

A Connection Between

TRANSPORT PHENOMENA AND THERMODYNAMICS

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The core subjects of thermodynamics and transport phenomena, taught in separate courses, tend to be internalized by students as seemingly unrelated subjects, despite the significant overlaps in their underlying physical principles. In introductory thermodynamics the macroscopic energy balance usually is presented by constructing a macroscopic envelope, defining the accumulation, and identifying various flow terms through the envelope (*e.g.*, Reference 1, Eq. 3.1-4, Reference 2, Eq. 3-63). The result is then readily applied to many useful problems. Even so, complications may arise in correctly representing the terms that appear. Examples include possible work by shear forces at the boundary, proper integration of work and heat fluxes when not uniform over areas, and proper integration of velocities for kinetic energy and internal energies when not uniform over the volume or flow areas.

Macroscopic entropy balances can be developed similarly, although the macroscopic entropy generation term appears. This macroscopic balance tends to receive less application. In practical cases the generation term often evades simple determination, and application is often limited to idealized reversible processes.

Many practical problems involve fluids contained within solid boundaries, and so the heat and work flows and their irreversibilities can be understood by examining a fluid continuum with diffusion of momentum (Newton's law) and heat (Fourier's law). The microscopic energy and entropy balances developed in transport phenomena^[3] capture the details of behavior at each point. Additionally, these balance equations may be formally integrated to arrive at the macroscopic balances. In the process, the proper forms for the various integrated terms are naturally obtained, and irreversibilities are precisely identified and explained. Moreover, one may further show that the fundamental relations taught in thermodynamics do not require assumptions about reversible changes, but hold quite generally, and naturally accommodate irreversibilities. With the assumption only of local equilibrium, most common macroscopic system behaviors can be represented.

Presentation of this analysis can help clarify many of the complications that may make the thermodynamics balances seem vague. It can also help students unify their understanding of the two subjects. It is particularly interesting to see how the

dissipation terms are absorbed and cancel in the result. While easily presented in a graduate course, a version of the main ideas for an undergraduate course should likewise be possible.

The general procedure involves integrating the microscopic balances over a macroscopic volume $V(t)$ and then converting from the fixed frame to the frame of the material within $V(t)$. The conversion is accomplished by combining the Leibniz formula

$$\frac{d}{dt} \int_{V(t)} f dV = \int_{V(t)} \frac{\partial f}{\partial t} dV + \int_{A(t)} \mathbf{n} \cdot f \mathbf{u} dA \quad (1)$$

with the Gauss divergence theorem

$$\int_{V(t)} \nabla \cdot f \mathbf{u} dV = \int_{A(t)} \mathbf{n} \cdot f \mathbf{u} dA \quad (2)$$

to obtain the relation

$$\frac{d}{dt} \int_{V(t)} f dV = \int_{V(t)} \frac{\partial f}{\partial t} dV + \int_{V(t)} \nabla \cdot f \mathbf{u} dV \quad (3)$$

R. Byron (Bob) Bird received his B.S. in chemical engineering from the University of Illinois (UIUC) in 1947 and his Ph.D. in chemistry from the University of Wisconsin-Madison in 1950. In 1953, Professor Olaf Hougen invited Bob to join the faculty at UW, to take over the responsibility for the courses in thermodynamics. However, shortly before Bob's arrival in Madison, Bob Marshall was elevated to be associate dean of the College of Engineering, and Bob had to take over the courses in fluid dynamics and mass transfer. In the ensuing years, he worked with W.E. Stewart and E.N. Lightfoot to develop a textbook on transport phenomena and never taught a course in thermodynamics!



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In Eqs. (1)–(3), \mathbf{u} is the velocity of the boundary of $V(t)$. Below we will choose \mathbf{u} to be the local fluid velocity \mathbf{v} , and so obtain fundamental closed system macroscopic balances. We note that alternatively choosing $V(t)$ to be fixed in space will lead to open system macroscopic balances after integration and application of Eq. (2) to convert the divergence terms to the surface integrals defining the flow terms.

