It is a simple matter to verify that the action

$$I = -\tfrac{1}{4} \int_\Omega (V_{\mu\nu} - V_{\nu\mu})(V^{\mu\nu} - V^{\nu\mu}) d^4x$$

$$+ \int_R \{p_\nu \dot{y}^\nu - [(p_\nu - eA_\nu)(p^\nu - eA^\nu)]^{1/2}\} d\tau \quad (24)$$

is unchanged under such a transformation. Assuming $\beta = 1 + \epsilon$, where ϵ is an infinitesimal parameter, we see that

$$\Delta A_n(x) = \epsilon[A_n(x) + V_{\nu n} x^\nu], \quad (25)$$

$$\Delta y^\nu(\tau) = \epsilon[-y^\nu(\tau) + \dot{y}^\nu(\tau)\tau], \quad (26)$$

$$\Delta \tau_{1,2} = -\epsilon \tau_{1,2}, \quad (27)$$

$$\delta x^\nu = -\epsilon x^\nu. \quad (28)$$

Thus, Eq. (19) takes the form

$$\int_S \left(-Lx^\nu + \frac{\partial L}{\partial V_{\nu n}}(A_n + V_{\mu n} x^\mu) \right) d^3 S_\nu$$

$$+ \left(M\tau - p_\nu y^\nu \right)_{\tau 1}^{\tau 2} = 0. \quad (29)$$

If the space-time region Ω is taken to be the region between the two planes $x^0 = t_1$ and $x^0 = t_2$, then our

conservation law can be written as

$$-\tfrac{1}{2}t \int F_{\mu\nu}(\mathbf{r},t) F^{\mu\nu}(\mathbf{r},t) d^3r - \tfrac{1}{2} \int F^{0\mu}(\mathbf{r},t) A_\mu(\mathbf{r},t) d^3r$$

$$+ M\tau - p_\nu y^\nu = \text{const}, \quad (30)$$

where $F_{\mu\nu} = V_{\mu\nu} - V_{\nu\mu}$.

It is apparent that, because of the term involving the proper time τ, the above equation is not a "conservation law" in the usual sense unless some means exist for determining τ without a knowledge of the particle's trajectory. If τ cannot be measured directly, then the above relationship is useful in that it allows the value of the proper time to be determined from a knowledge of the field, momentum, and position variables at one instant.

This conservation law is not new. It has been previously derived from the equations of motion by Havas.[8]

[8] P. Havas, Phys. Rev. 87, 898 (1952).

Third Law of Thermodynamics and Electromagnetic Zero-Point Radiation

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It is pointed out that the third law of thermodynamics, which has been verified experimentally for systems with electromagnetic interactions, is not part of traditional classical theory, and indeed is violated by hypothetical systems, such as an ideal gas, which exhibit equipartition of energy. In the context of quantum theory, the law may be understood from the description of thermodynamic systems as quantum systems having discrete energy levels. Along the same lines as a recent derivation of the blackbody radiation spectrum from classical theory involving classical electromagnetic zero-point radiation, it is shown that the third law holds in classical theory for all thermodynamic systems which interact (no matter how weakly) with electromagnetic radiation.

INTRODUCTION: SIGNIFICANCE OF THIRD LAW

THE third law of thermodynamics holds an ambiguous role in theoretical physics. Whereas the first two laws of thermodynamics express the fundamental ideas that heat is a form of energy and further that heat is disordered energy, no such fundamental significance can be ascribed to the third law. In the context of traditional classical theory, the third law is merely an experimental result for some systems with

electromagnetic interactions, which is indeed violated by the favorite model of classical theory, the ideal gas. Only within the context of quantum mechanics do we obtain a conceptual understanding of the third law. Phrased succinctly, the third law may be regarded as a statement that the experimentally observed thermodynamic systems are quantum systems having discrete energy levels.

