ENTROPY-INCREASE PRINCIPLE. PART 4*

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The paper discusses Heaviside's concept on universal energy dissipation applied to elucidate irreversibility.

Phenomenological thermodynamic theory raises at least two questions: 1) why thermodynamic laws wer discovered early and 2) why they have the universality inherent in fundamental laws of nature?

The answer to the first is almost obvious: heat is important in life and in human activities, and there are macroscopic sensors for it enabling one to sense heat and cold and to observe phenomena accompanying thermal processes, which thus provides for interpretation and generalization.

The second question is more difficult and requires examination. Heuristically speaking, interest attaches to extending Maxwell's electromagnetic theory to describe phenomena related to those for which it was set up, and the reasons of success in this.

The second law of thermodynamics (in view of its universality) is important in answering the second question: elucidation of the physical meaning (establishing the fundamental laws) of entropy increase (or the nature of irreversibiltity). Max Planck devoted much fruitful attention to these aspects, so I formulate the second question and avoid using many words by following his approach for two of the explanations he gave.

"The Carnot–Clausius principle is sometimes termed energy dissipation, particularly by English-speaking physicists, but that reflects only one aspect. There are irreversible processes whose final states show exactly the same, for example the diffusionof two ideal gases or further dilution to an already very dilute solution. Such a process does not produce any appreciable heat effect and in general no finite energy conversion (energy disaggregation does not exist); it occurs spontaneously for the unique reason thqt it corresponds to entropy increase. However, the most general and exhaustive expression for the content of the second law can be given only in terms of the entropy, whose increase is the most general measure of irreversibility" (pp. 102-103 of [1]).

"Nature in fact is interested only in entropy increase. By that statement I understand only that entropy in fact always increases precisely in the way that energy in fact always remains constant. Whether entropy has any more ghostly features is a topic I leave aside, since at present I am satisfied with the knowledge that it is a quantity that can be measured unambiguously.

However, I categorically deny the concept formulated by Heaviside, against which I have always battled, namely universal energy dissipation. If it is true that the energy of an ideal gas is dependent only on temperature, but not on volume, then the energy of a mixture of gases after mutual diffusion should remain precisely as it was at the start. Where here is the energy dissipation? That example in any case requires explanation.

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*The author proposes a model he uses to explain the relation between phase-transition enthalpies and certain other properties on the one hand and thermal-radiation characteristics on the other, which does not reflect the editors' view. The paper is published because it deals with major aspects of the relation between matter and thermal radiation. In previous parts, there is a close agreement between the calculated and experimental data, which may indicate a deeper relation between matter and thermal radiation than has so far been envisaged. The material in the paper should familiarize the reader with thinking in this area.

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I understand very well that the concept on energy dissipation can be preserved by introducing the concept of available or free energy, as has been done by Lord Rayleigh and by Helmholz. The irreversibility measure, as irreversibilty is universal and is equally applicable to all cases, can be found uniquely only in entropy increase" (pp. 109-110 of [1]).

I draw the following conclusions from Planck's statements.

1. Planck preferred an operational definition for entropy, which enables one to perform exact calculations.

2. Entropy is a state function, whose change is an unambiguous measure of the irreversibility in the process that transfers the system from one state to another. Entropy may be compared with the part of an iceberg above water, which can be measured and if that quantity is known for two states in the system, one can state how it would move (in the sense of increasing the above-water part). Planck leaves aside the causes or mechanisms providing this motion.

3. Planck uses the spontaneous concept in defining entropy increase in order not to consider the reasons (processes or mechanisms) leading to the increase and to avoid the need to consider the ghostly (physical) properties of entropy. Subsequently (in considering what constraints and why are imposed on it), that concept acted as a brake, in the same way as the instinct concept in biology (before bee language was interpreted).

4. Irreversibility (entropy increase) makes itself felt in the most general form and most clearly in thermal processes, and consequently it was used by Clausius in introducing the entropy concept. Thermal motion is a characteristic feature of the world in which we live [2].

