Second Law Violations by Means of a Stratification of Temperature Due to Force Fields

Andreas Trupp

Fachhochschule der Polizei Brandenburg -University of Applied Science-, Prenzlauer Str. 66-70, 16352 Basdorf, Germany; E-mail: atrupp@aol.com

Abstract: In 1868 J.C. Maxwell proved that a perpetual motion machine of the second kind would become possible, if the equilibrium temperature in a vertical column of gas subject to gravity were a function of height. However, Maxwell had claimed that the temperature had to be the same at all points of the column. So did Boltzmann. Their opponent was Loschmidt. He claimed that the equilibrium temperature declined with height, and that a perpetual motion machine of the second kind operating by means of such column was compatible with the second law of thermodynamics. Extending the general idea behind Loschmidt's concept to other force fields, gravity can be replaced by molecular forces acting on molecules that try to escape from the surface of a liquid into the vapor space. Experiments proving the difference of temperature between the liquid and the vapor phase were conducted in the 19th century already.

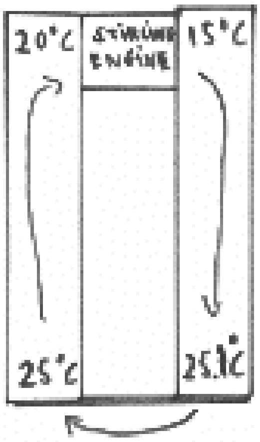

FIG 1

I. Maxwell addressed the question whether or not the temperature of a column of gas (or of any other substance) subject to gravity was stratified or uniform. His answer was the following, which linked that question to the Second Law of thermodynamics (see also fig. 1):

> "*In fact, if the temperature of any substance, when in thermic equilibrium, is a function of the height, that of any other substance must be the same function of the height. For if not, let equal columns of the two substances be enclosed in cylinders impermeable to heat, and put in thermal communication at the bottom. If, when in thermal equilibrium, the tops of the two columns are at different temperatures, an engine might be worked by taking heat from the hotter and giving it up to the cooler, and the refuse heat would circulate round the system till it was all converted into mechanical energy, which is a contradiction to the second law of thermodynamics. The result as now given is, that temperature in gases, when in thermal equilibrium, is independent of height, and it follows from what has been said that temperature is independent of height in all other substances.*"

Boltzmann sided with Maxwell. Their common opponent was Loschmidt. He claimed that the equilibrium temperature declined with height, and that a perpetual motion machine of the second kind operating by means of such column was compatible with the second law of thermodynamics.

The construction of a model gas (that shall not be discussed here) suggests that Maxwell and Boltzmann are right in case the ascent of molecules in a gravity field is at the expense of their *vertical* component of velocity only. It seems, however, that Loschmidt is right in case the ascent of the molecules, due to their mutual collisions, is at the expense of all three components of velocity.

II. One might wonder why Boltzmann did not attack Loschmidt with a simple argument: He could have pointed at the apparent fact that there is no difference in equilibrium temperature between liquid water and its vapor, though the molecules rising from the surface of the liquid have to overcome a force field generated by Van-der-Waals forces in very much the same way as air molecules have to overcome a gravity field when gaining height. Doesn‘t that shatter the position of all those who believe the ascent of molecules against a force field would have to result in a decline of equilibrium temperature?

The answer is in the negative. Let us see why. Both the behaviour of the vapor and the liquid can be described -to a fairly good approximation- by Van-der-Waals‘ formula for real gases. The general gas law

(1)

$$pV = RT$$

is modified by the assumption of mutual attractions between the molecules. In the interior of a gas, those attractive forces are supposed to cancel each other, but near the surface of a spherical volume containing many molecules, these forces will add up to form a force directed towards the center of that sphere and hence opposed to the external pressure of the gas. That „internal pressure“ can be supposed to be proportional to the square of the density (at a given temperature). It is easy to realize why: The more molecules within the volume, the stronger the force on a single molecule near the surface of the sphere. Moreover, the more molecules within the volume, the greater the number of molecules that hit the spherical wall per second. This is why the general gas law converts to (= Van-der-Waals-Law):

(2)

$$(p + \frac{a}{V^2})(V - b) = RT$$

The term „b“ denotes the volume proper of the molecules (per mol) that are no longer regarded as point particles. The term „a“ denotes the constant of proportionality linking the internal pressure with the square of the density.