Recently, it has been noted[1] that many aspects of phenomena generally described in terms of quantum statistical thermodynamics have quite natural explana-

[1] T. H. Boyer, Phys. Rev. 182, 1374 (1969). See, also, T. H. Boyer, ibid. 186, 1304 (1969).

tions in terms of continuous classical physics provided we recognize the possibility of fluctuating radiation in the universe—electromagnetic zero-point radiation. In this paper, we wish to point out that in this context the third law of thermodynamics may also be brought within the scope of classical theory. In this view, the third law is the expression of the fact that the observed thermodynamic systems interact with electromagnetic radiation.

As in our previous work, we will use the term "classical physics" to refer to physics involving continuous processes, in contrast to "quantum physics" involving discontinuous processes. By "traditional classical physics," we mean the physics developed along the lines laid down before the innovations of quantum theory at the beginning of this century.

STATEMENT OF THIRD LAW

The Nernst-Simon form of the third law asserts the following: The entropy change associated with any isothermal reversible process of a condensed system approaches zero as the temperature approaches zero. Other equivalent statements[2] of the third law, such as the Fowler-Guggenheim form involving the unattainability of the absolute zero, also appear in the literature. However, the Nernst-Simon form will be convenient for our present remarks.

An idea of what is involved in the third law may be obtained as follows. Assume we fix the mechanically available parameters a (such as volume) of some thermodynamical system. Starting at some temperature T_1, we decrease the temperature of the system toward $T \to 0$. We can, at least in principle, make accurate experimental measurements of the heat energy removed from the system and of the work done by the system. Assigning an arbitrary value of entropy to the system at temperature T_1 and then using the thermodynamic definition for change of entropy in a quasistatic reversible process

$$dS = \frac{dQ}{T} = \frac{dU + dW}{T}, \tag{1}$$

we obtain a curve for the entropy versus temperature such as the line AB in Fig. 1. Next we change some mechanical parameter of the system (such as the volume) from a to $a + \Delta a$ by a quasistatic, reversible isothermal process, and then again reduce the temperature reversibly to obtain the curve $AA'B'$.

From the ideas of heat expressed in the first two laws of thermodynamics, it is not clear that there is any relationship between the points B and B'. The third law of thermodynamics asserts that the entropy separation between B and B' vanishes as $T \to 0$,

$$\lim_{T \to 0} [S(a + \Delta a, T) - S(a, T)] = 0. \tag{2}$$

[2] See, for example, M. W. Zemansky, *Heat and Thermodynamics* (McGraw Hill Book Co., New York, 1957), 4th ed., pp. 396–401.
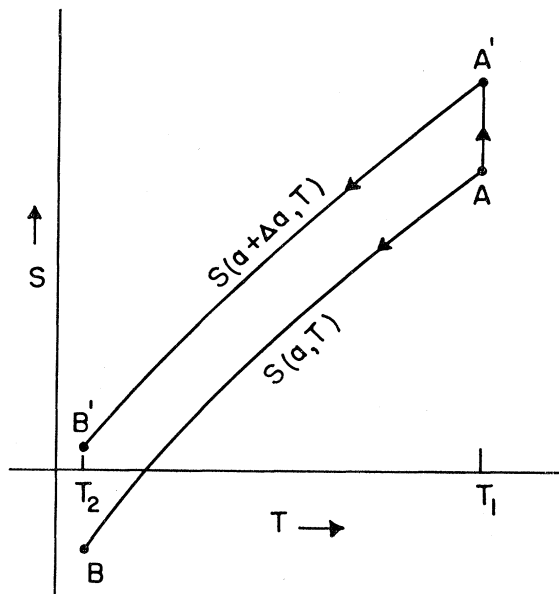

FIG. 1. Hypothetical curve of thermodynamic entropy versus temperature.

QUANTUM-THEORETICAL CONTEXT

On the traditional classical level, the third law is one of the supplementary postulates of thermodynamics, added in the light of experimental observation. However, in quantum theory, this thermodynamic postulate can be derived from the discreteness of quantum levels in statistical mechanics. The third law may thus be regarded as a statement of the quantum nature of the observed thermodynamic systems.

