Forms of the Microscopic Energy Balance

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When one derives the microscopic mass balance, one inevitably obtains the continuity equation,

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho \mathbf{v}) \quad , \tag{1}$$

where ρ is the mass density, **v** is the center-of-mass velocity, and *t* is time. We understand very clearly that the LHS is an accumulation term and the right hand side is a convection term. The only assumption in equation (1) is that mass is not created or destroyed in the system, meaning that there are no nuclear reactions in our system. In our text book, this is equation (3.1-4) on page 77 [1].

When one derives the microscopic mass balance on a single component within a multicomponent system, one typically obtains

$$\rho \frac{\partial w_A}{\partial t} = -\rho \mathbf{v} \cdot \nabla w_A - \nabla \cdot \mathbf{j}_A + \sum_{i=1}^{N_R} r_{i,A} \quad , \tag{2}$$

where w_A is the mass fraction of component *A*, $\mathbf{j}_A$ is the diffusive mass flux of component *A* relative to the center-of-mass velocity, N_R is the number of independent chemical reactions in the system, and $r_{i,A}$ is the rate of production of component *A* in reaction *i*, in units of mass/volume/time. The functional form of $\mathbf{j}_A$ depends on the choice of the form of the constitutive equation, i.e. Fick's law, that one chooses to employ. This diffusive flux can include the Soret effect, in which there is mass transfer due to a temperature gradient. We understand that the LHS is an accumulation term. The first term on the RHS is the convection term, the second term on the RHS is the diffusion term and the third term is the reaction term. Again, this equation neglects nuclear reaction. In our text book, this is equation (19.1-14) on page 584 [1].

When one derives the microscopic momentum balance, one typically obtains

$$\rho \frac{\partial \mathbf{v}}{\partial t} = -\rho \mathbf{v} \cdot \nabla (\mathbf{v}) - \nabla p - \nabla \cdot \tau - \rho \nabla \hat{\Phi} \quad , \tag{3}$$

where *p* is the pressure, τ is the extra stress tensor, and $\hat{\Phi}$ is the specific external field imposed by, for example, gravity. If gravity is the source of the external field then we have $\mathbf{g} = -\nabla \hat{\Phi}$. Again, the functional form of the extra stress tensor must be determined by the choice of constitutive equation. One common constitutive equation is Newton's law of viscosity. We understand that the LHS is an accumulation term. The first term on the RHS is the convection term, the second term on the RHS represents the momentum transport due to molecular transport due to a gradient in the pressure, the third term is the momentum transport due to molecular transport due to viscous dissipation, and the fourth term is due to an external potential such as gravity. This equation is a the difference of equation (3.2-9) on page 80 of our textbook [1] and the continuity equation , equation(1). There are numerous assumptions in this equation. It assumes that there is no coupling of the momentum and reaction.

When one derives the microscopic energy balance, one obtains

$$\frac{\partial \rho\left(\frac{1}{2}v^2 + \hat{U} + \hat{\Phi}\right)}{\partial t} = -\nabla \cdot \rho\left(\frac{1}{2}v^2\mathbf{v} + \hat{U}\mathbf{v} + \hat{\Phi}\mathbf{v}\right) - \nabla \cdot \mathbf{q} - \nabla \cdot p\mathbf{v} - \nabla \cdot (\tau \cdot \mathbf{v}) \quad , \tag{4}$$

where $\hat{U}$ is the specific (per mass) internal energy, $\hat{\Phi}$ is the specific potential energy due to an external field, and **q** is the heat flux due to conduction. The term on the LHS is the accumulation term. The first term on the RHS is the convection term. The second term on the RHS is the conduction term. The third term on the RHS is the reversible rate of internal energy change per unit change in unit volume. Note that a compression will increase the internal energy. The last term on the RHS is the irreversible rate of internal energy increase per unit volume by viscous dissipation. This is equation (11.1-9) on page 336 in your text book.

We can add other terms to this energy balance to account for reactions and energy loss to the surroundings by other means.

Enthalpy vs. Internal Energy

Equation (4) is written in terms of the internal energy. The internal energy is always the correct thermodynamic function to start with in terms of a derivation. However, we know from experience that sometimes we write the energy balance in terms of the enthalpy. Let’s discuss when we use one or the other.

If there is no flow in the system, then the velocity is zero and equation (4) becomes

$$\frac{\partial \rho\left(\hat{U} + \hat{\Phi}\right)}{\partial t} = -\nabla \cdot \mathbf{q} \quad . \tag{5}$$

In this case, it is very clear that the internal energy is the correct and most convenient thermodynamic function to use.

