On some physical conditions of chemical affinity and on Brownian motion

Prof. Giovanni Cantoni ([1])

([1]) *Pavia*

Summary. — Dynamical heat theory easily offers itself to several checks involving rather different kinds of phenomena. Thus I attempt at collecting, in a simple and elementary form, certain true facts, that were deeply discussed by illustrious mathematicians and strong physicists, with no pretension of saying new things.

PACS 05.40.Jc, 46.65.+g, 83.10.Mj – Brownian motion.
(Translated by G. Gallavotti, comments in bold and in square brackets).

1. –

In one of my Memoirs published in 1862, [1, 2, 3, 4, 5], I did remark that if perchance the Black and Wilke discovery, that a different amount of heat is required to produce an equal temperature increment in equal weights of different bodies, had been thought over with a little attention, it should have suggested to physicists to pose the following problem: to determine for different metals the weight proportions needed so that equal heat exchanges could occur under an equal temperature variation. So that since that time would have been known the ratios under which, at least approximately, metals combine with each other or with metalloids.

If furthermore such weight ratios, derived from Black's law and which merit to be called *thermal equivalents*, had attained recognition in Science, before the chemists achieved determining their proportionality ratios on the basis of their reactions, then well earlier would have been accepted the scientific concept that the chemical reactions between undecomposed substances

[**"chemically homogeneous (*i.e.* pure) substances"**]

should take place according to those weight ratios with which equal amounts of heat can be mutually exchanged under equal temperature variations (or according to very simple multiples or submultiples of the same ratios). Thus the law discovered by Dulong and Petit would have assumed a meaning more precise and more useful than what did happen because the discovery of the chemical equivalents preceded that of the thermal equivalents. In any event, denoted c and c' the temperature calories per equal weights

     1

[“specific heats per unit weight”]

of two undecomposed substances, and m and m' the molecular weights of the same substances, the Dulong and Petit law is expressed by the relation $c\,m = c'\,m'$. And if instead p and p' represent, for the same two substances, the weights corresponding to the thermal equivalents the relation $c\,p = c'\,p'$ would still hold associated with the above posed problem. Now, denoting by c_1 or c'_1 respectively the temperature calories per masses proportional to the said molecular weights

[“specific heats per mole”],

or also per equal numbers of molecules of the said two substances, it will be $c_1 = c\,m$ and $c'_1 = c'\,m'$, and therefore by the Dulong's law, it will also be $c_1 = c'_1$, which is the same as saying that, given equal molecules numbers of two given different substances, the heat amounts necessary to induce equal temperature variations are equal.

2. –

But, even having recognized this correlation between thermal equivalents and chemical equivalents or molecular weights (a denomination that I consider preferable to that of atomic weights), the following other question still remained: which is the physical reason for such specific heat values? Which is the same as: how comes that different weights of the various substances are needed to produce equal thermal effects under given temperature variations? Now, in my opinion, this question is entirely analogous to the following other: why at a given temperature different densities are needed to generate the same pressure with different gases? But at the latter question, thanks to the molecular diffusion law of Graham, we are able to answer that the mentioned difference in density needed to produce the same pressure is a consequence of the different speed that molecules of different gases possess at the same temperature. We could even say, with better precision, that to produce an equal sum of impulsions (equal pressure) on a given surface in a given time with such projectiles with different speeds, it will be necessary to use them with relative masses m and m_1 inversely proportional to the square roots

[sic: it should be the square, as in the following]

of the respective speeds, in order that it will be $mv^2 = m_1 v_1^2$. And such is in fact the expression of Graham's law once the relative masses m and m_1 are replaced by the relative densities d and d_1, leading to the conclusion that the molecular masses in simple gases will be directly proportional to their densities at equal pressure and temperature, which is one of the important experimental discoveries of Gay-Lussac.

[and Avogadro?]