Thus consider the quantity

$$S = k \ln W, \tag{3}$$

where W is the number of ways of assigning particles among the discrete quantum states. If we assume that this quantity S really does reflect the thermodynamic entropy of the system, then at temperature $T = 0$ for a system with a unique ground state, all Bose-Einstein particles are in that unique state, $W = 1$ and $S = 0$. However, this proof that all quantum systems have $S = 0$ when $T = 0$ is somewhat unsatisfying. Suppose we think of noninteracting gas particles in a box. Then in going from A to A' by expanding the volume of the box and so changing all the quantum energy levels, it is not obvious that our thermodynamic measurements will give B' approaching B as $T \to 0$. The usual quantum proof is based upon the assumption that the stated *statistical* outlook really does represent the *thermodynamic* situation. It is not a direct proof of the coincidence of B and B' in the limit $T \to 0$.

Aside from the formal questions raised here, Kramers and Casimir[3] have criticized the usual derivation on the

[3] H. B. G. Casimir, Z. Physik **171**, 246 (1963). See also D. ter Haar, *Elements of Thermostatistics* (Holt, Rinehart and Winston, Inc., New York, 1966), 2nd ed., p. 292.

ground that it is irrelevant to the experimental situations in which the third law was discovered and is now invoked. The experimental question for macroscopic samples is not the separation off of the discrete ground state. Rather, it is the decrease in density of available quantum states as $T \rightarrow 0$ which may be said to account for the third law in the experimentally available temperature range.

THERMODYNAMICS INVOLVED IN PROOFS OF THIRD LAW

In order to derive the third law, it is clear that we must go outside of thermodynamics and into the domain of statistical mechanics. In this sense, all proofs of the third law require the assumption that the statistical outlook indeed represents the thermodynamic situation. However, there are many points at which we may choose to make the transition between statistics and thermodynamics. The following thermodynamic analysis gives a further understanding of the third law by shifting attention away from the Boltzmann relation[3] over to the energy-temperature relation in statistical mechanics. It also prepares the ground for a derivation of the third law in the context of classical theory with zero-point energy.

In a quasistatic, reversible, isothermal process, the change in thermodynamic entropy is given by Eq. (1). For explicitness in our analysis, we will take the parameter a in question as the volume of the system, and will assume that all work ΔW done on external surroundings is through the pressure p. Thus,

$$S(V+\Delta V, T) - S(V,T)$$
$$= \{U(V+\Delta V, T) - U(V,T) + p(V,T)\Delta V\}/T. \quad (4)$$

At temperature $T=0$, we must assume that the principle of virtual work holds; i.e., the increase in internal energy is due to the work performed *on* the system

$$\Delta U_0 + p_0 \Delta V = 0. \quad (5)$$

We emphasize that this assumption does not beg the question by assuming what is to be proved. For a universe at $T=0$, there is no heat energy available, and hence the first law requires Eq. (5), whereas the change in thermodynamic entropy from (1) involves zero divided by zero, and is indeterminate. In the case of a classical ideal gas, $\Delta W_0 = 0$ and $\Delta U_0 = 0$; for quantum particles in a box, the pressure at $T=0$ must be such that the change in the quantum energy levels equals the work done on changing the size of the box. Now assuming continuity in $U(T)$ and $p(T)$ as $T \rightarrow 0$,

$$U(V+\Delta V, T) \cong U(V+\Delta V, 0) + \left(\frac{\partial U(V+\Delta V, T)}{\partial T}\right)T,$$

$$U(V,T) \cong U(V,0) + \left(\frac{\partial U(V,T)}{\partial T}\right)T, \quad (6)$$

$$p(V,T) \cong p(V,0) + \left(\frac{\partial p(V,T)}{\partial T}\right)T.$$

Thus when we substitute the relations (6) and then simplify with (5), Eq. (4) becomes

$$S(V+\Delta V, T) - S(V,T) \cong \frac{\partial}{\partial T} U(V+\Delta V, T)$$
$$- \frac{\partial}{\partial T} U(V,T) + \left(\frac{\partial p}{\partial U}\right)_V \left(\frac{\partial U}{\partial T}\right)_V \Delta V. \quad (7)$$

Now every term on the right-hand side of Eq. (7) involves $(\partial u/\partial T)_V$. Provided that the pressure p does not change too rapidly with decreasing energy, the third law equation (2) follows if

$$\left(\frac{\partial U}{\partial T}\right)_V \rightarrow 0 \quad \text{as} \quad T \rightarrow 0. \quad (8)$$

This is the crucial aspect of the third law.

