We can elucidate the significance of the intensities by lumping all the subsystems but one into a "surroundings" assumed very large (in the limit, infinite) and characterized by values $P_1, P_2, \ldots, P_{r+1}$ of the intensities. Because the surroundings—a generalized reservoir—is large, transseeding $X_i$ to or from the much smaller subsystem does not change the corresponding $P_i$ of the surroundings.

The intensities are zeroth-order homogeneous functions of the extensive variables:

$$P_i = \frac{\partial U(X_1, \ldots, X_{r+1})}{\partial X_i} = P_i(X_1, \ldots, X_{r+1}).$$

$$U(\lambda X_1, \ldots, \lambda X_{r+1}) = \lambda U(X_1, \ldots, X_{r+1})$$

$$\Rightarrow P_i(\lambda X_1, \ldots, \lambda X_{r+1}) = \frac{\partial}{\partial \lambda X_i} \left[ \lambda U(X_1, \ldots, X_{r+1}) \right]$$

$$= \frac{\partial U(X_1, \ldots, X_{r+1})}{\partial X_i} = P_i(X_1, \ldots, X_{r+1}).$$

It follows that the intensities are functions of the densities $\chi_j = \frac{X_j}{X_{r+1}} = \frac{X_j}{V}$ alone, for

$$P_i = P_i(\frac{1}{V} X_1, \ldots, \frac{1}{V} X_r, \frac{V}{V}) = P_i(X_1, \ldots, X_r).$$

The relations of this sort, which arise through differentiation of the fundamental equations, are referred to as generalized equations of state.
The information contained in the complete set of generalized equations of state

\[ P_i = P_i(x_1, \ldots, x_r) \quad i = 1, 2, \ldots, r+1 \]

is equivalent to that of the fundamental equation.

To convince ourselves of this assertion, we note that, as a first-order homogeneous function \( U = U(x_1, \ldots, x_{r+1}) \) obeys

**Euler's theorem:**

\[
\frac{\partial}{\partial \lambda} U(\lambda x_1, \ldots, \lambda x_{r+1}) = \sum_{\lambda} \left[ \lambda U(x_1, \ldots, x_{r+1}) \right] = U(x_1, \ldots, x_{r+1});
\]

but

\[
\frac{\partial}{\partial \lambda} U(\lambda x_1, \ldots, \lambda x_{r+1}) = \sum_{i=1}^{r+1} \frac{\partial U(\lambda x_1, \ldots)}{\partial (\lambda x_i)} \frac{\partial (\lambda x_i)}{\partial \lambda} = \sum_i P_i x_i ;
\]

so

\[
U(x_1, \ldots, x_{r+1}) = \sum_{i=1}^{r+1} P_i x_i .
\]

**So**

\[
\sum_{i=1}^{r+1} P_i x_i .
\]

**We can reconstruct the fundamental equation**

**if we know all the**

\[ P_i = P_i(x_1, \ldots, x_{r+1}) = P_i(x_1, \ldots, x_r) !!! \]

Moreover, the different equations of state are not independent from each other, as they obey the **Maxwell relations**

\[
\frac{\partial P_i}{\partial x_k} = \frac{\partial P_j}{\partial x_i} .
\]

These obtain because of the equality of mixed second partial derivatives:

\[
\sum \frac{\partial U}{\partial x_k} \frac{\partial x_k}{\partial x_i} = \sum \frac{\partial U}{\partial x_i} \frac{\partial x_i}{\partial x_k} .
\]
Differentiating (1) from p. 40 and subtracting dU from p. 40 gives

\[ 0 = \sum_i (aP_i x_i + P_i dX_i) - \sum_i P_i dX_i = \sum_{i=1}^{r+1} x_i dP_i, \]

the Gibbs-Duhem relation. Dividing the GD relation by \( x_{r+1} \) gives

\[ 0 = \sum_{i=1}^{r} x_i dP_i + dP_{r+1}, \]

or

\[ -dP_{r+1} = \sum_{i=1}^{r} x_i dP_i. \]

