* curve, as Professor Cayley has termed it); while a bar occurs at the node of an *in-loop* curve. If, in Fig. 24, we interchange the summits and immits, the passes and bars, we see that, in the chart of an island-basin (Maxwell, on Hills and Dales, Philosophical Magazine, series 4, vol. 40, Dec. 1870, p. 427), a pass is represented by the node of an *in-loop* curve, and a bar corresponds to the node of an *out-loop* curve. If there were any advantage in having passes and bars always indicated by the node of the same kind of curve respectively, this could be attained by affixing the positive sign not constantly to the region on the same side of the level surface, but to the region towards which or from which the surface was moving.

As a particular case, two regions of elevation may run into each other at a number of points simultaneously. Of these points, one must be taken as a pass and the others as bars. We may have also singular points where, for example, three or more regions of elevation meet. Such points are termed *double*, *treble*, &c., passes. Similarly, we may have multiple bars.

Before a pass can be formed there must be two summits, and for every additional pass there is another summit. Thus the number of summits is one more than the number of passes. So also the number of immits is one more than the number of bars.

Slope-lines are lines drawn everywhere perpendicular to the contour-lines. Evidently the steepness of a district is indicated on a chart by the closeness of the contour-lines. There are two kinds of slope-lines, however, which are specially important. These are the slope-lines drawn from summits to passes or bars, and from passes or bars to immits. The first of these can never reach an immit, and are termed *water-sheds*. The second can never reach a summit, and are termed *water-courses*.

A perpendicular precipice is indicated on a chart by the running together of two or more adjacent contour-lines (Fig. 24, *f*). An over-hanging precipice is indicated by the lapping of the upper-level line over the lower-level line. Similarly any other characteristic feature of a country can be indicated.

There is no necessity for taking the level as the quantity which is constant over the intersecting surface. We might, for example, make the inclination of the tangent-plane to the vertical constant, and thus obtain another set of contour-curves by rolling this plane over the given surface.

As mentioned at the commencement of this paper, we can build up a solid, the surface of which represents the state of a substance with regard to three quantities We may then lay down, upon this surface, contour-lines, each point of each of which indicates the relation between these quantities when a fourth quantity, characteristic of the line, remains constant.

Let us take, as a particular example, the thermodynamic surface representing the state of water-substance with regard to volume, pressure, temperature, entropy, and energy. If we choose any three of these quantities to be measured along the axes, the value of the remaining two at any point of the surface formed may be given by contour-lines. The model of the surface, with volume, entropy, and energy, measured along the axes, has been constructed by Clerk-Maxwell, and is explained and figured in his *Theory of Heat.* Let us take volume, temperature, and pressure, as the quantities to be measured off. The surface so obtained was first studied, and some peculiarities connected with it pointed out, by Professor James Thomson. Suppose the surface to be cut by a plane of constant pressure, say p_1. We thus get a contour-line, the general nature of which is indicated in Fig. 25. At a low temperature the volume is small, the substance being solid. As the temperature rises the substance expands, until it reaches the liquifying point. Its volume then diminishes without rise of temperature until the substance is completely liquified. Its temperature then rises and its volume diminishes up to the maximum density point, after which it expands. When it reaches the boiling point its volume increases, but its temperature does not rise until the substance is entirely in the gaseous state, after which both increase together. The contour lines for slightly less pressures, (p_2, p_3, in the Fig.), are approximately parallel to p_1, but lie entirely on the right-hand side of it, since for a given temperature the volume increases as the pressure diminishes and the freezing point is lowered and the boiling point is raised by pressure. The freezing point and boiling point approach as the pressure diminishes, until finally they coincide (see p_1, Fig. 26). After this (p_2, Fig. 26) the substance changes directly from the solid into the gaseous state. The line AB indicates the *triple-point* temperature, that is, the temperature at which portions of the substance in the three states, solid, liquid, and gaseous, can exist together in equilibrium. The length of the boiling-point line continually diminishes as the pressure is increased until, finally, there ceases to be a boiling-point (C, Figs. 25 and 27). The temperature at which this occurs is called the *critical temperature.* Similarly, we may assume a critical temperature for the solid-liquid condition. That is to say, there may be a temperature such that, if the temperature of the solid have a less value, no amount of pressure will lower the freezing point sufficiently to admit of liquifaction. It is, perhaps, too much to assume that there is a critical temperature for the solid-gaseous condition,—in other words, that at a certain pressure and temperature the whole mass of the solid will become gaseous without evaporation.

