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Definition of Heat in Open Systems

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Abstract

Existing definitions of heat in open systems are considered with the aim of providing acceptable physical motivation in restricted circumstances. The extent to which these definitions are independent of the usual concept of heat in closed systems is clarified: they all have the feature that internal energy may be transferred by convection in workless adiabatic processes. The global definitions are compared with various definitions of heat flux in irreversible thermodynamics. As the domain of applicability of these definitions is wider than that of equilibrium thermodynamics, it is suggested that a minimal check for any definition of heat flux be that it agree with the global definition of heat flow between equilibrium states in as wide a range of circumstances as possible.

1. Introduction

The question of how best to define heat transfer in open systems is not yet settled, although it was first raised many years ago. That a real generalization of closedsystem thermodynamics is required has been emphasized by Münster (1970): thus it is possible to increase the internal energy of an open system without doing work and without heat flow simply by adding more mass at the same temperature and pressure under adiabatic conditions. It is therefore expected that the usual version of the first law of thermodynamics for closed systems, namely dU = dQ + dW, will not be valid for open systems. Despite this, it is true that open systems can often be analysed by considering the motion of a fixed mass of the working fluid, as is done in engineering texts. However, this reduction to closed system thermodynamics can only be made after agreement has been reached on a suitable definition of heat.

For one-component systems, an agreed definition of heat is used by engineers for flow problems (see e.g. Rogers and Mayhew 1967). For multicomponent systems, Gillespie and Coe (1933) proposed, and partially motivated, a definition which reduces to the engineering version when the number of components is unity. In Sections 2 and 3 below we attempt to provide physical motivation for these definitions. In doing this, a convention is established that the heat flow into an open system is zero when the system, its supply tank and discharge tank are all surrounded by an adiabatic enclosure. This convention is partly a consequence of conventional notions of heat and partly an arbitrary device, depending on the physical conditions. For simplicity, all systems considered here are assumed to consist of one phase only.

In irreversible thermodynamics, which is usually formulated as a local rather than a global theory, there exist several definitions of heat flux. That due to Prigogine (1947; see also Glansdorff and Prigogine 1971) is most widely used, although many authors employ several non-equivalent definitions (see e.g. de Groot and Mazur 1962), while Haase (1953, 1969) uses a different definition, the so-called reduced heat flux, exclusively. The Prigogine definition of heat flux is usually justified by showing that the balance equation for internal energy per unit mass, following the centre of mass motion, agrees with the second law of thermodynamics for *closed* systems. But the balance equations of irreversible thermodynamics apply to open systems also. When comparisons with the global definition of heat are made for *open* systems, it is found that Prigogine's heat flux is consistent with the global definition only for systems of one component, but Haase's reduced heat flux is consistent in all cases.



Fig. 1. Thermodynamic process for a one-component fluid involving mass addition: (a) To the system, which is the fluid of the main chamber, (b) fluid is added by removing the common wall between the two chambers, and then (c) work and heat are supplied to the resulting closed system.

There are additional tests that can be used to discriminate between the various definitions. Both the Prigogine and the Haase definitions of heat flux are invariant under Galilean transformations. However, Haase's definition is also superior in that it is invariant under changes of standard values for the partial internal energies and entropies (Tolhoek and de Groot 1952).

2. Open One-component Systems

We will take the global definition of heat to refer only to a process connecting equilibrium states. No progress can be made until we have some notion of adiabatic processes for these systems. We choose to define adiabatic processes in these systems by requiring that the process for the original system plus its infinitesimal added mass, which together form a closed system, is adiabatic in the usual sense. With this definition it is possible to have workless adiabatic processes which increase the internal energy (see Fig. 1). Hence for open systems the first law of thermodynamics must be of the form

$$\mathrm{d}U = \mathrm{d}W + \mathrm{d}Q + \mathrm{d}R,\tag{1}$$

where dW is work done on the system, dQ is heat added according to the above convention and dR accounts for changes by addition of mass. Before dR can be specified we need to know the thermodynamic states of the original system and the added mass. Each state can be specified by two intrinsic variables, namely temperature and pressure, with values T and P for the system and T' and P' for the added mass. Furthermore, the initial state in each system is in equilibrium and therefore homogeneous, so the internal energies are U(T, P) and u(T', P')dM for the original system and the added mass respectively.