Now, if \( \bar{P}_i = P_i(x_1, \ldots, x_r), \quad i = 1, \ldots, r, \) (see p. 42), can be solved for the densities,

\[ x_i = x_i(P_1, \ldots, P_r), \quad i = 1, \ldots, r, \]

Then these can be substituted in

\[ U(x_1, \ldots, x_r) = \sum_{i=1}^{r} P_i x_i + P_{r+1} \] (see p. 43)

to yield

\[ -P_{r+1} = \sum_{i=1}^{r} P_i x_i(P_1, \ldots, P_r) - U(x_i(P_1, \ldots, P_r), \ldots) \]

\[ \equiv \Psi(P_1, \ldots, P_r). \]

Since \( -P_{r+1} = P \), \( \Psi(P) \) is the actual pressure of the system.
What is the necessary condition allowing the densities to be expressed in terms of the intensities, as in (A)?

Consider small variations in the original, convert expression on p. 42:

$$\delta P_i = \sum_{k=1}^r \frac{\partial P_i(x_1, \ldots, x_r)}{\partial x_k} \delta x_k,$$

or in the form of a system of linear equations,

$$
\begin{pmatrix}
\delta P_1 \\
\vdots \\
\delta P_r
\end{pmatrix} =
\begin{pmatrix}
\frac{\partial P_1}{\partial x_1} & \cdots & \frac{\partial P_1}{\partial x_r} \\
\vdots & \ddots & \vdots \\
\frac{\partial P_r}{\partial x_1} & \cdots & \frac{\partial P_r}{\partial x_r}
\end{pmatrix}
\begin{pmatrix}
\delta x_1 \\
\vdots \\
\delta x_r
\end{pmatrix}.
$$

Is the determinant of this matrix, termed the Jacobian

$$D_r = \begin{vmatrix}
\frac{\partial P_1}{\partial x_1} & \cdots & \frac{\partial P_1}{\partial x_r} \\
\vdots & \ddots & \vdots \\
\frac{\partial P_r}{\partial x_1} & \cdots & \frac{\partial P_r}{\partial x_r}
\end{vmatrix} = \frac{\partial(P_1, \ldots, P_r)}{\partial(x_1, \ldots, x_r)},$$

is nonzero, then the matrix can be inverted to obtain the $\delta x_k$ in terms of the $\delta P_i$. Conversely, we can obtain the $P_i$ from the $x_k$ in some neighborhood, provided

$$D_r^{-1} = \frac{\partial(x_1, \ldots, x_r)}{\partial(P_1, \ldots, P_r)} \neq 0.$$
Tisza mentions that $D_r$ approaches zero for heterogeneous and critical equilibria, while $D_r^{-1}$ goes to zero near absolute zero. Regular states are those for which both Jacobians are nonzero, and the intensity/density relations can be run in either direction.

With the streamlined notation $P = (p_1, ..., p_r)$ and $x = (x_1, ..., x_r)$, the function defined at the bottom of p. 44 can be written

$$\Psi(P) = \sum_{i=1}^{r} x_i p_i - u(x)$$

$\Psi$ is said to be a Legendre transform of the fundamental equation $u = u(x)$. Note that this transformation is carried out using densities; the size of the system being unexpressible in terms of the intensities alone.

Tisza defines a function

$$w(x'; P) = u(x') + \Psi(P) - \sum_{i=1}^{r} x'_i p_i$$

The densities represented by $x' = (x'_1, ..., x'_r)$ are distinct from the $x$ of the system in equilibrium with the surroundings; in fact, $w(x; P) = 0$, as follows directly from its definition.
We can show that \( W(x'; P) \) can only increase if the \( x' \) move away from \( x \):

\[
W(x' ; P) = u(x') - u(x) - \sum_{i} (x'_i - x_i) P_i .
\]