ENERGY BALANCE

In the recently published textbook, *Introductory Transport Phenomena*,^[3] the equation of change for the total energy (*i.e.*, kinetic plus internal energy) for a pure fluid is given in Eq. 11.1-7 as

$$\frac{\partial}{\partial t} \left(\frac{1}{2} \rho v^2 + \rho \hat{U} \right) + \nabla \cdot \left(\frac{1}{2} \rho v^2 + \rho \hat{U} \right) \mathbf{v} = -\nabla \cdot (\mathbf{q} + \mathbf{w}) + \rho \mathbf{v} \cdot \mathbf{g} \quad (4)$$

Here \hat{U} is the internal energy per unit mass of fluid, \mathbf{g} is the gravitational acceleration vector, \mathbf{q} is the heat flux vector, and $\mathbf{w} = [\boldsymbol{\pi} \cdot \mathbf{v}] = [(\rho \boldsymbol{\delta} + \boldsymbol{\tau}) \cdot \mathbf{v}] = \rho \mathbf{v} + [\boldsymbol{\tau} \cdot \mathbf{v}]$ is called the work flux vector; p is the pressure, $\boldsymbol{\delta}$ is the unit tensor, $\boldsymbol{\pi}$ is the total stress tensor, $\mathbf{v}(\mathbf{r}, t)$ is the local fluid velocity vector with respect to fixed coordinates, and $\boldsymbol{\tau}$ is the viscous stress tensor. Eq. (4) is obtained in Reference 3 by applying the law of conservation of energy to a differential element fixed in space, through which a pure fluid is flowing.

In the textbook, it is intimated that one can get from Eq. (4) to the usual statement of the first law of thermodynamics

$$\Delta U = Q + W \quad (5)$$

although a justification of this statement is not presented. This equation states that the internal energy of a closed system changes as one goes from one equilibrium state to another equilibrium state because heat is added to the system and/or work is done on the system. Although some might say that it is obvious that Eq. (5) comes from Eq. (4), we feel that a presentation of the proof is warranted.

We select a volume $V(t)$ moving and deforming with the fluid, and this will be the system of interest; this element does not exchange mass with the surrounding fluid. The volume element $V(t)$ has a surface area $A(t)$, every element of which is moving with the local velocity $\mathbf{v}(\mathbf{r}, t)$. Integration of Eq. (4) over the volume $V(t)$ gives

$$\int_{V(t)} \frac{\partial}{\partial t} \left(\frac{1}{2} \rho v^2 + \rho \hat{U} \right) dV + \int_{V(t)} \nabla \cdot \left(\frac{1}{2} \rho v^2 + \rho \hat{U} \right) \mathbf{v} dV = - \int_{V(t)} \nabla \cdot (\mathbf{q} + \mathbf{w}) dV + \int_{V(t)} \rho \mathbf{v} \cdot \mathbf{g} dV \quad (6)$$

Application of Eq. (3) then gives

$$\frac{d}{dt} \int_{V(t)} \left(\frac{1}{2} \rho v^2 + \rho \hat{U} \right) dV = - \int_{A(t)} \mathbf{n} \cdot (\mathbf{q} + \mathbf{w}) dA + \int_{V(t)} \rho \mathbf{v} \cdot \mathbf{g} dV \quad (7)$$

We may integrate this equation with respect to time from t_1 to t_2 to get

$$\left[\int_{V(t)} \left(\frac{1}{2} \rho v^2 + \rho \hat{U} \right) dV \right]_{t_1}^{t_2} = - \int_{t_1}^{t_2} \int_{A(t)} \mathbf{n} \cdot (\mathbf{q} + \mathbf{w}) dA dt + \int_{t_1}^{t_2} \int_{V(t)} \rho \mathbf{v} \cdot \mathbf{g} dV dt \quad (8)$$

We now define the following quantities

$$U(t) = \int_{V(t)} \rho \hat{U} dV = \text{the total internal energy within } V(t) \quad (8.1)$$

$$K(t) = \int_{V(t)} \frac{1}{2} \rho v^2 dV = \text{the total kinetic energy within } V(t) \quad (8.2)$$

$$Q = -\int_{t_1}^{t_2} \int_{A(t)} \mathbf{n} \cdot \mathbf{q} dA dt = \text{the total heat added to } V(t) \text{ between } t_1 \text{ and } t_2 \quad (8.3)$$

$$\begin{aligned} W &= -\int_{t_1}^{t_2} \int_{A(t)} \mathbf{n} \cdot \mathbf{w} dA dt + \int_{t_1}^{t_2} \int_{V(t)} \rho \mathbf{v} \cdot \mathbf{g} dV dt \\ &= \text{the total work done on } V(t) \text{ between } t_1 \text{ and } t_2 \end{aligned} \quad (8.4)$$

Then Eq. (8) may be rewritten as

$$[U(t_2) + K(t_2)] - [U(t_1) + K(t_1)] = Q + W \quad (9)$$

We now consider the two times t_1 and t_2 correspond to two equilibrium states. If we restrict consideration to initial and final systems at rest, there will be no kinetic energy within $V(t)$ at t_1 and t_2 , and the terms $K(t_1)$ and $K(t_2)$ may be omitted, leaving us with

$$\Delta U = U(t_2) - U(t_1) = Q + W \quad (10)$$

in which ΔU represents the increase in internal energy in the system as one goes from one equilibrium state to another, because of heat being added to the system and work being done on the system. For some fascinating reading about the history of Eq. (10) and the personalities involved, see the text leading up to Eq. 3.37a of Reference 4.

