Specific Heats of Fluids and Elastic Solids

1.1 Thermodynamics of Fluids

Using the free energy per unit mass $\psi$ as a thermodynamic potential, we have the caloric equation of state,

$$\psi = \hat{\psi}(\theta, \nu),$$

and the thermal equations of state,

$$s = \hat{s}(\theta, \nu) = -\frac{\partial \hat{\psi}(\theta, \nu)}{\partial \theta},$$

$$p = \hat{p}(\theta, \nu) = -\frac{\partial \hat{\psi}(\theta, \nu)}{\partial \nu},$$

where $\theta$ is the absolute temperature, $s$ is the entropy per unit mass, $\nu$ is the specific volume, and $p$ is the pressure.

Other combinations of thermodynamic state variables may be used. The internal energy per unit mass is

$$u = \psi + s \theta.$$  

Solving the relation $s = \hat{s}(\theta, \nu)$ for $\theta$, we have

$$\theta = \hat{\theta}(s, \nu).$$

Therefore, $u$ can be expressed by

$$u = \hat{\psi}(\hat{\theta}(s, \nu), \nu) + s \hat{\theta}(s, \nu) = \tilde{u}(s, \nu),$$

and

$$\frac{\partial \tilde{u}(s, \nu)}{\partial s} = \frac{\partial \hat{\psi}(\theta, \nu)}{\partial \theta} \frac{\partial \hat{\theta}(s, \nu)}{\partial s} + s \frac{\partial \hat{\theta}(s, \nu)}{\partial s} + \hat{\theta}(s, \nu)$$

$$= -s \frac{\partial \hat{\theta}(s, \nu)}{\partial s} + s \frac{\partial \hat{\theta}(s, \nu)}{\partial s} + \hat{\theta}(s, \nu) = \hat{\theta}(s, \nu),$$

and

$$\frac{\partial \tilde{u}(s, \nu)}{\partial \nu} = \frac{\partial \hat{\psi}(\theta, \nu)}{\partial \nu} + \frac{\partial \hat{\psi}(\theta, \nu)}{\partial \theta} \frac{\partial \hat{\theta}(s, \nu)}{\partial \nu} + s \frac{\partial \hat{\theta}(s, \nu)}{\partial \nu}$$

$$= -p - s \frac{\partial \hat{\theta}(s, \nu)}{\partial \nu} + s \frac{\partial \hat{\theta}(s, \nu)}{\partial \nu} = -\hat{p}(s, \nu),$$

where we have used (1.1.2). That is, corresponding to the caloric equation of state,

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1 For the derivation of the general equations see the book Continuum Mechanics by Ellis H. Dill, CRC Press 2007: Section 1.14.3 for fluids and Section 2.1 for elastic solids.
\[ u = \tilde{u}(s, \nu), \quad (1.1.8) \]

we have thermal equations of state
\[ \theta = \tilde{\theta}(s, \nu) = \frac{\partial \tilde{u}(s, \nu)}{\partial s}, \quad (1.1.9) \]
\[ p = \tilde{p}(s, \nu) = -\frac{\partial \tilde{u}(s, \nu)}{\partial \nu}. \]

The enthalpy per unit mass is
\[ h = u + p \nu. \quad (1.10) \]

Solving the equation of state \( p = \tilde{p}(s, \nu) \) for \( \nu \):
\[ \nu = \tilde{\nu}(s, p). \quad (1.11) \]

The enthalpy can therefore be expressed as
\[ h = \tilde{u}(s, \tilde{\nu}(s, p)) + p \tilde{\nu}(s, p) = \tilde{h}(s, p), \quad (1.1.12) \]

and
\[ \frac{\partial \tilde{h}(s, p)}{\partial s} = \frac{\partial \tilde{u}(s, \nu)}{\partial s} + \frac{\partial \tilde{u}(s, \nu)}{\partial \nu} \frac{\partial \tilde{\nu}(s, p)}{\partial s} + p \frac{\partial \tilde{\nu}(s, p)}{\partial s} \]
\[ = \theta - p \frac{\partial \tilde{\nu}(s, p)}{\partial s} + p \frac{\partial \tilde{\nu}(s, p)}{\partial s} = \bar{\theta}(s, p). \quad (1.1.13) \]