\( u(x') - u(x) \) is the change in internal energy density of the system, and

\[
- \sum_{i} (x'_i - x_i) P_i = - \sum_{i} \frac{x'_i - x_i}{x_{r+1}} P_i
\]

\[
= \frac{1}{x_{r+1}} \sum_{i} (x'_i \text{ surr} - x_i \text{ surr}) P_i
\]

\[
= \frac{1}{x_{r+1}} \sum_{i} [(x'_i \text{ surr} - x_i \text{ surr}) \frac{dU_{\text{surr}}}{dx_i \text{ surr}}]
\]

\[
= \frac{1}{x_{r+1}} [U'_{\text{surr}} - U_{\text{surr}}]
\]

This latter quantity is the change in energy of the surroundings divided by the scale-factor (volume) of the system. \( W(x'; P) \) is seen to be the minimum work that must be supplied in order to transfer \( x_i - x'_i \), \( i = 1, ..., r \) (viz \( S - S', N_1 - N'_1, ..., N_c - N'_c \)) from the system to the surroundings (divided by the volume of the system).

Since the combined system (system + surroundings) is thereby displaced from equilibrium, this quantity can only be nonnegative.
The resulting relation,
\[ w(x'; P) = 0 \]
may be considered a minimum principle when the \( x' \) are varied at constant \( P \).

One often uses fundamental equations in terms of mixed sets of variables say \( P_1, \ldots, P_n, x_{n+1}, \ldots, x_{n+1} \).

For the corresponding Legendre transform, we shall sometimes use the notation

\[-U[P_1, \ldots, P_n] = \sum_{i=1}^{n} X_i P_i - U(X_1, \ldots, X_{n+1})\,.

Common names apply to some of these transforms. For example, with \( U = TS - pV + \sum_{j} u_j N_j \) by Euler's theorem [(+)] on p.43], the Gibbs function (also known as Gibbs free energy) is

\[ G(T, p, N_1, \ldots, N_n) = U[T, p] = U - TS + pV \,.

Tisza next discusses some properties of pressure, the intensity governing mechanical equilibrium. Although the mechanical coupling of two fluids can often be regarded as an "exchange of volume" between two subsystems, other types of coupling are possible. Suppose the volume of two subsystems are controlled by rigidly connected pistons of different cross section $A'$ and $A''$.

The virtual process is

$$\frac{\delta V'}{A'} + \frac{\delta V''}{A''} = 0.$$ 

The total length of the two cylinders is here an additive invariant, rather than the total volume! The equilibrium condition is

$$0 = \delta U + \lambda \left( \frac{\delta V'}{A'} + \frac{\delta V''}{A''} \right)$$

$$= -p' \delta V' - p'' \delta V'' + \lambda \left( \frac{\delta V'}{A'} + \frac{\delta V''}{A''} \right) \quad \text{(see p. 41)}$$

$$= \left( \frac{\lambda}{A'} - p' \right) \delta V' + \left( \frac{\lambda}{A''} - p'' \right) \delta V''.$$
For this equality to be obeyed in the case of arbitrary and independent changes $\delta V'$ and $\delta V''$, it must be that

$$p'A' = p''A'' = \text{constant}.$$

It is noted that, with an adiabatic piston separating two subsystems, volume exchange becomes a one-variable process, provided that we work in the energy scheme.

$$\delta V' + \delta V'' = 0, \quad \delta S' = \delta S'' = 0.$$ 

Within the entropy scheme, we'd have to consider a two-variable process:

$$\Delta U' + \Delta U'' = 0$$

$$\Delta V' + \Delta V'' = 0,$$

because the energies of the two subsystems change (through work) when the piston moves.