Note that the diameter of the spherical volume has not entered the formula. This is

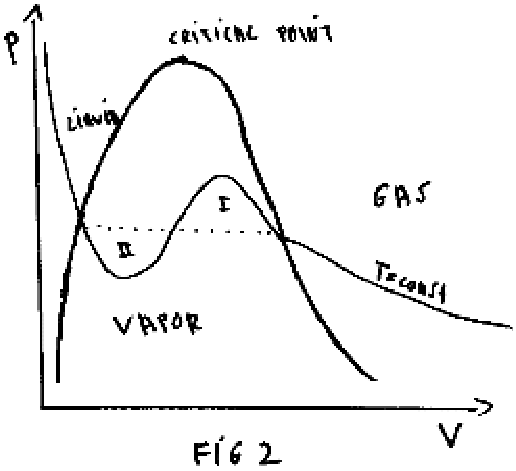

FIG 2

somewhat astonishing. If the molecular forces of attraction declined with $1/R^2$ (as do electrostatic and gravitational forces), the internal pressure would increase with the radius: At a given density, the mass (or charge) thought to be concentrated in the center would increase with the third power of the radius, while the force would decline with $1/R^2$ only. This is why the Van-der-Waals-formula makes the tacit assumption that the forces decline "faster“ than by $1/R^2$ (that feature of the formula is seldom mentioned in textbooks). Such an assumption is, of course, justified by the fact that the internal pressure has never been observed to depend on the volume of the sphere (a modification is, however, necessary if spheres of very small diameters are considered, as can be found in capillary tubes).

Re-arranging (2) leads to
(3)

$$p(V) \; ' \; \frac{RT}{V\&b} \; \& \; \frac{a}{V^2}$$

Plotting different curves (for different temperatures) on a p,V-chart results in the well known borderline separating gas phase, liquid phase and vapor phase from each other (fig. 2). The vapor phase is represented by the area on the chart where each isothermal curve displays two dips. For each curve representing a certain temperature, the two borders of the vapor phase (gas/vapor, and vapor/liquid) are marked by the intersection of a horizontal line which, in turn, is defined by the condition that two areas 1 and 2 in figure 2 have to be equal in size.

Within the vapor area, the curves represent metastable states of the substance (hence the „vapor area“ should be better called „metastable area“ rather than vapor area; in a strict sense, only those points that constitute the right slope of the hill -the top of which is marked by the critical point- represent vapor states). Near the border gas/vapor, the metastable state is called a „supercooled vapor“, near the border liquid/vapor, the substance is called a „superheated liquid“. As soon as the metastable state collapses, the substance -when being subject to constant pressure from outside- moves either to the right or to the left until it hits the borderline vapor/liquid or vapor/gas. It moves to the right (that is: it hits the borderline vapor/gas), if the metastable state has been a superheated liquid; it moves to the left (that is: it hits the borderline vapor/liquid), if the metastable state has been a supercooled vapor.

Now comes an inportant recognition: The sameness of temperature between water boiling at atmospheric pressure and the vapor evolving from its surface stems from the fact that the substance, when moving along the curve of constant temperature, does not enter the deep interior of that area, but abandons the metastable state in the vicinity of the border already.

There is an easy way to check out whether this analysis is correct. In case the journey goes deeper into the realm of metastable states than in an ordinary case, the horizontal shift to the right (in case of a superheated liquid) will hit the borderline vapor/gas somewhat below the point where the isothermal curve meets that borderline (see fig. 3). That is to say: When water vapor evolves from superheated liquid water (of, say, 180°C) the external pressure of which is 1 bar, the vapor has to have a temperature of just 100°C. This is exactly what any textbook is telling students who want to determine the boiling point of a liquid! It is for this reason that they are adviced to hold the thermometer into the vapor, not into the liquid (that might be superheated).

Unfortunately, the process cannot be reversed (see fig. 3 again). After having condensated all of the vapor (at an invariant pressure of 1 bar), you would have arrived at point 3 in fig. 3. The temperature of the liquid would then be 100°C only, and not 180°C.