5. Heaviside's approach is very interesting (by virtue of the clear physical significance), as are Planck's objections.

Planck gives an example and correctly notes that this requires an explanation. Not only that example, but virtually all physical phenomena and processes require explanations and new interpretations (from the energy dissipation viewpoint), i.e., a set of problems arises, and only the use of the spontaneous concept enable us to eliminate them on abandoning Heaviside's approach (we do not know the fundamental laws leading to irreversibility, and for that reason we assign the right to perform that part of the operation to the physical system, while the observational results are used in phenomenological theory).

Research on thermal phenomena can thus provide much towards explaining the factors causing irreversibility (entropy increase), and this in turn has a bearing on the interaction of thermal radiation with matter and leads to the approach given by Heaviside.

There is one clearly established reference point on this long and so far not entirely clear-cut path. When a high-energy photon interacts with matter, it may vanish and give rise to an electron—positron pair, i.e., we can say that a photon (radiation) on interacting with matter is localized in space and acquires entirely new features as regaards propagation and interaction with matter. One thus naturally suggests that the absorbed (localized) radiative component in the matter interacting with it acts as a medium having properties different from a radiation component in vacuum (such as the establishment of thermal equilibrium between bodies in a closed cavity whose wall temperature is kept constant). In research on radiation-matter interactions, considerable interest attaches to phase transitions, since one of the fundamental parameters difficult to reproduce, namely T, remains constant.

In [3], there are data on the latent heats of fusion and evaporation calculated from

$$Q_{\mathrm{m}} = \frac{a}{n} T_{\mathrm{m}}, \qquad (1)$$

$$Q_{\mathrm{e}} = 2aT_{\mathrm{e}}, \qquad (2)$$

where a comparison was made with measurements for elements in the periodic table, which gave satisfactory agreement.

(1) and (2) have been derived from the following physical concepts. A phase transition occurs at constant temperature and pressure, so the decisive part may be played by the component of the radiation at the maximum in the emission, i.e., photons having wavelength

$$\lambda = \frac{2898}{T_e}, \tag{3}$$

freuqency $\nu = c_0T_e/2898$ and energy $h\nu = hc/2898T_e$.

A photon is indivisible, and a molecule (atom) interactring with it obtains (localizes) the energy, while the energy obtained by one mole of substance if each molecule localizes one photon is

$$Q = Nh\nu = \frac{Nhc}{2898} T_e, \tag{4}$$

in which $a = Nhc/2898 = 41.28$ J/K.

Experiment gives the phase-transition heat as

$$Q_e = 2aT_e. \tag{5}$$

This expression can be interpreted as each molecule using (localizing) two photons at a certain frequency during the phase transition and acquiring new qualities (interaction in a new state of aggregation). The close agreement [3] between the calculated and measured values for all the elements indicates that this view has the right to be considered and tested.

In [4], wavelengths were calculated from (3) defining the peak emission at the transition temperature for each of the elements in the table and for certain compounds. There was close agreement with the lines in the spectra of these substances. The wavelengths at the peak emission at the transition temperatures for various substances and the absorption peaks coincided with those calculated from (3).

In [5], there is a comparison of wavelengths governing the maximum emission at the transition temperatures with measured laser wavelengths when the medium is provided by that substance. The agreement is satisfactory.

In view of this agreement, one concludes that radiation and its interactions with matter play a larger part in physics than has so far been assumed. Heaviside's approach to irreversibility (universal energy dissipation) is preferable to Planck's operational definition, since it has a clear-cut physical meaning, but in any case, as Planck remarks, it requires explanation. Particularly, one requires explanations for fundamental concepts such as energy forms, transformation mechanisms, and propagation laws. We consider Planck's statement: "If it is true that the energy of an ideal gas is dependent only on temperature, but not on volume, then the energy in a mixture of gases after they have diffuse into one another should remain precisely as it was before the start of diffusion. Where is the energy dissipation?"

