Entropy in Physics

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Abstract

Following worries that the entropy functions of classical thermodynamics and statistical thermodynamics were not equivalent, attention is drawn here to work by Lazar Mayants indicating that this is not the case and the two are, in fact, equivalent.

Introduction

Entropy has proved to present problems for physicists, both professionals and students, almost from the moment the idea was introduced. At least part of the problem has been associated with the question of what precisely entropy is physically. This is a question which has never been answered. However, an added issue has been the existence of something called 'entropy' in classical physics, where it's change is directly related to a change of heat, and in both statistical thermodynamics and information theory where entropy itself is defined in terms of probabilities. Seemingly, the first must be different from the other two and the question has been raised [1] as to whether all three may be thought the same, since the basis of the first is so different from that of the other two. However, just as studying the ideas of relatively unknown people, Wesley [2] and Mandelker [3], has led to a new approach to deriving the useful results normally associated with special relativity [4] and the study of the ideas of Lazar Mayants [5] has led to a different understanding of the nature of photons and light, so further study of the writing of Lazar Mayants [6] leads to a realisation that at least the first two functions referred to as entropy - those of classical and statistical thermodynamics - are seemingly one and the same. This seems an important point to publicise, particularly since it could well lead to a lessening of confusion about the whole idea of entropy as far as students especially are concerned. Note though that the new ideas presented here originate in the work of Lazar Mayants.

Some Useful Thermodynamic Preliminaries

The starting point for many discussions in classical thermodynamics is usually either the First Law or one of the traditional statements of the Second Law – either that due to Clausius or that due to Kelvin. It should be remembered from the outset that these two forms of the Second Law are at the heart of the subject; any other so-called forms of the Second Law –

apart from that due to Carathéodory - are, at best, derivations from one or other of these basic statements.

It often proves useful to consider the equation

$$d'Q = dU - d'W$$

which is a mathematical statement of the First Law and where dU is the difference in internal energy between two states and d'Q and d'W are increments of heat and work respectively. If an increment of purely mechanical work is considered then d'W = -pdV, where p represents pressure and V volume. The dashes indicate that d'Q and d'W are mathematically inexact differentials.

After some detailed argument [7], the Second Law may be used to show that the absolute temperature, T, is an integrating factor for the inexact differential d'Q and the result is normally written symbolically as

$$dS = d'Q/T.$$

It is this new function *S* which is termed the entropy in classical thermodynamics although, as may be noted from this basic equation, only *changes* in entropy are introduced in classical thermodynamics, *not* an absolute value. Also, it is clear that this new function is totally dependent on a heat change for its existence.

It is straightforward to note that combining the above two equations symbolising the First and Second Laws leads to

$$TdS = dU + pdV$$

provided attention is restricted to cases where the increment of work considered is of the purely mechanical kind.

Another function which often crops up in thermodynamics is the Helmholtz Free Energy which is defined by

$$F = U - TS$$

from which may be derived the incremental form

$$dF = dU - TdS - SdT.$$

Eliminating dU between this equation and that representing the combined First and Second Laws leads to dF = -pdV - SdT,

from which it is seen that

$$S = -\left(\frac{\partial F}{\partial T}\right)_V.$$

It then follows that

$$\frac{U}{T^2} = \frac{F}{T^2} + \frac{S}{T} = \frac{F}{T^2} - \frac{1}{T} \left(\frac{\partial F}{\partial T}\right)_V = -\frac{\partial}{\partial T} \left(\frac{F}{T}\right)_V$$

This is one of the neat steps introduced by Mayants [6] in his discussion of the point to be highlighted here. Up to this point, all the formulae and manipulations have been well-known; it is the introduction of this relationship which makes what follows feasible.

Relevant Results in Statistical Mechanics

If attention is restricted to the canonical ensemble, the equilibrium value of the probability p that the system of the ensemble has energy ε is given by

$$p = Z^{-1} \exp(-\beta \varepsilon)$$

where

$$Z = \sum \exp(-\beta\varepsilon)$$

is the partition function.

It follows that the average or internal energy is given by

$$U = \sum_{i=1}^{n} \frac{1}{Z} \varepsilon e^{-\beta \varepsilon}$$

and it readily follows [8] that

$$U = kT^2 \left(\frac{\partial lnZ}{\partial T}\right)_V$$

Comparing with the last equation of the previous section, it is seen that F = -kT lnZ

Then

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V} = k lnZ + kT \left(\frac{\partial lnZ}{\partial T}\right)_{V} = k lnZ + \frac{U}{T}$$

Again, from the expression for the probability that the system of the ensemble has energy ε , it follows that

$$lnp = -\frac{\varepsilon}{kT} - lnZ$$

Therefore, the mathematical expectation of $\ln p$ is easily seen to be

$$\overline{lnp} = -\frac{U}{kT} - lnZ$$

Hence, it follows that

where

$$lnW = -\overline{lnp}$$

S = klnW

These two final equations give a probabilistic interpretation of the entropy normally associated with classical thermodynamics and hence with that entropy whose change is irrevocably associated with a change in heat at some specified value of the absolute temperature.

Conclusion

It does seem from the above considerations that the entropies of classical thermodynamics and of statistical thermodynamics are the same even though their backgrounds are seemingly totally different. Although not considered here, the entropy associated with information theory would seem to be the same also since it and that of statistical thermodynamics are so similar. However, this final point possibly deserves further, more specific, examination.

References

[1] J. Dunning-Davies; "Entropy, or Entropies, in Physics?" http://viXra.org/abs/1610.0030 [2] J. P. Wesley; 2002, Selected Topics in Scientific Physics, (Benjamin Wesley, Blumberg) [3] J. Mandelker; 1954, Matter Energy Mechanics, (Philosophical Library, New York) [4] J. Dunning-Davies; 2013, Hadronic J.36, 1 http://viXra.org/abs/1304.0152 [5] L. Mayants; 1994, Beyond the Quantum Paradox, (Taylor & Francis, London) [6] L. Mayants; 1984, The Enigma of Probability and Physics, (Dordrecht, Reidel) [7] J. Dunning-Davies; 1996, Concise Thermodynamics, (Albion Publishing, Chichester) [8] E. S. R. Gopal; 1974, Statistical Mechanics and Properties of Matter, (Ellis Horwood Ltd., Chichester)