For another view of the problem at hand, we can subtract the equation of change for kinetic energy (Eq. 3.3-1 of Reference 3)

$$\frac{\partial}{\partial t} \left(\frac{1}{2} \rho v^2 \right) + \nabla \cdot \frac{1}{2} \rho v^2 \mathbf{v} = -\nabla \cdot \rho \mathbf{v} + \rho \nabla \cdot \mathbf{v} - \nabla \cdot [\boldsymbol{\tau} \cdot \mathbf{v}] + \boldsymbol{\tau} : \nabla \mathbf{v} + \rho \mathbf{v} \cdot \mathbf{g} \quad (11)$$

from Eq. (4) above and obtain the equation for internal energy (Eq. 11.2-1 of Reference 3):

$$\frac{\partial}{\partial t} (\rho \hat{U}) + \nabla \cdot \rho \hat{U} \mathbf{v} = -\nabla \cdot \mathbf{q} - p \nabla \cdot \mathbf{v} - \boldsymbol{\tau} : \nabla \mathbf{v} \quad (12)$$

Then, integrating Eq. (12) over the volume $V(t)$, we apply Eq. (3) to the terms on the left and the Gauss divergence theorem to the first term on the right, to give

$$\frac{d}{dt} \int_{V(t)} \rho \hat{U} dV = -\int_{A(t)} \mathbf{n} \cdot \mathbf{q} dA - \int_{V(t)} p \nabla \cdot \mathbf{v} dV - \int_{V(t)} \boldsymbol{\tau} : \nabla \mathbf{v} dV \quad (13)$$

Integrating over time, we get

$$\left[\int_{V(t)} \rho \hat{U} dV \right]_{t_1}^{t_2} = -\int_{t_1}^{t_2} \int_{A(t)} \mathbf{n} \cdot \mathbf{q} dA dt - \int_{t_1}^{t_2} \int_{V(t)} p \nabla \cdot \mathbf{v} dV dt - \int_{t_1}^{t_2} \int_{V(t)} \boldsymbol{\tau} : \nabla \mathbf{v} dV dt \quad (14)$$

We denote the first two terms of Eq. (14) as we did in going from Eq. (8) to Eq. (9). In the third term, we replace the variable p by its average value

$$\bar{p} = \frac{\int_{V(t)} p \nabla \cdot \mathbf{v} dV}{\int_{V(t)} \nabla \cdot \mathbf{v} dV} \quad (15)$$

and apply the Gauss divergence theorem to the resulting term. This gives

$$U(t_2) - U(t_1) = Q - \int_{t_1}^{t_2} \bar{p} \int_{A(t)} \mathbf{n} \cdot \mathbf{v} dA dt - \int_{t_1}^{t_2} \int_{V(t)} \boldsymbol{\tau} : \nabla \mathbf{v} dV dt \quad (16)$$

Next, we take $t_2 - t_1$ to be differentially small, dt . Noting that

$$dV = \int_{A(t)} \mathbf{n} \cdot \mathbf{v} dA dt, \text{ we may then write}$$

$$dU = dQ - \bar{p} dV - \int_{V(t)} \boldsymbol{\tau} : \nabla \mathbf{v} dV dt \quad (17)$$

Many practical problems involve fluids contained within solid boundaries, and so the heat and work flows and their irreversibilities can be understood by examining a fluid continuum with diffusion of momentum (Newton's law) and heat (Fourier's law).

The last term in this equation is an irreversible term containing a sum of products of velocity gradients (for Newtonian fluids). It indicates that, to get from one thermodynamic state to another, some irreversible processes must occur if there is volume change or deformation. (While the integral itself is negative, the dissipation term is positive because $(-\boldsymbol{\tau} : \nabla \mathbf{v})$ is positive^[3, §3.3])

ENTROPY BALANCE

To proceed further, we introduce the equation of change for entropy. By combining Eqs. 24.1, 2, and 3 of Reference 3, we get

$$\rho \frac{D\hat{S}}{Dt} = -\nabla \cdot \mathbf{s} + g_s = -\nabla \cdot \frac{1}{T} \mathbf{q} - \left(\frac{1}{T^2} \mathbf{q} \cdot \nabla T + \frac{1}{T} \boldsymbol{\tau} : \nabla \mathbf{v} \right) \quad (18)$$

in which \hat{S} is the entropy per unit mass, \mathbf{s} is the entropy flux vector, and $g_s \geq 0$ is the rate of entropy generation. The last two terms in Eq. (18) are, respectively, the thermal and viscous dissipation terms.