We should immediately note how the proofs of the third law from quantum statistical mechanics apply at this juncture between statistics and thermodynamics. At very low temperatures when the lowest quantum state does actually split off, then

$$U \propto \exp(-\epsilon_0/kT) \quad (9)$$

and

$$\frac{\partial U}{\partial T} \propto -\frac{\epsilon_0}{kT^2} \exp(-\epsilon_0/kT) \rightarrow 0 \quad \text{as} \quad T \rightarrow 0, \quad (10)$$

so that the third law indeed holds. In line with the criticism of Kramers and Casimir, we note that $\partial U/\partial T$ is a continuous function, and for all known substances becomes small for experimentally accessible temperatures so that the effects of the third law are indeed observed.

TRADITIONAL CLASSICAL IDEAL GAS

In order to emphasize that the significance of the third law of thermodynamics lies outside the ideas of traditional classical thermodynamics, we here review the behavior of a classical ideal gas at low temperatures. The equation of state is

$$PV = NkT, \quad (11)$$

while the internal energy is

$$U(T) = \tfrac{3}{2}NkT. \quad (12)$$

The entropy can be found accordingly[4] as

$$S = N\left[\tfrac{3}{2}k \ln\left(\frac{T}{T_0}\right) + k \ln\left(\frac{V}{N}\right) - k \ln\left(\frac{V_0}{N_0}\right) + s_0\right], \quad (13)$$

where T_0, V_0, N_0, and s_0 are constants appropriate to the choice of an entropy standard.

We first notice that

$$(\partial U/\partial T)_V = \tfrac{3}{2}Nk \quad (14)$$

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[4] See, for example, F. Reif, *Fundamentals of Statistical and Thermal Physics* (McGraw-Hill Book Co., New York, 1965), p. 160.

does not become small as $T \to 0$, so that we cannot immediately apply our proof of the third law. Moreover,

$$(\partial S/\partial V)_T = k/V \qquad (15)$$

does not become small as $T \to 0$, so that the system does not even satisfy the third law. Finally, holding N and V fixed,

$$S \to -\infty \quad \text{for } T \to 0,$$

so that the change in entropy as $T \to 0$ is infinite.

Clearly a classical ideal gas is entirely out of touch with the third law of thermodynamics. Moreover, it should be noted that the same is also true for every system satisfying the traditional classical equipartition theorem. For all these systems, we find the same basic behavior as for the classical ideal gas; energy varies linearly with temperature as $T \to 0$. One aspect of this situation is that there is no scale parameter (as there *is* in quantum theory) to indicate what is a low temperature. It seems apparent that some new understanding outside of traditional classical theory is necessary.

BLACKBODY RADIATION

We have just seen that the failure of classical systems to obey the third law of thermodynamics may be connected to the ideas of classical energy equipartition. It is most interesting to recall at this point that historically quantum mechanics was introduced precisely so as to avoid classical energy equipartition for radiation. In view of this historical connection, we will consider the blackbody radiation in terms of the third law.

Use of Maxwell's radiation pressure and of classical thermodynamics leads to the relations

$$U = \sigma T^4 V, \qquad (16)$$

$$S = \tfrac{4}{3}\sigma T^3 V, \qquad (17)$$

where U and S are the heat energy and entropy of electromagnetic radiation in a cavity of volume V. Here

$$(\partial U/\partial T)_V = 4\sigma T^3 V \to 0 \quad \text{as} \quad T \to 0, \qquad (18)$$

while

$$p = \tfrac{1}{3}U/V, \qquad (19)$$

so that our proof of the third law applies. Differentiating explicitly, we find

$$(\partial S/\partial V)_T = \tfrac{4}{3}\sigma T^3 \to 0 \quad \text{as} \quad T \to 0. \qquad (20)$$

In other words, thermal radiation satisfies the third law, and also the form of proof given above.

