## Last Time

### Diffusion of a Single Independent Mobile Species

### Relation of Thermodynamics of Solution Behavior to Diffusivity

### Relation of Mobility to Diffusivity

### Self-Diffusivity

### Intrinsic Diffusivity

### Vacancy Diffusion in a Substitutional Crystalline Alloy

## 3.21 Spring 2002: Lecture 5

## Lattice Motion (Darken's Analysis)

Consider the effect of the net motion of vacancies on a lattice.

From the perspective of the lab frame, the lattice appears to move with the velocity "marker atoms."

Because,

$$J_A^{lattice} = -D_A \nabla c_A \tag{5-1}$$

the apparent flux in the laboratory frame is

$$J_A^{lab} = -D_A \nabla c_A + v_{marker} c_A \tag{5-2}$$

The marker velocity must be related to the vacancy flux:

$$\begin{aligned} \vec{J}_V \text{ (Area) } \Delta t &= \text{number of sites destroyed} \\ &= \frac{\text{number of A and B}}{\text{volume}} (\text{volume swept}) \\ &= (c_A + c_B) v_{marker} \text{ (Area) } \Delta t \end{aligned} \tag{5-3}$$

Therefore

$$v_{marker} = \frac{J_V}{c_A + c_B} = -\frac{J_A + J_B}{c_A + c_B} \tag{5-4}$$

Putting this into Eq. 5-2,

$$J_A^{lab} = -D_A \frac{c_B}{c_A + c_B} \nabla c_A + D_B \frac{c_A}{c_A + c_B} \nabla c_B \tag{5-5}$$

If $X_V$ is small, and to good approximation $\nabla c_A = -\nabla c_B$:

$$J_A^{lab} = -(D_A X_B + D_B X_A) \nabla c_A \tag{5-6}$$

which is Darken's equation and defines the interdiffusivity $\tilde{D}$ for diffusion in an alloy.

## The Diffusivities

| Definitions and Relations for Diffusivities | | | |
|---|---|---|---|
| **Symbol** | **Name** | **Relation** | **Reference Frame** |
| $\tilde{D}$ | Interdiffusion Coefficient | $\vec{J}^{lab} = -\tilde{D}\nabla c$ | Laboratory |
| $\tilde{D}$ is the composition-dependent diffusion coefficient for the flux of concentration in a multi-component alloy. | | | |
| $D_i$ | Intrinsic Diffusivity | $\vec{J}_i^{lattice} = -D_i\frac{\partial c_i}{\partial x}$<br>$\vec{J}_i^{lab} = -D_i\frac{\partial c_i}{\partial x} + vc_i$<br>$\tilde{D} = X_A D_B + X_B D_A$ | Lattice<br>Laboratory |
| $D_i$ is the diffusivity that is related to the concentration gradient through the historical form of Fick's first law. $v$ is the velocity of the lattice planes with respect to the laboratory coordinates. The lattice frame is fixed to the crystal lattice and can move relative to the laboratory frame with velocity $v$. The $X_i$ are the mole fractions: $X_A = c_A/(c_A + c_B)$. The relationship to the interdiffusion coefficient is for binary alloys. | | | |
| $D_i^\star$ | Self-Diffusivity | $D_i = (1 + \frac{\partial \ln \gamma_i}{\partial \ln c_i})D_i^\star$ | Either frame can be used |
| $D_i^\star$ is the intrinsic self-diffusivity in a homogeneous solution. Also called the isotope diffusivity, reflecting the type of diffusion experiments which measure the self-diffusivity. | | | |