If there is flow in the system, then we can recall the definition of the specific enthalpy,

$$\hat{H} = \hat{U} + p\hat{V} = \hat{U} + \frac{p}{\rho} \quad . \tag{6}$$

If we examine the pressure term in equation (4) we can introduce the necessary density factor

$$-\nabla \cdot p\mathbf{v} = -\nabla \cdot \frac{\rho}{\rho} p\mathbf{v} = -\nabla \cdot \rho\left(\frac{p}{\rho}\mathbf{v}\right) \quad , \tag{7}$$

We substitute equation (7) into equation (4) to obtain

$$\frac{\partial \rho\left(\frac{1}{2}v^2 + \hat{U} + \hat{\Phi}\right)}{\partial t} = -\nabla \cdot \rho\left(\frac{1}{2}v^2\mathbf{v} + \hat{U}\mathbf{v} + \hat{\Phi}\mathbf{v}\right) - \nabla \cdot \mathbf{q} - \nabla \cdot \rho\left(\frac{p}{\rho}\mathbf{v}\right) - \nabla \cdot \left(\boldsymbol{\tau} \cdot \mathbf{v}\right) \quad , \qquad (8)$$

Rearranging we have

$$\frac{\partial \rho\left(\frac{1}{2}v^2 + \hat{U} + \hat{\Phi}\right)}{\partial t} = -\nabla \cdot \rho\left(\frac{1}{2}v^2\mathbf{v} + \hat{U}\mathbf{v} + \frac{p}{\rho}\mathbf{v} + \hat{\Phi}\mathbf{v}\right) - \nabla \cdot \mathbf{q} - \nabla \cdot \left(\boldsymbol{\tau} \cdot \mathbf{v}\right) \quad , \qquad (9)$$

We can substitute equation (6) into the convection term of equation (9):

$$\frac{\partial \rho\left(\frac{1}{2}v^2 + \hat{U} + \hat{\Phi}\right)}{\partial t} = -\nabla \cdot \rho\left(\frac{1}{2}v^2\mathbf{v} + \hat{H}\mathbf{v} + \hat{\Phi}\mathbf{v}\right) - \nabla \cdot \mathbf{q} - \nabla \cdot \left(\boldsymbol{\tau} \cdot \mathbf{v}\right) \quad . \qquad (10)$$

So, it is straightforward to obtain the enthalpy in the convection term. However, we still have the internal energy in the accumulation term. If we substitute equation (6) into the accumulation term of equation (9) we have

$$\frac{\partial \rho\left(\frac{1}{2}v^2 + \hat{H} - \frac{p}{\rho} + \hat{\Phi}\right)}{\partial t} = -\nabla \cdot \rho\left(\frac{1}{2}v^2\mathbf{v} + \hat{H}\mathbf{v} + \hat{\Phi}\mathbf{v}\right) - \nabla \cdot \mathbf{q} - \nabla \cdot \left(\boldsymbol{\tau} \cdot \mathbf{v}\right) \quad , \qquad (11)$$

Rearranging we have,

$$\frac{\partial \rho\left(\frac{1}{2}v^2 + \hat{H} + \hat{\Phi}\right)}{\partial t} - \frac{\partial p}{\partial t} = -\nabla \cdot \rho\left(\frac{1}{2}v^2 \cdot \mathbf{v} + \hat{H}\mathbf{v} + \hat{\Phi}\mathbf{v}\right) - \nabla \cdot \mathbf{q} - \nabla \cdot \left(\boldsymbol{\tau} \cdot \mathbf{v}\right) \quad , \qquad (12)$$

So, the change from internal energy to enthalpy dictates that the time derivative of the pressure appear explicitly. If the system is at steady state, then the time derivative terms drop out. Otherwise, we need both of them.

One other general trick is to cancel those terms that equate to the continuity equation, equation (1). We use the product rule on the accumulation and convection terms of equation (12),

$$\begin{aligned}&\left(\frac{1}{2}v^{2}+\hat{H}+\hat{\Phi}\right)\frac{\partial\rho}{\partial t}+\rho\frac{\partial\left(\frac{1}{2}v^{2}+\hat{H}+\hat{\Phi}\right)}{\partial t}-\frac{\partial p}{\partial t}=\\&-\left(\frac{1}{2}v^{2}+\hat{H}+\hat{\Phi}\right)\cdot\nabla\rho\mathbf{v}-\rho\mathbf{v}\nabla\cdot\left(\frac{1}{2}v^{2}+\hat{H}+\hat{\Phi}\right)-\nabla\cdot\mathbf{q}-\nabla\cdot\left(\tau\cdot\mathbf{v}\right)\end{aligned}\quad. \tag{13}$$