Thus, from this comparison between the said two questions, and according to the principles of the dynamical theory of heat, it seems to me that analogously it can be said that to have equal quantities of heat from different bodies for an equal temperature variation, different masses are required, because different are the molecular speeds at the same temperature: therefore, to obtain equal heat exchanges between two different bodies, it will still have to be $mv^2 = m_1 v_1^2$. However, by the mentioned Dulong's law, since $c\,m = c'\,m'$, it will also be $v^2 : v_1^2 = c : c_1$; *i.e.* the molecular speed variations of two substances for a given temperature variation are directly proportional to the square roots of their temperature calories.

3. −

Remark that to the above deduction it is possible to arrive by another path. Suppose that a unit weight of a given substance falls, freely covering the space s, at the end of which it is suddenly stopped. The corresponding dynamical work would also be represented by s_1 (keeping the weight equal to 1): and this work, becoming heat, will generate a number of calories expressed by $s_1 = c\,t\,E$, where c denote the calories of temperature per unit weight,

[**"specific heat per unit weight"**]

t the temperature increase that will take place, and E the dynamical equivalent of one calorie. Suppose then that s and v express respectively the fall height and the speed acquired so that the said temperature increase in the body corresponds to $t = 1^o$; it will then be $s_1 = cE$. And since $v^2 = 2gs_1$ it will also be $cE = \frac{v^2}{2g}$. For another body of different nature, but in the same site, it will analogously be $c_1 E = \frac{v_1^2}{2g}$, so that $c : c_1 = v^2 : v_1^2$. Therefore the speed that should be acquired by the molecules of two substances to generate an increment of 1°, and in general to generate an equal temperature increase, will be directly proportional to the square roots of their respective specific heats: just as found above.

4. −

But let us return to our first argument, and let us ask ourselves again: to what can the specific heat be related when considering the chemical reactions of heterogeneous bodies? Suppose to have two gases, for instance oxygen and hydrogen. At a given temperature their molecular velocities will be inversely proportional to the square roots of their respective densities, as stated above. But as the temperature varies their respective molecular speed will change in a different ratio: because as their dilatation coefficients change with the temperature, also the ratio of their densities will change, and therefore again that of the speeds necessary to exert the same pressure.

[**This is strange because in a mixture of perfect gases, or of classical particles in a Gibbs equilibrium state, at constant pressure the kinetic energy of each particle is the same**]

Now I think that the chemical reactions, associations and dissociations, correspond to a class of mechanical phenomena, analogous to that of the resonances and dissonances of sounds: which is the same as saying that for chemical combinations the existence of simple molecular masses ratios it is not sufficient, but certain harmonic ratios are required between the molecular speeds for which a suitable temperature is needed. Since as the temperature of considered substances increases, those speed limits would be reached by their respective molecules, for which a resonance or a harmonic vibration can take place. And on the other hand, increasing the temperature of a compound, its resolution into components would ensue whenever their molecular speed ratios would become incompatible.

[**The above paragraph is not clear, because the premise seems incorrect as remarked above.**]

More, remaining with this example of two different gases the analogy between the harmonic acoustic vibrations and the thermal harmonics should be reinforced by the fact

that, even in the sound propagation, different gases show speed of transmission which, at given temperature and pressure, are inversely proportional to the square roots of their respective densities, just as mentioned above for the relative gases diffusivity, and for their thermal velocity. In fact, according to LAPLACE's formula, since $v^2 = g\frac{c}{d} \cdot \frac{c}{c_1}(1 + \delta c)$, supposing the two gases at equal temperature and pressure, it will be possible to take δ and $\frac{c}{c_1}$ very slightly different from each other, so that it will be $v^2 : v_1^2 = d_1 : d$.