CLASSICAL THEORY WITH ELECTROMAGNETIC ZERO-POINT RADIATION

It is entirely consistent with the argument developed here to find that blackbody radiation indeed satisfies the third law of thermodynamics. Blackbody radiation was the first system to demonstrate clearly the failure of

energy equipartition in statistical mechanics, and we have noted that the failure of energy equipartition is connected with the validity of the third law of thermodynamics. In the terminology familiar today, the failure of energy equipartition is ascribed to quantum effects, and accordingly the third law of thermodynamics is to be regarded as an expression of this quantum nature of the observed thermodynamic systems.

However, it has been pointed out[5] within the context of classical theory that the traditional arguments for energy equipartition are erroneous. The arguments fail to recognize that all particles considered by traditional equilibrium thermodynamics must have electromagnetic interactions and must radiate on striking the container walls. Thus, for example, the traditional ideal gas fails to exist *in principle* for particles of finite mass. It has been shown that the inclusion of the ideas of interaction with the electromagnetic field leads naturally through classical theory to the idea of random fluctuating radiation in the universe. This electromagnetic zero-point energy leads to a derivation of the blackbody radiation spectrum and of the average energy of a classical oscillator which are in agreement with the results of quantum mechanics. The presence of electromagnetic zero-point energy will also cause a zero-point energy for all particles which have electromagnetic interactions (no matter how weak), and hence a reformulation of the thermodynamics of low temperatures is required. We will see that this reformulation of classical thermodynamics leads directly to the third law of thermodynamics. Thus in our view, the third law is an expression of the fact that the experimentally observed systems interact with electromagnetic radiation.

We will now show how zero-point energy of systems gives rise within classical theory to the condition (8) required for validity of the third law of thermodynamics.[6] It has been shown by Einstein and by others[7] that entropy S due to disordered energy should be connected to accompanying energy fluctuations ϵ as

$$k(\partial^2 S/\partial U^2)^{-1} = \langle \epsilon^2 \rangle, \qquad (21)$$

where U is the average energy. Throughout this section, the partial derivatives involve energy changes without work being performed by the system. If there is electromagnetic zero-point radiation present in the universe, then there are two sources for fluctuations: zero-point radiation, and caloric (heat) energy above the zero-point energy. The caloric entropy S_{cal} in thermodynamics [Eq. (1)] reflects only fluctuations due to heat energy associated with temperature T, and accordingly the caloric entropy must be connected only to fluctuations associated with heat energy. Assuming that the zero-point and caloric energy fluctuations are

[5] See the second work in Ref. 1.

[6] That the principle of virtual work required in Eq. (5) indeed holds for electromagnetic zero-point radiation can be shown in the case of the Casimir effect involving radiation between parallel plates: T. H. Boyer, Phys. Rev. **174**, 1631 (1968). See also L. S. Brown and G. J. Maclay, *ibid.* **184**, 1271 (1969).

[7] A. Einstein, Physik. Z. **10**, 185 (1909). See also Ref. 4.

independent, the mean squares will add:

$$k(\partial^2 S_{cal}/\partial U_{cal}{}^2)^{-1} = \langle \epsilon_{cal}{}^2 \rangle = \langle \epsilon_{tot}{}^2 \rangle - \langle \epsilon_0{}^2 \rangle. \quad (22)$$

The thermodynamic temperature T may be introduced through the definition (1) for thermodynamic entropy:

$$\partial S_{cal}/\partial U_{cal} = 1/T. \quad (23)$$

By differentiating (23) once with respect to U_{cal}, we obtain

$$\frac{\partial^2 S_{cal}}{\partial U_{cal}{}^2} = -\frac{1}{T^2}\frac{\partial T}{\partial U_{cal}}. \quad (24)$$