But the process *can* be reversed as soon as some salt (or some other solid) has dissolved in the liquid, bringing about the effect of a reduction of vapor pressure (or of a boiling point elevation). Let‘s see how this would affect the Van-der-Waals-formula. Re-arranging (3) leads to:

(4)

$$T_1 \;'\; (p_0 \;\%\; \frac{a}{V_1^2}) \; \frac{(V_1\&b)}{R}$$

The term p_0 denotes the pressure of 1 bar, V_1 denotes the specific volume of the vapor at the borderline vapor/gas.

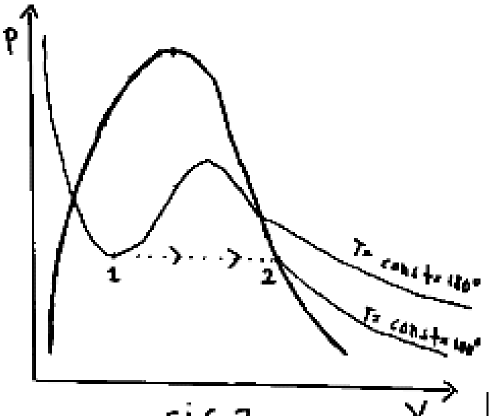

FIG. 3

In case a solute is present in the liquid, that solute will act as if the attractive forces between the molecules would have become stronger, resulting in an increase of the constant „a“. The volume (per mol) V shall be the *reduced* volume, that is the volume of the solvent (water) alone. Let V_2 be the unknown specific (reduced) volume of the liquid at the borderline liquid/vapor (point

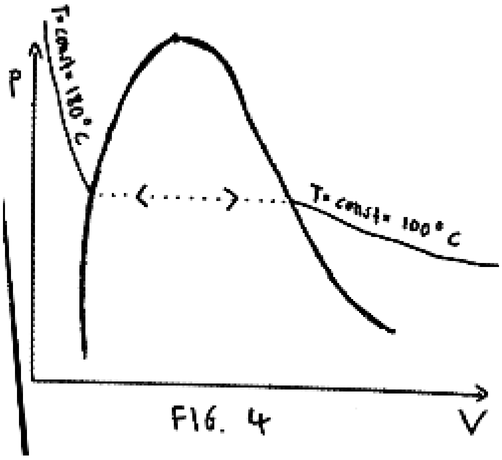

FIG. 4

2 in fig. 4), and let „k“ be a factor greater than unity. Then we have (if „k“ is great enough):
(5)

$$T_2 \text{ ' } (p_0 \ \% \ \frac{ka}{V_2^2}) \ \frac{V_2 \& b}{R} > T_1$$

Thus, when vapor is evolving from the surface of the -just slightly superheated- solution at 1 bar, the vapor (T_1=100°C, point 1 in fig. 4) is cooler than the liquid (e.g., T_2=180°C). Quite different from the case of the vapor evolving from the extremely superheated (pure) liquid, the process is reversible (see fig. 4): Slightly supercooled vapor of 100°C (1 bar +dp) is capable of condensating on the surface of the liquid the temperature of which is T_2. That is to say: The two horizontal lines -representing horizontal shifts (from vapor to liquid, and from liquid to vapor) when metastable states are being abandoned- coincide at full length (more precisely: their mutual distance is vanishingly small).

The result is confirmed by more sophisticated calculations that -due to a lack of space- cannot be presented here.