The history of the development of this equation—which is not a conservation equation—is discussed in the book by de Groot and Mazur.^[5] Use of Eqs. 3.5-6 and A.4-19 of Reference 3 then allows us to write

$$\frac{\partial}{\partial t} (\rho \hat{S}) + \nabla \cdot \rho \hat{S} \mathbf{v} = -\frac{1}{T} \nabla \cdot \mathbf{q} - \frac{1}{T} \boldsymbol{\tau} : \nabla \mathbf{v} \quad (19)$$

Integrating over the volume $V(t)$ and applying Eq. (3) to the terms on the left, we get

$$\frac{d}{dt} \int_{V(t)} \rho \hat{S} dV = -\frac{1}{T} \int_{V(t)} (\nabla \cdot \mathbf{q} + \boldsymbol{\tau} : \nabla \mathbf{v}) dV \quad (20)$$

In going from Eq. (19) to Eq. (20), we have replaced $1/T$ by

$$\frac{1}{\bar{T}} = \frac{\int_{V(t)} \frac{1}{T} (\nabla \cdot \mathbf{q} + \boldsymbol{\tau} : \nabla \mathbf{v}) dV}{\int_{V(t)} (\nabla \cdot \mathbf{q} + \boldsymbol{\tau} : \nabla \mathbf{v}) dV} \quad (21)$$

and moved it outside the volume integral.

Next we apply the divergence theorem and integrate from t_1 to t_2

$$S(t_2) - S(t_1) = -\int_{t_1}^{t_2} \frac{1}{\bar{T}} \int_{A(t)} \mathbf{n} \cdot \mathbf{q} dA dT - \int_{t_1}^{t_2} \frac{1}{\bar{T}} \int_{V(t)} \boldsymbol{\tau} : \nabla \mathbf{v} dV dt \quad (22)$$

in which $S(t)$ is the total entropy within $V(t)$.

We now take $t_2 - t_1$ to be differentially small, dt , so that Eq. (22) becomes

$$\frac{1}{\bar{T}} dQ = dS + \frac{1}{\bar{T}} \int_{V(t)} \boldsymbol{\tau} : \nabla \mathbf{v} dV dt \quad (23)$$

Finally we get

$$dQ = \bar{T} dS + \int_{V(t)} \boldsymbol{\tau} : \nabla \mathbf{v} dV dt \quad (24)$$

When Eq. (24) is combined with Eq. (17), the viscous dissipation terms cancel one another, and we get one of the most fundamental equations of equilibrium thermodynamics (Reference 6, Eq. 12.3, which embodies both the first and second laws)

$$dU = \bar{T} dS - \bar{p} dV \quad (25)$$

Normally in dealing with a succession of equilibrium states, the temperature will be constant throughout the system in any state, and the bar may be omitted from T . By similar arguments, the bar may be omitted from p as long as a pressure gradient in the system due to gravity may be safely neglected. For the history of the development of Eq. (25), and the individuals who created it, see the text leading up to Eq. 4.28 of Reference 4.

Although it is evident how the viscous dissipation terms cancel in obtaining Eq. (25), the vanishing of the analogous heat conduction dissipation term $(1/T^2) \mathbf{q} \cdot \nabla T$ in Eq. (18) is less obvious. In going from Eq. (18) to Eq. (19), the heat conduction dissipation term is combined with the entropy flux (written in terms of \mathbf{q}) to give the term $(1/\bar{T}) \nabla \cdot \mathbf{q}$. This term becomes the first term on the right side of Eq. (22), which gives the dQ in Eq. (24). The latter then cancels the dQ of Eq. (17). After this chain of

operations, the heat conduction dissipation contribution no longer appears explicitly in the final result, Eq. (25). Both thermal and viscous dissipation terms reside within $\bar{T}dS$.

The succession of equilibrium states is often called a “quasi-static process.” To quote Callen^[7, § 4.2]: “A quasi-static process is thus defined as a dense succession of equilibrium states. It is to be stressed that a quasi-static process therefore is an idealized concept, quite distinct from a real physical process, for a real process always involves nonequilibrium intermediate states having no representation in the thermodynamic configuration space.” This distinction between quasi-static processes and real physical processes is an important one.

Here we have succeeded in showing that, starting from the equations of change for total energy, internal energy, and entropy, we get two well-known results from equilibrium thermodynamics: Eq. (10) and Eq. (25). No assumption of reversible processes has been invoked in either case. Although this exercise does not produce any new results, it does emphasize the connection between two subjects: transport phenomena and equilibrium thermodynamics.

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