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Comment on "A Classical Test of the Entropy Production Function. Compatibility with Kinetic Laws and Local Equilibrium"

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Sir: Chasteen and Spitzer[1] have given an expression for the local entropy production for constant volume systems which are capable of heat and mass transfer. This expression, which does not include the assumption of local equilibrium, is reproduced here[2] as follows:

$$\dot{\eta} = \vec{J}_q \cdot \vec{\nabla}\left(\frac{1}{T}\right) - \frac{1}{T}\sum \vec{J}_i \cdot \vec{\nabla}\mu_i + \left(\frac{\partial s}{\partial t} - \frac{1}{T}\frac{\partial u}{\partial t} + \frac{1}{T}\sum \mu_i \frac{\partial c_i}{\partial t}\right) \tag{1}$$

This is formula 4.1 of ref 1. When the accepted mathematical forms of the fluxes (namely, Fourier's law of heat conduction and Fick's law of mass diffusion) together with the definition of chemical potential for ideal solutions are substituted into 1, the result is

$$\dot{\eta} = \frac{\kappa}{T^2}|\vec{\nabla}T|^2 + R\sum \frac{D_i}{c_i}|\vec{\nabla}c_i|^2 + \left(\frac{\partial s}{\partial t} - \frac{1}{T}\frac{\partial u}{\partial t} + \frac{1}{T}\sum \mu_i \frac{\partial c_i}{\partial t}\right) \tag{2}$$

This is formula 4.2 of ref 1. The authors of ref 1 remarked[1] that (i) formula 1 is correctly reduced to the accepted expression for the local entropy production at a "stationary state" where the time derivatives of all thermodynamic state variables vanish, and (ii) each of the first two terms and the bracketed term in the second member of (2) are either positive or zero, therefore, $\dot{\eta} \geq 0$ as must be. Chasteen and Spitzer[1] then propose to perform a further and more stringent test on their expression by integrating $\dot{\eta}$ with respect to time and space for processes taking place in isolated conditions and between well-defined and conveniently chosen initial and final states. They[1] indicate that the thus computed net entropy changes, if compared to the values obtained by classical thermodynamic techniques, must give identical results. However, in practice they[1] found that, after assuming the applicability of the quoted kinetic laws, it was also necessary to assume local equilibrium (i.e., that the bracketed term of (2) vanishes for all times and at all positions) in order to obtain agreement between the results of the two methods for computing the net entropy changes. Therefore, we find that Chasteen and Spitzer[1] conclude that there are evidently connections between the assumptions of local equilibrium and accepted linear kinetic laws; they stated[1] that "one of only two possibilities must prevail; namely, either (1) local equlibrium and accepted linear kinetic laws accurately describe such nonequilibrium systems at all positions and times or (2) at some positions and/or some times both fail". This means such systems proceed following either both assumptions or neither, but never one without the other; local equilibrium implies and is implied by accepted linear kinetic laws.

In this comment we present an argument by which we disagree with the above-reproduced conclusions of Chasteen and Spitzer.[1] To this end it is sufficient to examine the particular case of heat transfer in a system identical with that described by them.[1] Such a system consists of an infinite flat plate of pure solid of thickness L. The faces are maintained at constant and equal temperatures, T_2, by contact with isothermal surroundings. The system is initially at a uniform temperature T_1, and spontaneously proceeds at constant volume to the final state of temperature T_2. The combination of the system and its surroundings constitutes an isolated system. The net entropy change between initial and final states of system and surroundings is[1] $\Delta S = \Delta S_{sys} + \Delta S_{surr}$. By introducing ρC_v (the constant volume heat capacity per unit volume) and assuming it to be independent of temperature, one can show by usual thermodynamic techniques that

$$\Delta S = \rho C_v AL\left[\ln \frac{T_2}{T_1} - \frac{(T_2 - T_1)}{T_2}\right] \tag{3}$$

which is formula 2.1 of ref 1.

Let us now consider the time and space integral of $\dot{\eta}$ in this heat-transfer case, ignoring the assumption of local equilibrium. Thus formula 1 is reduced to

$$\dot{\eta} = \vec{J}_q \cdot \vec{\nabla}\left(\frac{1}{T}\right) + \left(\frac{\partial s}{\partial t} - \frac{1}{T}\frac{\partial u}{\partial t}\right) \tag{4}$$

and following ref 1 we have

$$\Delta S = \int_0^\infty \int_V \dot{\eta}\, dV\, dt \tag{5}$$

where the volume integral is over the volume of the flat plate corresponding to the chosen area A. When the first term of the second member in (4) is integrated by parts, its contribution to ΔS is

$$A\int_0^\infty \left[\frac{J_q}{T}\bigg|_L - \frac{J_q}{T}\bigg|_0\right] dt - \int_0^\infty \int_V \frac{1}{T}\vec{\nabla}\cdot\vec{J}_q\, dV\, dt \tag{6}$$

Considering that (i) for every possible transition[3] (FEPT) between the already specified initial and final states of system and surroundings the net energy change is

$$\Delta U = \Delta U_{sys} + \Delta U_{surr} = 0 \tag{7}$$

(ii) ρC_v is a quantity defined from two fundamental ones: energy and entropy; from its definition in our case we have

$$\rho C_v = \Delta U_{sys}/AL(T_2 - T_1) \tag{8}$$

(iii) From the definition of $\vec{J}_q$, in our case we have FEPT

$$\partial U_{surr}/\partial t = A(J_q|_L - J_q|_0) \tag{9}$$

(iv) The faces of the plate are maintained at the temperature T_2; then FEPT

$$\frac{J_q|_L}{T_2} = \frac{J_q}{T}\bigg|_L \qquad \frac{J_q|_0}{T_2} = \frac{J_q}{T}\bigg|_0 \tag{10}$$