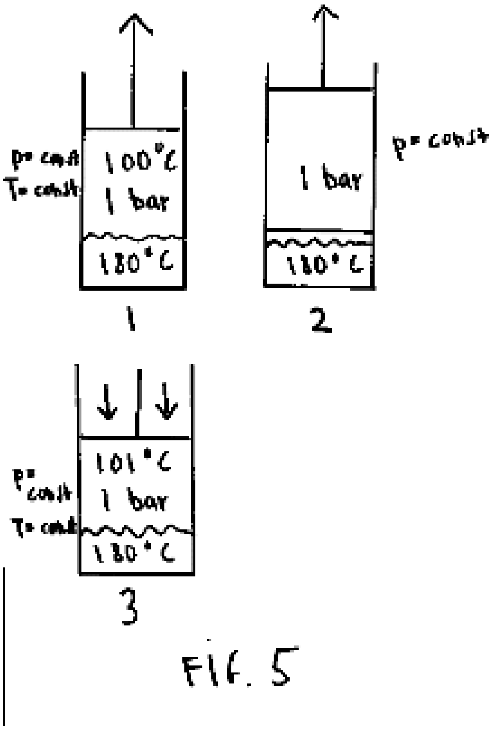

FIG. 5

III. With a stratification of temperature being present in the system liquid/vapor, it is no surprise to realize that a perpetual motion machine of the second kind can be conceived of to operate also in such a system, and not only in a gravity field. The easiest way to show this would be to place one part of a Stirling-engine in the liquid, and the top in the vapor (with the volume of the container -housing the liquid solution and the vapor in contact with that liquid- being invariant). But there is even a more effective device one could conceive of (fig. 5): As a first step of the cycle, vapor (100°C) is evolving from a saturated solution of of calcium chloride in water that has a temperature of 180°C +dT at a pressure of 1 bar. As a second step, the vapor is separated from the solution, and is expanded isobaricly (but not isothermally) by letting heat flow into the vapor from a reservoir the temperature of which is slightly above 100°C. As a third step, the vapor is again brought into contact with the solution, and is compressed isobaricly (still at 1 bar) until it has completely condensed in the liquid. The temperature of the liquid shall be kept constant at 180°C -dT during the condensation. The net mechanical work spent or yielded approaches zero (under ideal circumstances).

Though no net mechanical energy was invested, the device acted as a heat pump: During the last step, more condensation heat must have *left* the liquid than had *entered* the liquid during the *first* step, with the temperature of the liquid being 180°C (+ - dT) during both steps; for without that difference between condensation heat and evaporation heat, the cycle would have „swallowed" the amount of heat that entered the vapor during the *second* step (when the vapor was expanded isobaricly but not isothermally). Moreover, according to the First Law of thermodynamics, that difference between condensation heat and evaporation heat must *equal* the amount of heat that entered the vapor during the second step. But the heat that entered the vapor during that second step came from a heat reservoir the temperature of which was only slightly above 100°C, and hence far below 180°C. So heat was lifted across a „distance" of 80 degrees. Since any heat pump not requiring mechanical work for its operation represents a perpetual motion machine of the second kind, this device, too, would constitute a Second Law violation.

IV. It is amazing to learn that the crucial experiments -the purpose of which was to determine whether or not the vapor evolving from a solution had the same temperature as the liquid phase- were conducted about 150 years ago; first by Rudberg, and then by Regnault. Both scientists, who explored the effect of boiling point elevation (or vapor pressure reduction) due to the presence of a solute, found the vapor to have the same temperature as if it evolved from the pure liquid (solvent) at the given pressure. Regnault faced difficulties in accounting for this surprising result. Though the phenomenon did not depend on the vivacity of boiling, he held the evaporation of small droplets -that were ejected from the surface during the boiling process- responsible for the cooling off of the vapor. This explanation can be doubted, since it is the loss in kinetic energy suffered by the molecules (when overcoming the force field generated by the other molecules) that accounts for the drop in temperature; the effect is hence related to the well known effect of a cooling of a real gas that is expanding into vacuum. But even if Regnault's explanation were correct, it would not disable the operation of the cycle described above.

The capability of vapor, be it saturated or superheated, to condensate at the (reduced) equilibrium pressure of the solution -though the liquid is hotter than the vapor- has also been detected in the 19th century already (Sakurai, Landsberger), and has been used to determine the elevation of the boiling point of solutions.

Both the experiments by Sakurai and by Regnault are in the process of being repeated.

References:

J.C. Maxwell, The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science 35, 215 (1868);
J. Sakurai, Journal of the Chemical Society (London) 61, 989 (1892);
M.V. Regnault, Memoires de l'Academie des Sciences de l'Institut Imperial de France, Tome XXVI, Paris 1862, p. 84;

A. Trupp, Physics Essays 12, 614 (1999).