The intensity conjugate to a mole number is the corresponding chemical potential. There is an analogy, which Tisza develops, between mass flow (change of mole numbers), heat flow, and volume exchange on one hand, and chemical potential, temperature, and pressure on the other.
For a one-component system, we may choose $N = X_{r+1}$ as the scale factor. Then $P_{r+1} = \mu$.

\[ U = TS - pV + \mu N \quad (*) \]

leads to

\[ \mu = \frac{U}{N} = TS - pv + \mu \quad \text{or} \quad \mu = u - Ts + pv. \]

The Gibbs-Duhem relation follows from

\[ dU = Tds - pdV + \mu dN \quad \text{(differential of fundamental relation)} \]

and

\[ dU = Tds + SdT - pdV - Vdp + u dN + N d\mu \quad \text{(from (*)}, \text{ which combine to give} \]

\[ 0 = SdT - Vdp + N d\mu \quad \text{(GD)} \]

or

\[ d\mu = -SdT + Vdp. \]

Thus, the chemical potential is both the intensity conjugate to the number of moles and the Legendre transform of the molar energy - the molar Gibbs free energy.
While there exist walls restrictive to mass flow but nonrestrictive to energy (i.e., diathermic partitions), the converse constraint (a wall restrictive to energy but not mass) is not generally available. Consequently, virtual processes involve simultaneous independent variations of mole numbers and entropy:

\[ \delta N'_i + \delta N''_i = 0 \]
\[ \delta S'_i + \delta S''_i = 0 \]

The corresponding conditions of equilibrium are

\[ u'_i = u''_i \]

and

\[ T' = T'' \]

But Tsizza mentions the interesting case of a narrow capillary, which acts, for liquid He II, as an entropy filter. It inhibits the entropy-containing normal fluid, but transmits the zero-entropy superfluid. The capillary is non-restrictive to mass, but restrictive to entropy! For two containers thus connected, \( \Delta m = 0 \), but \( \Delta T \) may be nonzero.

Hence, from \( A'p' = A''p'' \) (see p. 52) and the Gibbs-Duhem relation (p. 51), we have

\[ s dT = v dp \quad \text{or} \quad \frac{\Delta p}{\Delta T} = \frac{s}{v} = s \rho \text{ molar density} \]
VI 1st phase rule

Is the possible phases of a Thermodynamic system are known and are specified in terms of their primitive fundamental relations (see p. 13), then the basic problem of phase equilibrium is to predict the actual heterogeneous structure of a simple system specified in terms of its extensive variables.

This problem is solved in principle by appropriate entropy maximum postulate (Pd2) on p. 15, but this solution is unwieldy because it involves, on equal terms, all possible phases of the system.

A more practical, but strictly equivalent solution can be found by using the concept of a generalized reservoir. We single out one modification in a heterogeneous system for special consideration, and study its equilibrium with the (much larger) rest of the system regarded as a reservoir.

The intrinsic properties of the modification are specified by a set of densities, \( X_1^{(w)}, \ldots, X_r^{(w)} \); its size is given by \( X_r^{(a)} \).

The modification can be kept in equilibrium either by completely restrictive walls or by contact with a generalized reservoir with appropriate intensities \( P_1, \ldots, P_r+1 \). These intensities are related to each other by the differential GD relation (see p. 44):

\[
-dP_{r+1} = \sum_{i=1}^{r} X_i^{(w)} dP_i \quad (+) 
\]

These densities are the \( X_i^{(a)} \) of the modification under consideration, as defined on p. 19.
The integral version (same page) \( P_{r+1} = \Psi(P_1, \ldots, P_r) \) associates an \( r \)-dimensional surface in \( P \)-space with the modifications of a single phase. This means that only \( r \) intensities are capable of independent variation while still providing the environment for the same phase in one of its modifications.

In the case of a heterogeneous system—consisting of \( m \) modifications, rather than a single one—each of the modifications is in equilibrium with the same reservoir. Thus, the phases are in equilibrium with each other; we say they coexist. A differential GD relation of the form (↑) applies for each modification \( \alpha = 1, \ldots, m \) with the intensities \( P_{1\alpha}, \ldots, P_{r+1\alpha} \) having the same values in all coexisting modifications. The densities \( \Omega_i(P_1, \ldots, P_r) \), however, take values characteristic of each modification.