and
\[ \frac{\partial \tilde{h}(s, p)}{\partial p} = \frac{\partial \tilde{u}(s, \nu)}{\partial \nu} \frac{\partial \tilde{\nu}(s, p)}{\partial p} + p \frac{\partial \tilde{\nu}(s, p)}{\partial p} + \tilde{\nu}(s, p) \]
\[ = -p \frac{\partial \tilde{\nu}(s, p)}{\partial p} + p \frac{\partial \tilde{\nu}(s, p)}{\partial p} + \tilde{\nu}(s, p) = \tilde{\nu}(s, p). \quad (1.14) \]

That is, corresponding to the caloric equation of state,
\[ h = \tilde{h}(s, p), \quad (1.1.15) \]

we have thermal equations of state
\[ \theta = \bar{\theta}(s, p) = \frac{\partial \tilde{h}(s, p)}{\partial s}, \quad (1.1.16) \]
\[ \nu = \tilde{\nu}(s, p) = \frac{\partial \tilde{h}(s, p)}{\partial p}. \]

The free enthalpy per unit mass (Gibbs function) is
\[ g = h - s\theta \quad (1.1.17) \]
Solving the equation of state \( \theta = \bar{\theta}(s, p) \) for \( s \):

\[
s = \bar{s}(\theta, p). \tag{1.18}
\]

Therefore, the free enthalpy can be expressed as

\[
g = \bar{h}(\bar{s}(\theta, p), p) - \theta \bar{s}(\theta, p) = \bar{g}(\theta, p), \tag{1.1.19}
\]

and

\[
\frac{\partial \bar{g}(\theta, p)}{\partial \theta} = \frac{\partial \bar{h}(s, p)}{\partial s} \frac{\partial \bar{s}(\theta, p)}{\partial \theta} - \theta \frac{\partial \bar{s}(\theta, p)}{\partial \theta} - \bar{s}(\theta, p)
\]

\[
= \theta \frac{\partial \bar{s}(\theta, p)}{\partial \theta} - \theta \frac{\partial \bar{s}(\theta, p)}{\partial \theta} - \bar{s}(\theta, p) = \bar{s}(\theta, p),
\]

and

\[
\frac{\partial \bar{g}(\theta, p)}{\partial p} = \frac{\partial \bar{h}(s, p)}{\partial p} + \frac{\partial \bar{h}(s, p)}{\partial s} \frac{\partial \bar{s}(\theta, p)}{\partial p} - \theta \frac{\partial \bar{s}(\theta, p)}{\partial p}
\]

\[
= \nu + \theta \frac{\partial \bar{s}(\theta, p)}{\partial p} - \theta \frac{\partial \bar{s}(\theta, p)}{\partial p} = \bar{\nu}(s, p).
\]

That is, corresponding to the caloric equation of state,

\[
g = \bar{g}(\theta, p), \tag{1.22}
\]

we have thermal equations of state

\[
s = \bar{s}(\theta, p) = \frac{\partial \bar{g}(\theta, p)}{\partial \theta},
\]

\[
\nu = \bar{\nu}(s, p) = \frac{\partial \bar{g}(\theta, p)}{\partial p}.
\]

Relations between the various equations of state are expressed by Maxwell’s reciprocal relations:

\[
\frac{\partial s}{\partial \nu} = -\frac{\partial^2 s}{\partial \theta \partial \nu} = \frac{\partial p}{\partial \theta} \bigg|_\nu,
\]

\[
\frac{\partial \theta}{\partial \nu} = \frac{\partial^2 \nu}{\partial s \partial \nu} = -\frac{\partial p}{\partial s} \bigg|_\nu,
\]

\[
\frac{\partial \theta}{\partial p} = \frac{\partial^2 \nu}{\partial s \partial p} = \frac{\partial \nu}{\partial s} \bigg|_p,
\]

\[
\frac{\partial s}{\partial \theta} = -\frac{\partial^2 \nu}{\partial \theta \partial \theta} = -\frac{\partial \nu}{\partial \theta} \bigg|_p.
\]

\[
\text{(1.1.24)}
\]
The specific heat at constant volume is

\[ c_v = \frac{\partial u}{\partial \theta} \bigg|_v = \frac{\partial u}{\partial s} \bigg|_v \frac{\partial s}{\partial \theta} \bigg|_v = \theta \frac{\partial s}{\partial \theta} \bigg|_v. \]  

