

states accumulates the largest fraction of molecules.

The terms “enthalpy,” “entropy,” and “free energy” do not appear in the preceding outline, but they are present as weighted summations over the distribution functions.

Whether we use the language of thermodynamics or of statistical mechanics, we are concerned with huge assemblies of atoms and molecules. It is highly misleading to discuss the properties of a single molecule, large or small, in terms of changes in its free energy or chemical potential. Analysis of what happens to a long protein molecule under stress is properly treated in terms suitable for a mechanical model.

With that criticism aired, I applaud the authors for an otherwise fine article.

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Nelson, Powers, and Goldstein reply: We agree with Simon Bauer’s points, and we regret if we inadvertently implied anything to the contrary. In fact, we believe that the rise of single-molecule biophysics demands more than ever that we present a statistical-mechanical viewpoint of the concepts of entropy and free energy.

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Gap in Einstein’s Early Argument for Existence of Photons

During this the centennial year of Albert Einstein’s epochal papers from his miraculous year, I was prompted to read again his paper on the quantum nature of radiation.¹ Surprisingly, I found a gap in his earliest argument for the existence of photons, a gap that apparently has remained unnoticed up to the present.

Einstein’s argument was based on his proof that for sufficiently large frequencies the entropy of thermal radiation varies logarithmically with the volume, in the same manner it does in an ideal gas. He concluded that “monochromatic radiation of low density (within the range of validity

of Wien’s radiation formula) behaves thermodynamically as if it consisted of mutually independent quanta [photons] of magnitude $h\nu$,²¹ where ν is the frequency of the radiation and h is Planck’s constant. In a footnote Einstein also gave a derivation, based on his entropy–volume relation, for the familiar pressure–volume formula of an ideal gas. But substituting in this formula Einstein’s relation for the number of photons—that is, the energy of the monochromatic thermal radiation divided by $h\nu$ —results in an incorrect expression for the pressure. This

pressure is one-third of the energy density of the radiation, as was originally shown by Maxwell for the case of electromagnetic waves. Moreover, a kinetic-theory calculation of the pressure shows that this relation is also valid for photons.

Maxwell’s relation also played a fundamental role in Boltzmann’s derivation of the dependence of thermal radiation on the fourth power of the temperature, and in Wien’s derivation of the general dependence of the thermal energy density on both frequency and temperature. I have not found any evidence, however,

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