[**This seems to refer to Laplace's formula for the speed of sound in a gas $v_{sound}^2 = g\,h\,(1 + \frac{\delta c}{c_v})$ where g is gravity acceleration and h is the height of a homogeneous gas of density d which would produce the given pressure p, c_v is the specific heat at constant volume, δc is the difference between specific heat at constant pressure c_p and c_v. This leads correctly to $v^2 : v_1^2 = d_1 : d$ and can also be written $v_{sound}^2 = \frac{p}{d}(1 + \frac{\delta c}{c_v})$ and in a perfect gas this would be $v_{sound}^2 = \frac{\delta c\, T}{M_0}\gamma = \frac{RT}{M_0}\gamma$ with M_0 the atomic mass, R the gases constant and $\gamma = \frac{c_p}{c_v}$.**
However the arguments developed in the text are not clear: the appearance of g, c, c_1, undefined here together with δc, seems to refer to Sec. 3 and to the connection developed there between specific heat, acceleration g and height s_1 of fall developing a heat equivalent of kinetic energy, hence related to the specific heat c. Furthermore the $v^2 : v_1^2 = d_1 : d$ the first part of this footnote indicated that the ratio is $v^2 : v_1^2$ is constant as a function of T, so that the text of this Sec. 4 seems in error. For Laplace's formula see P.S. LAPLACE, Traité de Mécanique Céleste, XII, p. 137, Paris, 1825]

Also the phenomena of the partial dissociations of the components at certain temperatures, like the ones studied by SAINT CLAIRE DEVILLE, and the water decomposition at high temperature observed by GROVE, seem to me that they can support this point of view, which would also be supported by the ingenious studies of HELMHOLTZ on the combination of various harmonic sounds in the same musical note.

5. −

I just said that, as the temperatures of the samples changes the ratios of the molecular speeds should change: therefore their specific heats change. In solids the increase is not very relevant, in general; however it seems larger in less coherent materials. In liquids the latter increase is stronger, and more so in those with smaller coherence, while in gases it has not yet been determined with sufficient precision.

[**Here it seems that the Author has not yet grasped the equipartition of energy: the ratio of the squares of the molecular speeds is constant as temperature changes. The ratio of the specific heats changes whenever the substance is not a perfect gas.**]

Very relevant is the increase of the specific heat connected with the change from the liquid to the aerial state. In my lectures given in Milan in 1860 at the schools of the "Cassa d'incoraggiamento", I tried to prove that specific heat is related above all with the relative coherence of different samples, and that, to make evident the relation, rather than determining the calories of temperature per equal weights of the different samples one should determine the dilatation calories of the same samples, *i.e.* the calories needed to produce equal volume increases. And in fact when we see the specific heat to increase in solids and liquids with the temperatures we also observe their dilatation coefficients

increase, and the latter increase is very relevant when the solid substance changes state into a liquid. Thus I have been able to prove that, both with the increase of temperature in solids and with their liquefaction,the dilatation calories decrease in correspondence to the decrease in coherence that the samples undergo in such cases. And in this way some objections that could be brought up towards the theory of heat have been eliminated.

However here I want to remark that the above specific heat variations reveal also modifications of the molecular velocities that deserve all our attention, in particular about the matters discussed above.

According to the determinations of Dulong and Petit the different metals not only present a capacity increase as temperatures grow, but this increase has a very different value for different metals: thus, for instance, in copper it is larger than in platinum, in a ratio three to two, and in iron it is the double of what it is in the platinum itself. From that we see how much should also change in such metals, as the temperatures change, the ratios of their molecular velocities: therefore the above mentioned resonance–dissonance conditions should vary considerably. Hence, even from such viewpoint, the importance of a similar experimental study on the specific heat variations appears.

And since solids, becoming liquids, show an increase in the specific heats, we must admit a corresponding increment of their molecular velocities (which implies a remarkable decrease in material coherence); and we shall therefore find in the liquid a condition more suitable for chemical reactions, according to the old say *corpora non agunt nisi sunt soluta*. And together with such an increase of the molecular speeds a condition will be realized suitable to explain the considerable amounts of heat that become manifest at the moment of the various chemical combinations between liquids, or between liquids and solids: and we want to attribute this heat to a decrease of the molecular speed of the compound, compared to the molecular speeds of the components at the same temperature.