Three kinds of processes may be distinguished. In decreasing order of generality, they are:

- (A) completely irreversible;
- (B) mass-reversible, i.e. addition of mass takes place reversibly but the subsequent change is irreversible;
- (C) completely reversible.

Even in the general case A, a simple expression for dR follows by treating the original system plus added mass as a closed system, as suggested by Gillespie and Coe (1933). The internal energy change of this closed system in the process of Fig. 1 is (U+dU)-U-u'dM, so

$$dU - u' dM = dW + dQ \quad (case A)$$
(2)

is the normal statement of the first law for this closed system. This is of the form (1) with dR = u' dM. For mass-reversible processes, the temperatures and pressures of the two systems before addition must be equal. This is the case with continuous flow systems, although the conventional analysis of such systems is more general in that the initial and final states are not equilibrium states. Thus the added mass has the same intrinsic variables as the original system; in particular u' = u, so

$$dU = dW + dQ + u dM \quad (case B).$$
(3)

The technique of changing the boundary shows that no extra generality in the theory is required for open one-component systems. This can be verified explicitly for mass-reversible systems, where the total system (original system plus added mass) is initially homogeneous. We then expect that the work done and the heat entering per unit mass, namely

$$dw = dW/M$$
 and $dq = dQ/M$, (4)

obey the relation

$$\mathrm{d}u = \mathrm{d}w + \mathrm{d}q\,,\tag{5}$$

which is the first law for a closed system. This result follows immediately from equation (3).

For completely reversible processes, the work done can be expressed in terms of state variables. As the volume change is (V+dV) - V - v dM, we have

$$\mathrm{d}W = -P(\mathrm{d}V - v\,\mathrm{d}M) = -PM\,\mathrm{d}v,\tag{6}$$

showing that any work done necessarily changes the specific volume v. Addition of mass at the same density is a workless process. Substitution in equation (3) gives

$$dU = -P dV + dQ + h dM \quad (case C),$$
(7)

where h is the enthalpy per unit mass, that is, h = u + Pv.

Another way of expressing equation (7) is to write dq = T ds, which follows by using equations (4). This is a generalization of the Carnot-Clausius equality, and has the attractive feature that heat flow necessarily increases the entropy density. Thus in homogeneous one-component systems the mass is almost an irrelevant variable; all changes can be described by using the laws of closed-system thermo-dynamics on thermodynamic densities. This situation does not persist for multi-component systems.

The order of operations detailed in Fig. 1 is not important for an infinitesimal process. The system can suffer an infinitesimal closed change *before* mass is added rather than afterwards, the difference being of second order in infinitesimal quantities. The same equations can also be shown to apply to the case of mass loss if dM is negative.

3. Open Multicomponent Systems

For simplicity we consider multicomponent systems without external forces and chemical reactions, although the extensions required to include these are trivial.

For the completely irreversible case A, the addition of mass dM of a fluid with intrinsic variables T', P', x' (where the $x = x_1, ..., x_n$ are the mass fractions of the *n* components) to a fluid of mass *M* in state *T*, *P*, *x* leads to a first law of form (1) with

$$\mathrm{d}R = \sum_{i} u_i' \mathrm{d}M_i, \qquad (8)$$

where u'_i is the partial internal energy per unit mass of component *i*, dM_i is the added mass of that component, and the convention for defining heat is as proposed in Section 2. The usual definition of partial quantities is used, namely

$$u_i = (\partial U / \partial M_i)_{T, P, M'} \qquad (M' = \{M_j; j \neq i\}).$$

For a mass-reversible process (case B), each component must be added reversibly, with additional irreversible changes on the closed systems formed after each addition. Again, the order of operations is not important if the processes are infinitesimal. There are various physical arrangements for adding components reversibly, but the most convenient for our purposes is shown in Fig. 2. The added masses in each of the vertical cylinders are all at the same temperature, pressure and chemical composition as the main system, but each cylinder i (i = 1, ..., n) is fitted with a membrane permeable only to species i. Each vertical piston is used to displace an infinitesimal

mass dM_i into the main chamber. Subsequent changes of a closed-system variety can be carried out by clamping these pistons and using the piston of the main chamber. Thus $u'_i = u_i$ and $v'_i = v_i$, where u_i and v_i are values for the main chamber, and so



$$dU = dQ + dW + \sum_{i} u_{i} dM_{i} \quad \text{(case B)}.$$
(9)

Fig. 2. Process for a general change of state in a multicomponent fluid. Masses $dM_1, dM_2, ...$ of fluid at the same temperature, pressure and composition as the fluid of the main chamber are added through semipermeable membranes 1, 2, ... The net work done by all pistons is dW, and heat dQ enters through the surrounding wall.