(1.1.25)

The specific heat at constant pressure is

\[ c_p = \frac{\partial h}{\partial \theta} \bigg|_p = \frac{\partial h}{\partial s} \bigg|_p \frac{\partial s}{\partial \theta} \bigg|_p = \theta \frac{\partial s}{\partial \theta} \bigg|_p. \]  

(1.1.26)

The relation between the specific heats is found by using (1.1.12):

\[ c_p = \frac{\partial u}{\partial \theta} \bigg|_v + \frac{\partial u}{\partial v} \bigg|_v \frac{\partial v}{\partial \theta} \bigg|_p + p \frac{\partial v}{\partial \theta} \bigg|_p \]

\[ = c_v + \left( \frac{\partial u}{\partial v} \bigg|_v + \frac{\partial u}{\partial s} \bigg|_v \frac{\partial s}{\partial v} \bigg|_v + p \right) \frac{\partial v}{\partial \theta} \bigg|_p \]

\[ = c_v + \left( -p + \theta \frac{\partial s}{\partial v} \bigg|_v + p \right) \frac{\partial v}{\partial \theta} \bigg|_p \]

\[ = c_v + \theta \frac{\partial p}{\partial \theta} \bigg|_v \frac{\partial v}{\partial \theta} \bigg|_p, \]  

(1.27)

where we have used the Maxwell reciprocal relation \( \frac{\partial s}{\partial v} \bigg|_v = \frac{\partial p}{\partial \theta} \bigg|_v \).

The (volumetric) coefficient of thermal expansion is defined by

\[ \alpha = \frac{1}{v} \frac{\partial \theta}{\partial \theta} \bigg|_p. \]  

(1.28)

The coefficient of thermal stress at constant volume is

\[ \beta = \frac{\partial p}{\partial \theta} \bigg|_v. \]  

(1.29)

Therefore the specific heats are related by

\[ c_p - c_v = \theta v \alpha \beta. \]  

(1.30)
1.2 Thermoelasticity

The free energy per unit mass is a function of absolute temperature and the strain tensor \( \mathbf{E} \):

\[
\psi = \hat{\psi}(\theta, \mathbf{E}).
\]  

(2.1)

The Kirchhoff stress tensor \( \mathbf{S} \) and the entropy per unit mass are determined by

\[
s = -\frac{\partial \hat{\psi}(\theta, \mathbf{E})}{\partial \theta},
\]

\[
\mathbf{S} = \rho_0 \frac{\partial \hat{\psi}(\theta, \mathbf{E})}{\partial \mathbf{E}}.
\]  

(2.2)

Let us introduce measures per unit reference volume:

\[
\Psi = \rho_0 \psi, \quad \eta = \rho_0 s, \quad U = \rho_0 u, \quad H = \rho_0 h, \quad G = \rho_0 g.
\]  

(2.3)

Then,

\[
\eta = -\frac{\partial \hat{\Psi}(\theta, \mathbf{E})}{\partial \theta} = \hat{\eta}(\theta, \mathbf{E}),
\]

\[
\mathbf{S} = +\frac{\partial \hat{\Psi}(\theta, \mathbf{E})}{\partial \mathbf{E}} = \hat{\mathbf{S}}(\theta, \mathbf{E}).
\]  

(2.4)

Solve the thermal equation of state \( \eta = \hat{\eta}(\theta, \mathbf{E}) \) for \( \theta \):

\[
\theta = \hat{\theta}(\eta, \mathbf{E})
\]  

(2.5)

The internal energy per unit volume is then given by

\[
U = \Psi + \eta \theta = \hat{\Psi}(\hat{\theta}(\eta, \mathbf{E}), \mathbf{E}) + \eta \hat{\theta}(\eta, \mathbf{E}) = \hat{U}(\eta, \mathbf{E}),
\]  