Combining (22) and (24), we arrive at

$$\frac{k\,dU_{cal}}{\langle \epsilon_{tot}{}^2 \rangle - \langle \epsilon_0{}^2 \rangle} = \frac{dT}{T^2}. \quad (25)$$

In order to use the relation (25) to obtain information about $\partial U_{cal}/\partial T$, we must relate the magnitude of the energy fluctuations to the magnitude of the energy. Now the energy fluctuations of a system can be expected to depend directly upon the total energy of the system, being larger for larger total energy. Thus, for example, if we consider free particles in a box, the fluctuations in kinetic energy density follow this pattern.[8] In the case of radiation or of oscillatory motion generally, the mean-square fluctuation in energy per normal mode is equal to the mean energy squared,

$$\langle \epsilon_{\omega\,tot}{}^2 \rangle = U_{\omega\,tot}{}^2. \quad (26)$$

However, in all cases, we must separate out the zero-point energy U_0 present at zero temperature from the additional heat energy U_{cal}:

$$U_{tot} = U_{cal} + U_0. \quad (27)$$

Thus there arises an interference effect such that the fluctuations associated with heat energy are larger than if there were no zero-point energy present. For radiation,

$$\langle \epsilon_{\omega\,tot}{}^2 \rangle - \langle \epsilon_{\omega 0}{}^2 \rangle = U_{\omega\,tot}{}^2 - U_{\omega 0}{}^2 = U_{\omega\,cal}{}^2$$

$$+ 2U_{\omega 0}U_{\omega\,cal}. \quad (28)$$

This is precisely the additional fluctuation effect which in the presently familiar quantum theory is assigned to the presence of quanta, to the presence of discrete units or levels of energy. This zero-point energy interference

phenomenon is what is usually described as an effect of the density of quantum states.

From fluctuation interference analogous to (28), it is easy to see that for small T the left-hand side of (25) behaves as $U_{cal}{}^{-1}$, whereas the right-hand side depends upon T^{-2}, and therefore $\partial U/\partial T \rightarrow 0$ as $T \rightarrow 0$. In the specific case[9] of radiation or of a harmonic oscillator of frequency ω, we may use (25) and (28) to obtain

$$\frac{k}{2U_0}\ln\left(\frac{U_{cal}+2U_0}{U_{cal}}\right) = \frac{1}{T} + C \quad (29)$$

or

$$U = \frac{2U_0}{\exp[2U_0/kT + (2U_0/k)C] - 1} + U_0, \quad (30)$$

where C is a constant and $U_0 = \tfrac{1}{2}\hbar\omega$. If we wish to find $E \sim kT$ at high temperatures, then we require $C = 0$. In any case, it is clear that as $T \rightarrow 0$, $\partial U/\partial T \rightarrow 0$. We indeed have conditions for proof of the third law of thermodynamics from within the context of classical theory including electromagnetic zero-point radiation.

CLOSING SUMMARY

Two of the laws of thermodynamics are crucial to the structure of thermodynamics. The first law may be regarded as a definition of heat in a manner expressing conservation of energy. The second law expresses the disordered nature of heat energy. The third law of thermodynamics has made its way into the literature, not so much in our intrinsic understanding of thermodynamics as on the level of an observation relevant to 20th-century low-temperature experiments on systems with electromagnetic interactions. The fact that the traditional classical ideal gas violates this law illustrates its expendable nature in most thermodynamic arguments. In this paper we have suggested that in the presently familiar quantum view of physics the third law is a statement that the experimentally observed thermodynamic systems are quantum systems. Alternatively, in the classical theory including electromagnetic zero-point radiation, the third law is the statement that the observed thermodynamic systems interact with electromagnetic radiation.

ACKNOWLEDGMENT

I wish to thank Professor Claude Kacser for helpful criticisms.

[8] A. Einstein, Sitzber. Deutsch. Akad. Wiss. Berlin, Math.-Phys. Kl. 1, 3 (1925). See also Ref. 4.

[9] The analysis also holds for a rigid dipole rotator. See T. H. Boyer, Phys. Rev. D 1, 2257 (1970).