Integrating (9) with respect to time from the initial to the final states, and using (7) and (8), we obtain FEPT

$$\Delta U_{surr} = A\int_0^\infty (J_q|_L - J_q|_0)\, dt = -\Delta U_{sys} = -\rho C_v AL(T_2 - T_1) \tag{11}$$

(11) is simply a way of expressing energy conservation when using the definitions and the assumptions mentioned

above. Actually, (11) is in fact an integral condition which has to be imposed one way or another on any assumed kinetics (therefore to use the latter to reobtain (11) would necessarily imply a redundancy).

Finally, dividing (11) by T_2, and using (10), we can show that the first term of (6) must be FEPT

$$A\int_0^\infty \left[\left.\frac{J_q}{T}\right|_L - \left.\frac{J_q}{T}\right|_0\right] dt = -\rho C_v AL\frac{(T_2 - T_1)}{T_2} \quad (12)$$

which formally is the same expression as that in formula 2.13 of ref 1 but which has been shown here to be of absolute validity; Fourier's law and/or local equilibrium are irrelevant to the validity of eq 12.

For the second term of (6), if we do not assume local equilibrium the following equality is false:

$$-\int_0^\infty \int_V \frac{1}{T}\vec{\nabla}\cdot\vec{J}_q \, dV \, dt = \rho C_v AL \ln\left(\frac{T_2}{T_1}\right) \quad (13)$$

The reason for this is that when the system is not in local equilibrium it is not possible to write

$$-\rho C_v\left(\frac{\partial T}{\partial t}\right)_x = \vec{\nabla}\cdot\vec{J}_q \quad (14)$$

as is in the case of local equilibrium where then (13) is true. We explain this as follows: when there is no local equilibrium the state of the system at a given time is not determined only by the energy per unit volume u as a function of position but also by the set of the other field variables (needless to specify here and denoted generically by $\{\alpha\}$) which are not relaxed to their local equilibrium values $\{\alpha_{eq}\}$ as would be necessary, in fact, for local equilibrium (in our case the α_{eq}'s are only functions of u). Therefore, in the absence of local equilibrium, the time evolution of T is not simply $(\partial T/\partial t)_x = (dT/du)(\partial u/\partial t)_x$ with $dT/du = 1/\rho C_v$ as is in the case of local equilibrium, but the expression for $(\partial T/\partial t)_x$ is different due to the time variation of the $\{\alpha\}$ variables now being independent of that of u:

$$\left(\frac{\partial T}{\partial t}\right)_x = \left(\frac{\partial T}{\partial u}\right)_\alpha\left(\frac{\partial u}{\partial t}\right)_x + \sum_\alpha\left(\frac{\partial T}{\partial \alpha}\right)_u\left(\frac{\partial \alpha}{\partial t}\right)_x \quad (15)$$

Replacing $\partial u/\partial t = -\vec{\nabla}\cdot\vec{J}_q$ in (15) we obtain, after multiplication by $-\rho C_v$

$$-\rho C_v\left(\frac{\partial T}{\partial t}\right)_x = \rho C_v\left(\frac{\partial T}{\partial u}\right)_\alpha \vec{\nabla}\cdot\vec{J}_q - \rho C_v\sum_\alpha\left(\frac{\partial T}{\partial \alpha}\right)_u\left(\frac{\partial \alpha}{\partial t}\right)_x$$

which amounts to (14) in the case of local equilibrium because

$$\rho C_v = \left[\left(\frac{\partial T}{\partial u}\right)_{\alpha_{eq}} + \sum_\alpha\left(\frac{\partial T}{\partial \alpha}\right)_u\left(\frac{d\alpha_{eq}}{du}\right)\right]^{-1}$$

From our considerations on the two terms of (6) we see that (i) when there is no local equilibrium the bracketed term in (4) has a contribution other than zero to ΔS in every case of assumed kinetics, for example, a linear one such as $\vec{J}_q = -\kappa\vec{\nabla}T$;[4] therefore, to conclude that accepted linear kinetic laws imply local equilibrium would be wrong; (ii) in the case of local equilibrium the integral in (5) naturally is bound to give the result (3) in every case of assumed kinetics, either linear (Fourier's law) or not; therefore, to conclude that local equilibrium implies accepted linear kinetic laws would be wrong. Thus, we disagree with the conclusions of Chasteen and Spitzer[1] reproduced here.

References and Notes

(1) J. W. Chasteen and R. H. Spitzer, *J. Phys. Chem.*, **80**, 143 (1976).

(2) In this communication the undefined notation has the same meaning as that in ref 1.

(3) By "possible transition" we understand a path (on which energy is conserved and entropy does not decrease) in the set of all possible states of system and surroundings which is traversed at a certain rate; such a set includes every possible nonequilibrium state of the system, with or without local equilibrium.

(4) It must be made clear that we do not object to Chasteen and Spitzer's[1] formal use of T (and of $\vec{J}_q = -\kappa\vec{\nabla}T$) even in the case of no local equilibrium, as for example in their[1] eq 4.2.

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