

the SMI isn't just identical to the thermodynamic entropy, but the corresponding mathematical apparatus could in principle be used to formally derive the expressions for the latter. So that, yes, the functional interrelationship between the thermodynamic entropy and the probability is definitely plausible, but ... how could we formally prove this? Would it be possible at all?

The answer is affirmative, thank goodness! There are even several ways to fulfill the task. One of the conceptual keys to the solution had already been outlined by J. W. Gibbs in his famous book about statistical mechanics [17]. Specifically, he was one of the true adepts of the atomistic hypothesis, and had described his standpoint as follows:

... The laws of thermodynamics may be easily obtained from the principles of statistical mechanics, of which they are the incomplete expression, but they make a somewhat blind guide in our search for those laws. This is perhaps the principal cause of the slow progress of rational thermodynamics, as contrasted with the rapid deduction of the consequences of its laws as empirically established.

We may, therefore, confidently believe that nothing will more conduce to the clear apprehension of the relation of thermodynamics to rational mechanics, and to the interpretation of observed phenomena with reference to their evidence respecting the molecular constitution of bodies, than the study of the fundamental notions and principles of that department of mechanics to which thermodynamics is especially related.

Moreover, we avoid the gravest difficulties when giving up the attempt to frame hypotheses concerning the constitution of material bodies, we pursue statistical inquiries as a branch of rational mechanics. In the present state of science, it seems hardly possible to frame a dynamical theory of molecular action which shall embrace the phenomena of thermodynamics, of radiation, and of the electrical manifestations which accompany the union of atoms. Yet any theory is obviously inadequate which does not take account of all these phenomena. Even if we confine our attention to the phenomena distinctively thermodynamic, we do not escape difficulties in as simple a matter as the number of degrees of freedom of a diatomic gas. It is well known that while theory would assign to the gas six degrees of freedom per molecule, in our experiments on specific heat, we cannot account for more than five. Certainly, one is building on an insecure foundation, who rests his work on hypotheses concerning the constitution of matter.

Difficulties of this kind have deterred the author from attempting to explain the mysteries of nature, and have forced him to be contented with the more modest aim of deducing some of the more obvious propositions relating to the statistical branch of mechanics. Here, there can be no mistake in regard to the agreement of the hypotheses with the facts of nature, for nothing is assumed in that respect. The only error into which one can fall is the want of agreement between the premises and the conclusions, and this, with care, one may hope, in the main, to avoid".

J. W. Gibbs had clearly and logically perfectly shown how the notion of probability could in principle be introduced, when studying

experimental data, as well. Here we would only like to present a simple interpretational algorithm:

1. Thorough and systematic experimental data on EEC must first be obtained. But, mind that not every experimentally revealed EEC is a valid one [5-7]. Typically, one must use independent experimental approaches for one and the same specimen (set of specimens) to get enthalpy and entropy. If the latter both are obtained, say as a result of the conventional Arrhenius or van't Hoff analyses, this is not a physically-chemically interpretable EEC.
2. The conventional linear regression of the experimental enthalpy on the experimental entropy data must be found in the standard way, to reliably evaluate the a and T_c parameters in Equation 1. Only then, the "Carnot entropic parameter", a/T_c , can be determined.
3. The results thus obtained can be interpreted using own experimental data and the information known from the literature.

The algorithm is pretty easy in itself, with the third step being definitely the most non-trivial one. But this should not constitute any "inviolable fortification" for the specialists in the respective fields. A more detailed analysis and the corresponding examples could be borrowed from our recent publications [8,26,27], and the references therein).

Thermodynamics at nanoscale

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