For a completely reversible process (case C), the work done is

$$\mathrm{d}W = -P\left(\mathrm{d}V - \sum_{i} v_{i} \,\mathrm{d}M_{i}\right) \tag{10}$$

and hence

$$dU = -P dV + dQ + \sum_{i} h_i dM_i \quad \text{(case C)}, \qquad (11)$$

where $h_i = u_i + Pv_i$ is a partial enthalpy. This is the definition suggested by Gillespie and Coe (1933). There is an alternative form, namely

$$\mathrm{d}Q = T\sum_i M_i \,\mathrm{d}s_i$$

Note that the result (11) is different from what one gets by using the process of Fig. 1 with a multicomponent fluid. This would lead to equation (11) with the last term replaced by $\bar{h} dM$, where

$$\bar{h} = M^{-1} \sum_{i} h_i M_i \tag{12}$$

is the mean enthalpy per unit mass. The difference between the two terms is just the quantity $h_i(dM_i - M_i dM/M)$ summed over each component. In fact both results are correct in the context of Fig. 1, because that process merely adds more fluid of

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the same composition, that is, $dM_i/dM = M_i/M$. This illustrates an important point, namely that the processes considered must be sufficiently general to include all possible changes of state. To include composition changes and to carry them out reversibly requires the use of semipermeable membranes, as was realized by van't Hoff.

Other physical arrangements may be used to change composition, either reversibly or not. However, equation (8) remains true whatever apparatus is used. For massreversible processes, an alternative arrangement is to fill the vertical cylinders of Fig. 2 with infinitesimal amounts $dM_1, dM_2, ...$ of pure components of types 1, 2, ... and adjust the pressures in those cylinders to the membrane pressures $P_1, P_2, ...$ of the corresponding components in the main chamber. The temperatures in all chambers are to be equal. With the pure fluids prepared in this way, they will be in thermal, mechanical and chemical equilibrium with the main fluid mixture, and by pushing each vertical piston down to zero volume the mixing is again carried out reversibly. However, the work done, in general, is not given by equation (10). The work of mixing is formally equal to

$$\sum_{i} P_i v_i^{\phi}(T, P_i) \,\mathrm{d}M\,,\tag{13}$$

where v_i^{ϕ} is the specific volume of the pure component *i*. This should be compared with the result $Pv_i(T, P, x) dM_i$ appearing in equation (10). Formally, the membrane pressures are determined from the condition of chemical equilibrium, which for component *i* is

$$\mu_i(T, P, x) = \mu_i^{\phi}(T, P_i) \tag{14}$$

in terms of the chemical potentials (μ_i^{ϕ} is actually the Gibbs energy per unit mass for pure *i*). The specific volumes are also related through the expressions

$$v_i = (\partial \mu_i / \partial P)_{T,x}, \qquad v_i^{\phi} = (\partial \mu_i / \partial P_i)_T, \tag{15}$$

so that equations (14) and (15) determine P_i and v_i^{ϕ} in terms of the state variables of the mixture. For a perfect gas mixture one can show that $Pv_i = P_i v_i^{\phi}$, but in general this is not true and the two arrangements lead to different expressions for the heat increment.

We are thus confronted with the unsatisfactory situation that, even with the convention of Section 2 for adiabatic processes, the expression for heat in open multicomponent systems depends on the process chosen, even in the purely reversible case. To introduce some order into this situation, it is useful to distinguish the following two types of processes.

- (1) Processes of the first kind: the added fluid is at the same temperature, pressure and composition as the original fluid.
- (2) Processes of the second kind: the added fluid is in a different state.

Those of the first kind imply that the thermodynamic variables are continuous across the boundary of the original system. Thus it is these processes that can be compared with those of irreversible thermodynamics, where the existence of local equilibrium at each point of the fluid is assumed. Local equilibrium implies that the intrinsic thermodynamic variables are continuous functions of position.

If one is prepared to accept the restriction to processes of the first kind, then it appears likely that the arrangement of Fig. 2 is unique, at least for mass-reversible