Answer:

1) the gases constituting the mixture have differing spectral characteristics, so they localize different spectral ranges;

2) a gas contains localized radiation, and one feature of matter-radiation interaction is that a gas (the substance and the localized radiation) occupies all the volume accessible to it; and

3) if we have a mixture of gases, if this is inhomogeneous (in material or composition) and there is a radiative component (which the gas localizes selectively) that is distributed essentially unevenly, diffusion should be observed if 2) is correct.

Then to answer Planck's question, one needs to examine and elucidate the interaction between matter and thermal radiation. Here interest attaches to spectral characteristics in phase-transition regions, in particular the spectral dependence of the amount of heat taken up or given out by a body (material). Research on the interactions of laser radiation with matter can reduce the effort and produce an appreciable result more rapidly, particularly at last wavelengths corresponding to the emission maximum at phase transition points or in the temperature range covering the transition. A laser beam can play a part in researching the interaction of radiation with matter similar to that played by ideal gases and ideal crystals in research on the gaseous and solid states of aggregation.

An intersting point is that an excellent qualitative description exists for phenomena such as thermal conduction, thermoelectricity, diffusion, thermal diffusion, and the Peltier, Seebeck, Ettingshausen, Rigi—Leduc, and other effects (as regards order of magnitude for the thermal conduction, diffusion, and thermal diffusion), but at present the lack of the necessary data does not give a quantitative description when one considers irreversibility in the Heaviside approach.

Following Planck, we may formulate two topics whose elucidation whould improve substantially our concepts on irreversibilty (in Planck's or Heaviside's approaches).

1. Whether the simplicity in a gaseous system (homogeneous mixtures filling all the available volume) is the result of interaction between equilibrium thermal radiation and matter, i.e., whether the gas molecule motion and distribution is Brownian motion, whose cause arises from interaction with radiation (localized) in matter and equilibrium beteen the localized radiation and that entering from outside?

2. Whether the energy spectrum for a blackbody (Planck's radiation law) is a χ^2 distribution for the unobservable elementary interactions (of radiation and matter), which are subject to a Gaussian distribution, which appears attractive in view of the resonant form of interaction between matter and radiation.

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NEW CONSEQUENCES OF THE LINEAR MODEL OF THE PARAMETRIC EQUATION OF STATE

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New possibilities of applying the linear model of the parametric equation of state are shown; in reduced coordinates, this model is associated with a single determining similarity parameter b depending on the compressibility coefficient of the individual materials at the critical point Z_{cr}.

Analysis of the theoretical models and experimental data permits the hypothesis that the series of critical-amplitude complexes

$$A\Gamma/B^2,\ D\Gamma B^{\delta-1},\ \Gamma/\Gamma',\ A'/A,\ A_2/A \tag{1}$$

is universal [1], but only the universality of the complex

$$A_1\Gamma'/B^2 = \beta^2 \tag{2}$$

has been rigorously proven [2]. As well as the conventional notation for critical amplitudes [3], A_1 denotes the jump in isochoric specific heat at the boundary curve and A_2 is the corresponding quantity for the specific heat C_V at the boundary curve from the side of the single-phase reigon.

A linear model of the parametric equaiton of state is widely used to describe the thermodynamic properties of the individual materials in the critical region [4]

$$\begin{gathered}\Delta\mu = ar^{\beta\delta}\theta(1-\theta^2);\\ \Delta\rho = kr^{\beta}\theta;\\ t = r(1-b^2\theta^2),\end{gathered} \tag{3}$$

where $\Delta\mu = (\mu - \mu_\alpha)/(p_{cr}v_{cr})$; μ_α is an analytical function of the temperature; $\Delta\rho = \omega - 1 = \rho/\rho_{cr} - 1$, $t = \tau - 1 = T/T_{cr} - 1$. On the basis of the isolated curves, the variable θ has

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