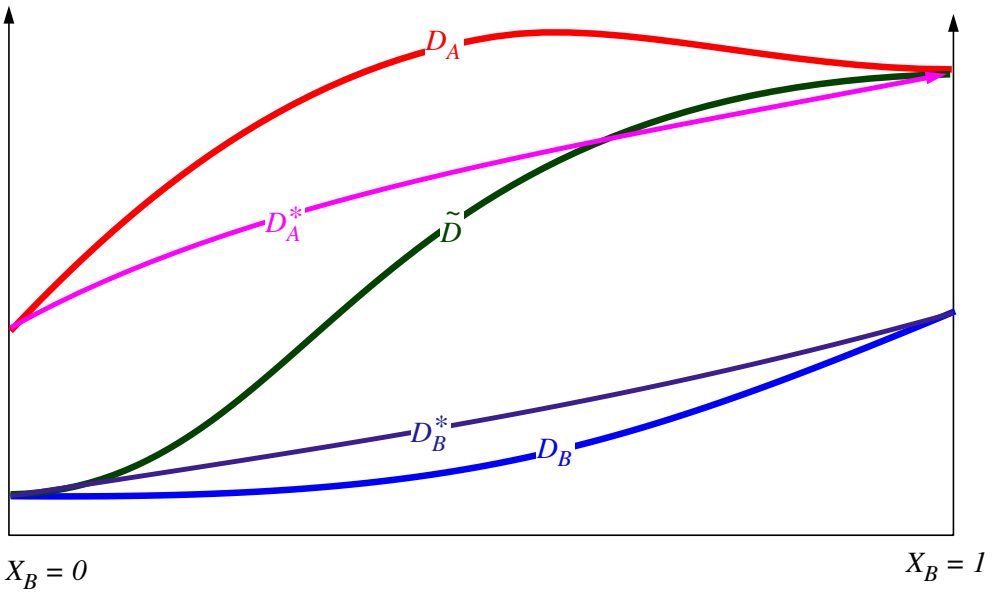


Figure 5-1: Graphical representation of the composition dependence of the various diffusivities.

## Motion of Marker Atoms

Last time, an equation for the average velocity of a inert "marker" atom was derived:

$$v_{marker} = \frac{J_V^{latt}}{c_A + c_B} = -\frac{J_A^{latt} + J_B^{latt}}{c_A + c_B} \tag{5-7}$$

Using the relationships for the intrinsic diffusivity,

$$v_{marker} = \frac{D_A \nabla c_A + D_B \nabla c_B}{c_A + c_B} \tag{5-8}$$

## Kirkendall Effect

For a nice historical discussion of the Kirkendall effect, see http://www.tms.org/pubs/journals/JOM/9706/Nakajima-9706.html. This weblet does a nice job of describing the intellectual resistance to the current understanding that the motion of markers is related to the differences (Zinc has an intrinsic diffusivity about 2.5 times that of Copper at the temperature of the Smigelskas-Kirkendall experiment, 785°C) in the intrinsic diffusion coefficients during interdiffusion in an alloy.

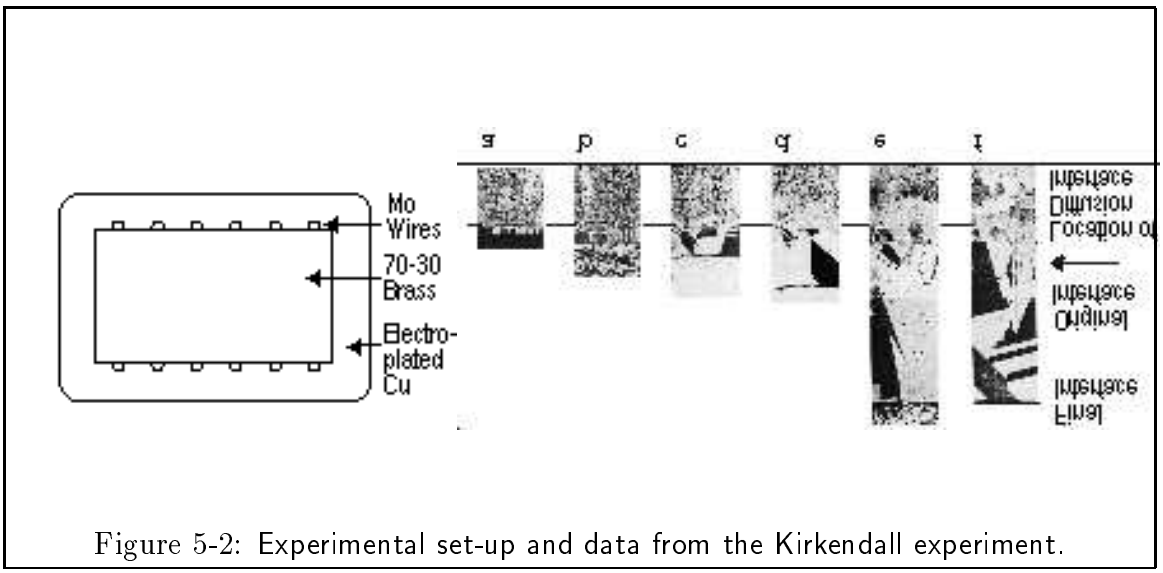


Figure 5-2: Experimental set-up and data from the Kirkendall experiment.