Each of the \( m \) equations (↑) can be used to eliminate one of the intensities, and we are left with \( \delta_i = r+1-m \) intensities capable of independent variation. \( \delta_i \) is the dimension of a region in \( P \)-space that represents the heterogeneous equilibrium of \( m \) distinct modifications. If it should happen, however, that only \( \tilde{m} \) of the (↑) are linearly independent, then \( \delta_i \) is increased to \( \delta_i = r+1-\tilde{m} = c+2-\tilde{m} \).

\[ \text{THE FIRST PHASE RULE} \]
Tisza considers more closely the properties of a system consisting of two modifications that differ in their densities. The complete description of this system is provided by $\delta_i = r + 1 - 2 = r - 1$ independent intensities $P_i, \ldots, P_{r-1}$ and the two scale factors $X_{r+1}'$ and $X_{r+1}''$. [For example, if we consider the coexistence of two "modifications" of a one-component substance, like ice and water, then $\delta_i = 1$, and the thermodynamic state of the system can be specified by the pressure $p$ (or the temperature $T$) and the mole numbers $N_{\text{ice}}$ and $N_{\text{water}}$.]

In a phase transition, the boundary between the two modifications is displaced, and

$$\Delta X_{r+1}' + \Delta X_{r+1}'' = 0,$$

while the system remains in contact with the same reservoir (which has fixed values of all $r$ intensities $P_i, \ldots, P_r$ — we were free to choose $r - 1$ of them). [In the water-ice example, the reservoir has fixed values of $p$ and $T$ (we may have specified the former, in which case the latter was fixed by the requirement of phase coexistence), while the total volume changes (decreasing, say, as some of the ice melts).] The reservoir supplies the quantities

$$\Delta X_i = \Delta X_i' + \Delta X_i'' = x_i' \Delta X_{r+1}' + x_i'' \Delta X_{r+1}'' = \Delta X_{r+1}'' (x_i'' - x_i').$$

[For the ice-water transition,]

$$\Delta V = \Delta N_{\text{water}} (V_{\text{water}} - V_{\text{ice}})$$

and

$$\Delta S = \Delta N_{\text{water}} (S_{\text{water}} - S_{\text{ice}}).$$

\[\text{molar volumes}\]

\[\text{molar entropies}\]
Note that \( T(\text{water} - \text{ice}) = \ell \), the latent heat of melting.

Tisza points out that by subtracting the differential GD relation (p. 44) of one coexisting phase from that of another, we obtain a generalized Clausius-Clapeyron equation,

\[
\sum_{i=1}^{n} (x''_i - x'_i) \, dP_i = 0,
\]

where the \( dP_i \) are intensity variations in the coexistence region.
VII Thermodynamic fundamental forms. Connection with experiment.

In order to investigate the intrinsic stability of a single homogeneous phase, we expand its primitive function through second order about a point \( x_1, x_2, \ldots, x_n \) in Gibbs space. Among these, the scale factor \( x_{n+1} \) is held constant, and we can write the expansion in terms of the densities:

\[
U(x_1, \ldots, x_n) \approx U_0 + \sum_{i=1}^{n} P_{io} \delta x_i + \frac{1}{2} \sum_{i,j} u_{ij} \delta x_i \delta x_j,
\]

where

\[
\delta x_i = x_i - x_{i0},
\]

\[
P_{io} = \left( \frac{\partial u}{\partial x_i} \right)_0
\]

and

\[
u_{ij} = \left( \frac{\partial^2 u}{\partial x_i \partial x_j} \right)_0 = \left( \frac{\partial P_{ij}}{\partial x_i} \right)_0 = \left( \frac{\partial P_j}{\partial x_i} \right)_0.
\]

The matrix \( \| v_{ij} \| \) is called the stiffness matrix. Let

\[
\Pi_i = \sum_{j} v_{ij} \delta x_j = \sum_{j} \left( \frac{\partial P_j}{\partial x_i} \right)_0 (x_j - x_{j0});
\]

then, clearly, for small enough displacements, \( \Pi_i = P_i - P_{io} = \delta P_i \).