Now, suppose the surface to be cut by a plane of constant temperature. The contour-lines so obtained are ordinarily termed *isothermals.*

Let the temperature first be above the triple point but below the critical point. Then, the substance being taken in the gaseous state, as the pressure increases the volume diminishes until the boiling-point is reached. At this stage the volume decreases, without variation of pressure, until all the substance is liquified. After this, a very great increase of pressure is required to produce even a small decrease of volume. Such an isothermal is indicated by the line WXYZ, Fig. 27. If we take an isothermal below the triple-point, we find that the solid state is intermediate between the liquid and the gaseous. As the pressure increases the volume decreases until the point of sublimation is reached, when the pressure remains constant, the volume diminishing until all is solidified. Then the volume decreases slowly for increase of pressure until the melting-point is reached, when the pressure becomes constant, the volume diminishing, until all is melted, when the volume again decreases slowly for increase of pressure. Thus there are two kinds of isothermals having their transition stage at the triple-point temperature. We have seen that, similarly, at the triple-point pressure the transition stage for the two kinds of lines of equal pressure occurs. The form of the isothermals beyond the critical temperature is indicated in Fig. 27. Evidently, a second transition temperature for the isothermals is that of the solid-liquid critical temperature, if sublimation occurs at temperatures where liquifaction has ceased. It is probable that, as Professor James Thomson has indicated, the true form of the isothermals is not indicated by the part of the line parallel to the v-axis (Fig. 27), but by, for example, the waved line XY. Part of this line represents an unstable state since pressure and volume increase together. Hence the substance can only be obtained in nature in states represented by parts of this line.

On the surface, various contour-lines might be laid down. For example, we might have lines along which either of the quantities $\frac{dp}{dt}$ or $\frac{dp}{dv}$ was constant. Or we might have lines of constant energy, or of constant entropy. These latter are ordinarily termed adiabatics ; that is, as the substance passes from one state to another along such a line, no heat enters or leaves it. The properties of these lines in a region where $\frac{dp}{dt}$ has a negative value are rather interesting. This condition is satisfied when the temperature of the substance is between the maximum-density point and the freezing-point.

This part of the surface is indicated in Fig. 28, which represents the projection of lines of equal volume upon the plane (p, t). MN, TC, TN, TS, are the projections respectively of the maximum-density curve, and the water-steam, water-ice, and ice-steam surfaces. In the region TMN, therefore, $\frac{dp}{dt}$ has a negative value. If the substance be in a state represented by a point in this part, and be allowed to expand adiabatically, its temperature rises until the maximum-density curve is reached. The adiabatic, however, cannot pass to the right-hand side of the curve, since the curve slopes upwards from left to right, and, in the region to the right, adiabatic expansion is accompanied by fall of temperature. Hence we find that two adiabatics may intersect on the surface in this region. That is, the substance may have the same temperature, volume, and pressure, in two different states corresponding to different amounts of intrinsic energy.

After the adiabatic reaches the maximum-density curve, the temperature may either rise or fall. Let us suppose that, (as indicated by Rücker), the intrinsic energy is such that, having done work while expanding, its temperature must fall. In this case it is evident (Fig. 29), that an isothermal can cut an adiabatic twice. Hence, we can have an isothermal steeper than an adiabatic at their point of intersection. In Fig. 29 MN is the maximum-density curve, the dotted curve is an isothermal, and the continuous curve is an adiabatic. Fig. 30 represents the contour-lines of equal pressure.

In the representation of physical properties by models, use might be made of tortuous curves. Thus, if we take two quantities, one of which is a parabolic function of the other, say x and y where $y^2 = ax$, and therefore $y\frac{dy}{dx} = \frac{a}{2}$, we may measure $\frac{dy}{dx}$ along a third rectangular axis, and so obtain a tortuous curve the projection of which on the plane (x, y) is a parabola, while its projection on the plane $\left(y, \frac{dy}{dx}\right)$ is a hyperbola. If y represent the time during which a body has been falling under gravity, and x represent the space described from rest, then the reciprocal of the third co-ordinate quantity gives the velocity acquired.

P.S.—From the experimental determination of the amount by which the maximum-density point is lowered by pressure, and the theoretical determination of the steepness of the adiabatics in the plane (p, v), it seems that the latter are steeper than the former as regards inclination to the v-axis. Hence there is no point of maximum temperature on the adiabatic; but, on the other hand, there is a point of minimum temperature. This temperature for any given adiabatic, is that corresponding to the isothermal passing through the point of intersection of the adiabatic with the maximum-density curve. I have not altered the text above, however, as the remarks and figure may conceivably apply to some substance other than water.

The Theorems as far as Proposition 32, of the first book of Euclid's Elements, proved from First Principles.

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Proposition 4.

Given * $AB = DE$, $AC = DF$, $\angle A = \angle D$.

Suppose you start from B, and walk along BA a certain distance a to A; then at A you turn at a certain angle into another road AC; then you walk along AC a certain distance b to C. Again you start from E, walk a distance a along ED; turn off at D into DF at the same angle as before; then walk the distance b along DF to F. Since you have gone through the same set of movements in the two cases, and since *the same cause always produces the same result*,† the results in the two cases must be the same, that is, you will arrive in both cases, at the same distance from the starting point. Hence BC = EF.

Proposition 5.

Given $AB = AC$.

From a certain point A, two lines AB, AC are drawn. Two points B, C equally distant from A are joined. The same causes which determine the size of $\angle$ B also determine the size of $\angle$ C. Hence $\angle$ B = $\angle$ C.

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* For figures see Mackay's *Elements of Euclid.*

† This axiom, as well as its converse, is assumed in every Science.