[**Same comment as above: at a phase transition the specific heat can change but the average square velocity is the same in the two phases.**]

If then the specific heat is less in vapors than in the corresponding liquids, this is not a reason to suppose that the molecular kinetic energy results in vapors less than in liquids. First, in changing from liquid to gas state, molecules of a given substance receive all the thermal energy that corresponds to the vaporization calories of the liquid, so that such molecules decompose and diffuse through space against the external pressure. Second the temperature calories in the vapors, not having any longer to perform internal work, as in the liquid state, can be entirely used to perform external works, and therefore to generate heat upon combining with other bodies.

And for this reason it seems to us, at least in some cases, possible to submit, for what concerns the molecular speeds that given substances must have at the temperature of their reaction, to mathematical analysis whether the calories produced in the reaction result completely accounted, keeping into consideration the calories lost or gained as a consequence of the respective changes in the physical state.

6. –

I cannot restrain from remarking that the asserted different molecular speed in different bodies at the same temperature, finds a direct confirmation in the gaseous diffusion laws, so appropriately studied by Graham; and in the dissociations, as said above, it seems to me that it is confirmed by the decomposition phenomena that accompany the

expansion of liquid droplets or of solids laid at the surface of other liquids, according to the detailed observations of Fusinieri; by the gaseous condensations phenomena in porous solids and in liquids, and to a different extent for different gases and different temperatures; by the condensations and combustions that certain gases and vapors undergo at a the surface of spongy or laminar platinum, and by many other phenomena, commonly called of *presence* or of *contact*. These are phenomena for which no explanation has been proposed so far and that, nevertheless, seem to reveal the perturbation to the thermal vibrations of a given system of point masses due to vibrations very different in number or in extension of the other group of molecules that enters in contact with the first.

[**Diffusion speed does depend on the molecular speeds, which depend on temperature and the molecular mass. This however does not seem to support the arguments of Sec. 5.**]

7. –

But the repeated difference in the thermal vibrations seems to me even better confirmed by the curious motions called *Brownian*.

On such motions a lot has been already said. And certainly in some cases osmotic actions and reactions between the vibrating solid and the liquid around it could contribute to sustain them, as in the case of organic globules or vesicles. In other cases they could be caused by diffusion currents generated by a solid while dissolving in the medium, with different intensity in the verious points of its surface, thus provoking simoultaneous translation and rotation motions, depending on whether the resultant of the mutual pressures between liquid and solid passes or not throught the center of mass of the latter. But when considering inorganic solids or substances insoluble in the liquid, the above explanations of those motions cannot be easily accepted.

In fact I think the the dance-like motion of extremely minute solid particles within a liquid could be attibuted to the different speeds that, at the same temperature, must exist both in such solid particles and in the molecules of the liquid that hit them from every side.

I do not know whether others have already tried this way of explaining Brownian motions, but it seems to me that it is susceptible of testing. Because, other circumstances being equal, the same motions should be wider the more the differences in speed of the liquid and of the solid, i.e. of their specific heats. In fact for extremely small solid particles, being their surface very large compared to the volume, the action on them of the sum of the momenta communicated from the many liquid molecules, assiduously colliding with them because of their thermal vibrations, should be more effective.
[**Italics added**]

In order to subject such hypothesis to a check, I begun to observe that, for certain porous solids, finely grinded like a crunched brick, Brownian motions appear in the minutest particles and persist, even though they are left suspended in water for several days. Now, if such motions were due to wetting they should be over in a short time, or become less and less sensible.

Nor can one say that such motions arise from a slow and continuous dissolution of the solid within the liquid, because I observed that they are just slightly noticeable for minute particles of the water soluble solids; as it is easy to see with sodium chloride. Furthermore the fact that I observed, toghether with Prof. Oehl, that Brownian motions of some

organic globules, embedded in a thin liquid layer, between two microscope glasses sealed with asphalt, can continue beyond a year against any idea of wetting or solution as a cause for such motions.