The determinant of the stiffness matrix,

\[
\det(\| v_{ij} \|) = |\nu_{ij}| = Dr,
\]

is the Jacobian defined on p. 45.
In the regular case, $D_r \neq 0$ or $\infty$, the fundamental equation has a Legendre transform (see pp. 44 and 46)

$$\Psi(P_1, \ldots, P_r) = \sum_{i=1}^r x_i P_i - u(x)$$

with $x$ expressed in terms of $P$

$$= \sum_i (\xi_i + x_0) (\Pi_i + P_i) - u_0 - \sum_i P_i \xi_i - \frac{1}{2} \sum_{i \neq j} \xi_i \xi_j u_{i2} u_{j2}$$

with $\xi$ expressed in terms of $\Pi$

Because $D_r \neq 0$, the stiffness matrix has an inverse, and

$$\xi_i = \sum_{l \neq 2} \frac{(u^{-1})_{il}}{e} \sum_{2} u_{2l} \xi_{2l} = \sum_{l \neq 2} (u^{-1})_{il} \Pi_{l2}$$

Thus, $\xi_{i2}$

$$\Psi(P_1, \ldots, P_r) = \sum_{i=1}^r \sum_{l \neq 2} (u^{-1})_{il} \Pi_e (\Pi_i + P_i) + \sum_{i=1}^r x_i 0 (\Pi_i + P_i)$$

$\Psi_0 - \sum_i P_i \xi_i \sum_{l \neq 2} (u^{-1})_{il} \Pi_{l2}$

$- \frac{1}{2} \sum_{i \neq j} \xi_i \xi_j u_{i2} u_{j2} (\sum_{m} (u^{-1})_{2m} \Pi_{2m})$

$= (u^{-1})_{i2}$ since $\|u_{i2}\|$ and hence $\|u_{i2}\|$ are symmetric

$$\Psi(P_1, \ldots, P_r) = \Psi_0 + \sum_{i=1}^r x_i 0 \Pi_i + \frac{1}{2} \sum_{i \neq j} \Pi_{i2} \Psi_{i2}$$

The compliance form
where \( \Psi_0 = \sum_i x_{i0} P_i - u_0 \),

and

\[
\Psi_i\dot{\epsilon} = (\mathbf{U}^{-1})^{-1} = \left( \frac{\partial^2 \Psi}{\partial P_i \partial P_j} \right)_0
\]

\[
= \left( \frac{\partial^2 x_i}{\partial P_j} \right)_0 = \left( \frac{\partial \epsilon}{\partial P_i} \right)_0
\]

From the differential GD relation (p. 44),

\[
\sigma \equiv -dP_{i+1} = \sum_{i=1}^n x_i dp_i \quad \Rightarrow \quad \dot{\epsilon} = \frac{\partial \Psi}{\partial P_i}
\]

Tisza refers to the stiffness form and the compliance form jointly as the fundamental forms. In his notation,

\[
\| \Psi_i \| = \| u_i \|^{-1}
\]

(I don't understand his further statement that \( \| u_i \|^{1} = \| u_i \| \).)

The fundamental forms help establish contact between theory and experiment.

Let's focus on a one-component system and let \( x_1 = e \) and \( x_2 = u \) (the scale factor is \( x_3 = N \)), whence \( P_1 = T \) and \( P_2 = -p \). Here \( u, e, \) and \( v \) are molar quantities. The Legendre transform of the fundamental relation \( u = u(s,v) \) is

\[
\Psi(T, p) = -g(T, p) = Ts - pv - u
\]

where \( g(T, p) \) is the molar Gibbs function. The formalism developed from the fundamental relation \( g = g(T, p) \) is called the \( T, p \) scheme.
\[ \frac{d\mathbf{g}}{dt} = \dot{u} - \dot{\mathbf{e}} - \dot{\mathbf{s}} dT + p \dot{\mathbf{v}} + \dot{\mathbf{v}} dp \]

whence

\[ \frac{\partial \mathbf{g}}{\partial p} = \mathbf{v}(T, p) \quad \frac{\partial \mathbf{g}}{\partial T} = -\dot{\mathbf{a}}(T, p) . \]