(2.6)

and

\[
\frac{\partial \hat{U}(\eta, \mathbf{E})}{\partial \eta} = \frac{\partial \hat{\Psi}(\theta(\eta, \mathbf{E}), \mathbf{E})}{\partial \eta} + \eta \frac{\partial \hat{\theta}(\eta, \mathbf{E})}{\partial \eta} + \eta
\]

\[
= -\eta \frac{\partial \hat{\theta}(\eta, \mathbf{E})}{\partial \eta} + \eta \frac{\partial \hat{\theta}(\eta, \mathbf{E})}{\partial \eta} + \hat{\theta}(\eta, \mathbf{E}) = \hat{\theta}(\eta, \mathbf{E}).
\]  

(2.7)

and

\[
\frac{\partial \hat{U}(\eta, \mathbf{E})}{\partial \mathbf{E}} = \frac{\partial \hat{\Psi}(\theta(\eta, \mathbf{E}), \mathbf{E})}{\partial \mathbf{E}} + \hat{\Psi}(\hat{\theta}(\eta, \mathbf{E}), \mathbf{E}) \frac{\partial \hat{\theta}(\eta, \mathbf{E})}{\partial \mathbf{E}} + \eta \frac{\partial \hat{\theta}(\eta, \mathbf{E})}{\partial \mathbf{E}}
\]

\[
= \mathbf{S} - \eta \frac{\partial \hat{\theta}(\eta, \mathbf{E})}{\partial \mathbf{E}} + \eta \frac{\partial \hat{\theta}(\eta, \mathbf{E})}{\partial \mathbf{E}} = \hat{\mathbf{S}}(\eta, \mathbf{E}).
\]  

(2.8)
That is,
\[ \theta = \frac{\partial U(\eta, E)}{\partial \eta} = \tilde{\theta}(\eta, E), \]
\[ S = \frac{\partial U(\eta, E)}{\partial E} = \tilde{S}(\eta, E). \]

Solve the equation of state \( S = \tilde{S}(\eta, E) \) for \( E \) to obtain
\[ E = \tilde{E}(\eta, S) \]  \hspace{1cm} (2.9)

The enthalpy per unit volume is then given by
\[ H = U - S : E = \tilde{U}(\eta, \tilde{E}(\eta, S)) - S : \tilde{E}(\eta, S) = \tilde{H}(\eta, S), \]  \hspace{1cm} (2.10)
and
\[ \frac{\partial \tilde{H}(\eta, S)}{\partial \eta} = \frac{\partial \tilde{U}(\eta, E)}{\partial \eta} + \frac{\partial \tilde{U}(\eta, E)}{\partial \eta} \frac{\partial \tilde{E}(\eta, S)}{\partial \eta} - S : \frac{\partial \tilde{E}(\eta, S)}{\partial \eta} = \theta + S : \frac{\partial \tilde{E}(\eta, S)}{\partial \eta} - \tilde{E}(\eta, S) = \tilde{\theta}(\eta, S), \]  \hspace{1cm} (2.11)
and
\[ \frac{\partial \tilde{H}(\eta, S)}{\partial S} = \frac{\partial \tilde{U}(\eta, E)}{\partial E} : \frac{\partial \tilde{E}(\eta, S)}{\partial S} - S : \frac{\partial \tilde{E}(\eta, S)}{\partial S} - \tilde{E}(\eta, S) \]
\[ = S : \frac{\partial \tilde{E}(\eta, S)}{\partial \eta} - S : \frac{\partial \tilde{E}(\eta, S)}{\partial \eta} - \tilde{E}(\eta, S) = -\tilde{E}(\eta, S). \]  \hspace{1cm} (2.12)

That is,
\[ \theta = \frac{\partial \tilde{H}(\eta, S)}{\partial \eta} = \tilde{\theta}(\eta, S), \]  \hspace{1cm} (2.13)
\[ E = -\frac{\partial \tilde{H}(\eta, S)}{\partial S} = \tilde{E}(\eta, S). \]