8. –

It then happend to me to observe that all coloring substances prepared as painters commonly do show, although to a different extent, the said motions of their particles, which also remain for a long time suspended in water without dissolving. It even seems that their ability to float in the liquid, in spite of their larger specific weight, is due to their assiduous motion.

Then I thought of performing experiments on substances of well determined chemical composition, and therefore of known heat as well as specific density and correctly prepared and already reduced into minute dust by the exquisite kindness of my colleague BRUGNATELLI, chemistry professor.

I tried first with the metals, reduced from the respective oxydes by means of hydrogen, which appear in the form of the finest dusts. Silver, copper and iron suspended in distilled water, all show the dancing motion among their finest particles: but one must note that silver, although much denser, vibrates more rapidly than copper and the latter vibrates better than iron. These are differences which correspond to the lower specific heat of silver compared to copper, and of the latter compared to iron, so that for the first is largest the difference in specific heat with respect to water, a difference that gradually diminisces in copper and iron. Analogusly sulfur, which can also be obtained in extremely fine particles as a chemical precipitate, having a specific heat much larger even than that of iron, shows very limited motions and only in its minutest particles, even though its specific weight is barely a fifth of that of silver and a quarter of that of copper. Also carbon reduced to a fine dust, having a specific heat even higher than that of sulfur, exhibits a very scarse and shortly lived motions.[1]

Subsequently I tested some compounds with small specific heat, as mercury biiodure, mercury oxyde, lead oxyde, antimonium coated sulfur and lead carbonate, and all of them, which according to a micrometer are little different in size (wich is about $\frac{1}{1000}$ of a millimeter), did show very relevant dance like motions, and particularly the first three, whose specific heat is very small and yet have a large specific weight. All such particles, although so heavy, show a vorticous motion and at the same time a very rapid and extended vibratory one: and all such substances are insoluble in water. Using instead stronzium and zinc carbonate less extended motions were observed proportionally to their higher specific heat, and although their specific weight is less than that of lead carbonate. It is also worth pointing out the comparison between titanic acid and sulfide of antimonium $[Sb_2S_3]$, because they have almost equal density; but since specific heat of the first is almost double than in the second, the dance like motion is also much

---

[1] I have recently experimented with bismuth, lead, iridium, gold and platinum, also reduced into a very fine powder. Their specific heat is even less than that of silver. And, although their density is quite relevant, the Brownian motion was discernible in the smallest particles of all such materials, and quite stable in time, particularly in bismuth, lead and iridium. It is them worth noting that also small groups, formed by two or three gold particles, are seen to continue for a not short while their dance motion. Here it appears evident that in order that these metals particles, whose specific weight is between 18 and 20 times that of the liquid, can stay suspended and floating in water as an immediate effect and as a proof of heir assiduous state of motion.

Table I. – *In the following, for easier checks, the specific heat and the relative density of the tested subtances are reported*

Elements	Specific heats	Relative density	-	Compounds	Specific heats	Relative density
Bismuth	0.030	9.82	-	Lead. Iod	0.042	6.10
Lead	0.031	11.45	-	Lead Biox.	0.043	6.32
Gold	0.032	19.26	-	Lead Oxyd.	0.051	9.20
Platimun	0.032	19.50	-	Merc. Oxy.	0.052	11.00
Iridium	0.036	18.68	-	Antim. Sulf	0.084	4.33
Silver	0.057	10.47	-	Lead Carb.	0.086	6.73
Copper	0.095	8.70	-	Chrom. Stann	0.089	
Iron	0.114	7.60	-	Tin. Acid	0.093	6.70
Sulfur	0.203	2.07	-	Molib. Acid	0.032	
Carbon	0.241	1.50	-	Stron. Carb	0.141	3.65
			-	Zinc Carb	0.171	4.50
			-	Tit. Acid	0.172	4.25

smaller. Also the cobalt compounds, like the black oxyde and the arsenical colbat, having rather large specific heat, show very limited motions. On the opposite side the chromiun stannate and the sesquioxyde of uranium, which have small specific heat, are very interesting to watch, because of the turbinous agitation and the reciprocal collisions of their small vibrating particles.