 Thermal equation of state

 Caloric equation of state

 Thermodynamic volume is directly measurable, but caloric measurements yield only entropy differences. The stiffness matrix is

\[
\begin{bmatrix}
(\frac{\partial^2 T}{\partial \mathbf{v}})_{\mathbf{v}} & (\frac{\partial^2 T}{\partial \mathbf{v}})_{\mathbf{v}} \\
- (\frac{\partial^2 \mathbf{v}}{\partial \mathbf{v}})_{\mathbf{v}} & (\frac{\partial^2 \mathbf{v}}{\partial \mathbf{v}})_{\mathbf{v}}
\end{bmatrix}
= \begin{bmatrix}
\frac{T}{c_v} & \frac{\partial T}{\partial \mathbf{v}} \\
- \frac{\partial T}{\partial \mathbf{v}} & B_v
\end{bmatrix} \leftarrow \text{The equality of the two off-diagonal elements is of course a Maxwell relation}
\]

\( c_v = T \frac{\partial \mathbf{v}}{\partial T} \)

\( B_v = \mathbf{v} \frac{\partial^2 \mathbf{v}}{\partial \mathbf{v}} \) \leftarrow \text{adiabatic bulk modulus}

The compliance matrix is

\[
\begin{bmatrix}
(\frac{\partial^2 \mathbf{v}}{\partial \mathbf{v}})_{\mathbf{p}} & (\frac{\partial^2 \mathbf{v}}{\partial \mathbf{v}})_{\mathbf{p}} \\
(\frac{\partial^2 \mathbf{v}}{\partial \mathbf{v}})_{\mathbf{p}} & (\frac{\partial^2 \mathbf{v}}{\partial \mathbf{v}})_{\mathbf{p}}
\end{bmatrix}
= \begin{bmatrix}
\frac{\partial \mathbf{v}}{\partial T} & \mathbf{v} \alpha \\
\mathbf{v} \alpha & \mathbf{v} \chi_T
\end{bmatrix} \]  

where \( c_p \equiv T \frac{\partial \mathbf{v}}{\partial T} \) is the heat capacity at constant pressure,

\[ \alpha = \frac{1}{\mathbf{v}} \frac{\partial \mathbf{v}}{\partial T} \] is the coefficient of thermal expansion, and

\[ K_T = -\frac{1}{\mathbf{v}} \frac{\partial \mathbf{v}}{\partial p} \] is the isothermal compressibility.
One could seek the thermodynamic relations that follow from the fact that the compliance matrix is the inverse of the stiffness matrix...

The elements of the compliance matrix are directly measurable. With these data at hand, one can obtain the caloric equation of state by integration:

\[ \frac{\partial s}{\partial T} = -s(T, p) = - \int \left( \frac{s_p}{T} \, dT - \nu \, dp \right) \]

whence follows the fundamental relation in the \( T, p \) scheme:

\[ g(T, p) = u(T, p) + p \, v(T, p) - T \, s(T, p) \]

within two integration constants \( s_0 = s(T_0, p_0) \) and a reference enthalpy \( h_0 = u_0 + p_0 \, v_0 \).

The fundamental equations \( u = u(s, v) \) and \( g(T, p) = u(T, p) - T \, s(T, p) + p \, v(T, p) \) are only two of a wide variety of formally equivalent choices. Other equations include the Helmholtz free energy as a function of \( T \) \( \neq V \) and the enthalpy as a function of \( S \) \( \neq p \). Other possibilities arise if the volume, rather than the number of moles, is chosen as a scale factor.