The first term on the LHS and first term on the RHS cancel because of the continuity equation, leaving

$$\rho\frac{\partial\left(\frac{1}{2}v^{2}+\hat{H}+\hat{\Phi}\right)}{\partial t}-\frac{\partial p}{\partial t}=-\rho\mathbf{v}\nabla\cdot\left(\frac{1}{2}v^{2}+\hat{H}+\hat{\Phi}\right)-\nabla\cdot\mathbf{q}-\nabla\cdot\left(\tau\cdot\mathbf{v}\right)\quad. \tag{14}$$

What does the time derivative of the pressure look like? For a single-component ideal gas, we have

$$p=\frac{\rho RT}{m} \tag{15}$$

so the time derivative of the pressure is

$$\frac{\partial p}{\partial t}=\frac{RT}{m}\frac{\partial\rho}{\partial t}+\frac{\rho R}{m}\frac{\partial T}{\partial t}=-\frac{RT}{m}\nabla\cdot\left(\rho\mathbf{v}\right)+\frac{\rho R}{m}\frac{\partial T}{\partial t} \tag{16}$$

where we substituted in the continuity equation to get the final result. The energy balance will be converted into a differential equation for temperature, so the form of equation (16) is acceptable.

For an ideal gas binary mixture, we have

$$p=\frac{N}{V}RT=cRT=\left(\frac{w_A}{M_A}+\frac{w_B}{M_B}\right)\rho RT=\left(\frac{w_A}{M_A}+\frac{1-w_A}{M_B}\right)\rho RT\quad, \tag{17}$$

in which case the time derivative of the pressure can be expressed in terms of the fundamental variables as

$$\frac{\partial p}{\partial t}=\left(\frac{w_A}{M_A}+\frac{1-w_A}{M_B}\right)\rho R\frac{\partial T}{\partial t}+\left(\frac{w_A}{M_A}+\frac{1-w_A}{M_B}\right)RT\frac{\partial\rho}{\partial t}+\rho RT\left(\frac{1}{M_A}-\frac{1}{M_B}\right)\frac{\partial w_A}{\partial t}\quad. \tag{18}$$

It we again want to have the expression in terms of the time derivative of the temperature only, we have to substitute in the continuity equation and the material balance for component A, equation (2) to obtain

$$\begin{aligned}\frac{\partial p}{\partial t} &= \left(\frac{w_A}{M_A}+\frac{1-w_A}{M_B}\right)\rho R\frac{\partial T}{\partial t}-\left(\frac{w_A}{M_A}+\frac{1-w_A}{M_B}\right)RT\nabla\cdot(\rho\mathbf{v}) \\ &\quad+\rho RT\left(\frac{1}{M_A}-\frac{1}{M_B}\right)\left(-\mathbf{v}\cdot\nabla w_A-\frac{1}{\rho}\nabla\cdot\mathbf{j}_A\right)\end{aligned}, \tag{19}$$

where we have ignored the possibility of chemical reaction.

A similar treatment must be done for any equation of state. For example, for the single component van der Waal's equation of state, we have

$$p=\frac{RT}{V_m-b}-\frac{a}{V_m^2}=\frac{RT}{\frac{m}{\rho}-b}-\frac{a}{\left(\frac{m}{\rho}\right)^2}=\frac{\rho RT}{m-\rho b}-\frac{a\rho^2}{m^2} \tag{20}$$

so the time derivative of the pressure is

$$\frac{\partial p}{\partial t}=\frac{\rho R}{m-\rho b}\frac{\partial T}{\partial t}+\left(\frac{RT}{m-\rho b}+\frac{b\rho RT}{(m-\rho b)^2}-\frac{2a\rho}{m^2}\right)\frac{\partial\rho}{\partial t} \tag{21}$$

Eliminating the time derivative of the density through the continuity equation, we have

$$\frac{\partial p}{\partial t}=\frac{\rho R}{m-\rho b}\frac{\partial T}{\partial t}-\left(\frac{RT}{m-\rho b}+\frac{b\rho RT}{(m-\rho b)^2}-\frac{2a\rho}{m^2}\right)\nabla\cdot(\rho\mathbf{v}) \tag{22}$$

References

1. Bird, R.B., W.E. Stewart, and E.N. Lightfoot, *Transport Phenomena*. Second ed. 2002, New York: John Wiley & Sons, Inc.