It is a fact, then, that such inorganic particles motions are even more marked than those that micrographs revealed, since a long time, in globules and granules of several organic substances floating in water because, at least in general, the specific heat of these substances are less different from that of water than for the above inorganic substances.

To confirm the above explanation of Brownian motions I observed that alcohol exhibits them to a much less strong extent even in substances which are more mobile in water; because alcohol, having a much smaller specific heat than water, also shows a smaller difference between the specific heat of the liquid and that of the suspended solid. For an analogous reason the Brownian motions in benzine and ether are less strong.

Also the fact, on which Exner recently insisted, that such motions increase with temperature, is consistent with the princples exposed above about the different increment of molecular speed of the different substances as temperature increases.

At this point all the above illustrated cases contribute to conclude that the physical origin of Brownian motion resides in the different speed that molecules of different substances have at the same temperature. So that Brownian motion, so interpreted, provides us with one of the most beautiful and direct experimental proofs of the fundamental principles of the mechanical theory of heat, showing that an assiduous vibratory state has to exist both in liquids and solids even when their temperature does not change.
[**Italics added**].

Comment

[**The conclusion of this remarkable work, which in Sec. 8In f reports on a large number of experimentations on Brownian motion of different substances, is that the motion is due to collisions of the microparticles against the solvent molecules and that there is a strong anticorrelation between the specific heat and the intensity (*i.e.* diffusion coefficient) of the "dance" motion. In the first part of the paper an inverse proportionality between specific heat and molecular mass was discussed in simple metal ad gases. However the conclusions of this section indicate that at room temperature there is little correlation between molecular weight and specific heat or, therefore, Brownian motion intensity. Thus the paper may look somewhat contradictory: however it can be interpreted as saying that the inverse proportionality relation between specific heat and molecular weight which is observed in Dulong-Petit metals (high temperature) or rarefied gases breaks down when changing the temperature and what counts for the strength of the Brownian motion is really the specific heat. The explanation for the lack of inverse proportionality of the mean square speed to the density is not only not clear as presented, in particular through relations and analogies with sound speed theory or with a seemingly strange (and not convincing) account of chemical affinity, but it seems at odds with energy equipartition: which, however, in 1867 had not yet been discussed in Boltzmann's papers. One should retain the insight, ahead of times, of the molecular nature ot the "dance motions". See A. Pais, Subtle is the Lord: the science and the life of Albert Einstein, Oxford University Press, 1982, p.93.]. The works of Delsaulx and Carbonnelle published in the Royal Microscopical Society and in the Revue des Questions scientifiques, from 1877 to 1880 and of M. Gouy (1888), came much later.**

REFERENCES

[1] Cantoni G. , *Relazioni tra alcune proprietà termiche ed altre proprietà dei corpi,* Pavia, *Il Nuovo Cimento,* **14** (1861) ;
[2] Cantoni G. , *Relazioni tra alcune proprietà termiche ed altre proprietà dei corpi, (continuazione)* Pavia, *Il Nuovo Cimento,* **15** (1862) ;
[3] Cantoni G. , *Relazioni tra alcune proprietà termiche ed altre proprietà dei corpi, (continuazione)* Pavia, *Il Nuovo Cimento,* **15** (1862) ;
[4] Cantoni G. , *Relazioni tra alcune proprietà termiche ed altre proprietà dei corpi, (continuazione)* Pavia, *Il Nuovo Cimento,* **16** (1862) ;
[5] Cantoni G. , *Relazioni tra alcune proprietà termiche ed altre proprietà dei corpi, (continuazione e fine)* Pavia, *Il Nuovo Cimento,* **16** (1862) ;

Web: http://ipparco.roma1.infn.it