Invert the equation \( \theta = \tilde{\theta}(\eta, S) \) to obtain
\[ \eta = \tilde{\eta}(\theta, S) \]  \hspace{1cm} (2.14)

The free enthalpy per unit volume is then given by
\[ G = H - \eta \theta = \tilde{H}(\tilde{\eta}(\theta, S), S) - \theta \tilde{\eta}(\theta, S) = \tilde{G}(\theta, S), \]  \hspace{1cm} (2.15)
and
The specific heat at constant strain is

\[ C_E = \left. \frac{\partial U}{\partial \theta} \right|_E = \left. \frac{\partial \hat{U}(\eta,E)}{\partial \eta} \frac{\partial \hat{\eta}(\theta,E)}{\partial \theta} \right|_E = \theta \left. \frac{\partial \hat{\eta}(\theta,E)}{\partial \theta} \right|_E. \]  

(2.20)

The specific heat at constant stress is

\[ C_s = \left. \frac{\partial H}{\partial \theta} \right|_s = \left. \frac{\partial \hat{H}(\eta,S)}{\partial \eta} \frac{\partial \hat{\eta}(\theta,S)}{\partial \theta} \right|_s = \theta \left. \frac{\partial \hat{\eta}(\theta,S)}{\partial \theta} \right|_s. \]  

(2.21)

Alternative constitutive formulas for the internal energy are

\[ U = \hat{U}(\eta,E) = \hat{U}(\hat{\eta}(\theta,E),E) = \hat{U}(\theta,E) = \hat{U}(\theta,\hat{E}(\theta,S)) = \hat{U}(\theta,S). \]  

(2.22)
From (2.10),
\[ C_S = \frac{\partial \bar{U}(\theta, S)}{\partial \theta} - S : \bar{\mathbf{E}}(\theta, S) \]
\[ = \frac{\partial \bar{U}(\theta, E)}{\partial \theta} + \frac{\partial \bar{U}(\theta, E)}{\partial \mathbf{E}} : \frac{\partial \bar{\mathbf{E}}(\theta, S)}{\partial \theta} - S : \frac{\partial \bar{\mathbf{E}}(\theta, S)}{\partial \theta} \]
\[ = C_E + \left( \frac{\partial \bar{U}(\theta, E)}{\partial \mathbf{E}} + \frac{\partial \bar{U}(\theta, E)}{\partial \eta} \frac{\partial \eta(\theta, E)}{\partial \mathbf{E}} - S \right) : \frac{\partial \bar{\mathbf{E}}(\theta, S)}{\partial \theta} \]
\[ = C_E + \left( S + \theta \frac{\partial \eta(\theta, E)}{\partial \mathbf{E}} - S \right) : \frac{\partial \bar{\mathbf{E}}(\theta, S)}{\partial \theta} \]
\[ = C_E + \theta \frac{\partial \eta(\theta, E)}{\partial \mathbf{E}} : \frac{\partial \bar{\mathbf{E}}(\theta, S)}{\partial \theta}. \]

Using a Maxwell reciprocal relation,
\[ C_S - C_E = -\theta \frac{\partial \bar{S}(\theta, E)}{\partial \theta} : \frac{\partial \bar{\mathbf{E}}(\theta, S)}{\partial \theta} \]  \hspace{1cm} (2.24)

For small deformations:
\[ \mathbf{E} = \mathbf{e} = \alpha(\theta - \theta_0) \mathbf{1} - \frac{\lambda}{2\mu + 3\lambda} \text{tr} \left( \frac{\mathbf{\tau}}{2\mu} \right) \mathbf{1} + \frac{\mathbf{\tau}}{2\mu}, \]  \hspace{1cm} (2.25)
\[ \mathbf{S} = \mathbf{\tau} = -3\kappa\alpha(\theta - \theta_0) \mathbf{1} + \lambda(\text{tr} \mathbf{e}) \mathbf{1} + 2\mu \mathbf{e}, \]
and
\[ C_S - C_E = 9\theta \kappa \alpha^2 \]  \hspace{1cm} (2.26)

where \( \theta \) is the absolute temperature, \( \kappa \) is the bulk modulus, and \( \alpha \) is the coefficient of lineal expansion.