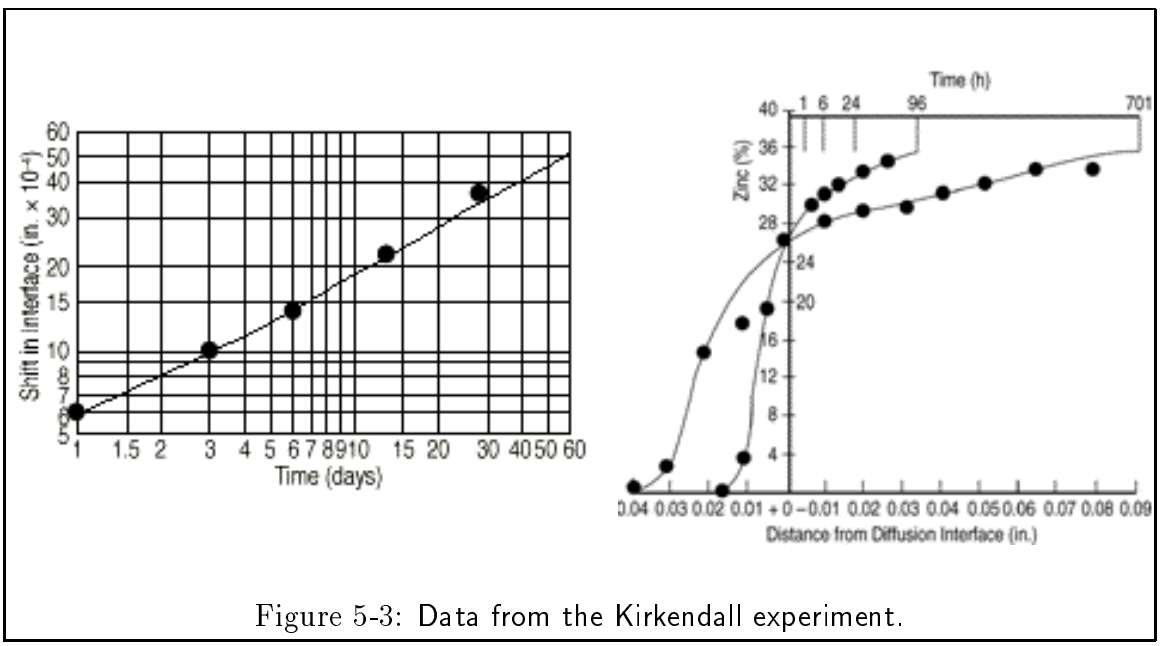


Figure 5-3: Data from the Kirkendall experiment.

The mechanism behind the marker motion can be understood physically by the removal of lattice planes by vacancy absorption during dislocation climb on the side towards which the marker moves and the emission of vacancies by climb on the other.

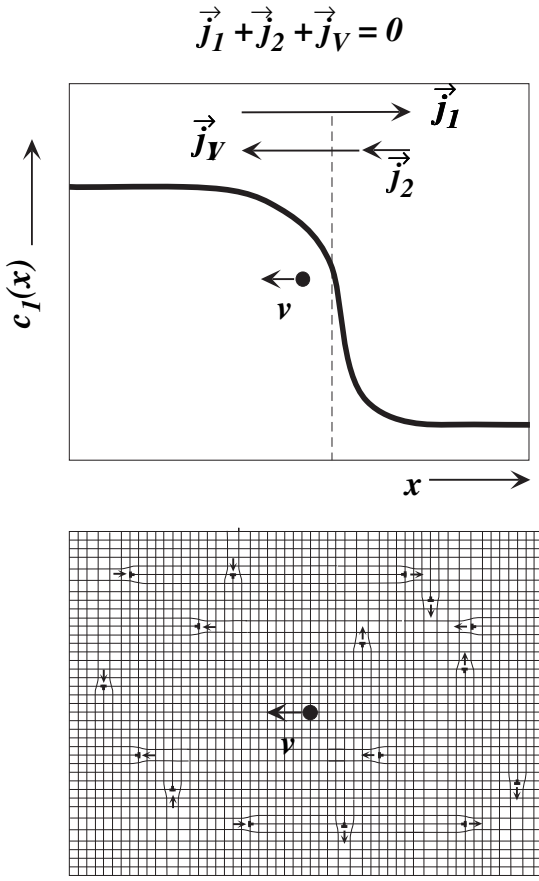


Figure 5-4: Illustration of the lattice mechanism for the Kirkendall effect.

However, the Kirkendall effect can also be explained with a very simple analogy to the interdiffusion of two gases with differing diffusivities. In fact, this phenomenon was known before the Kirkendall controversy.

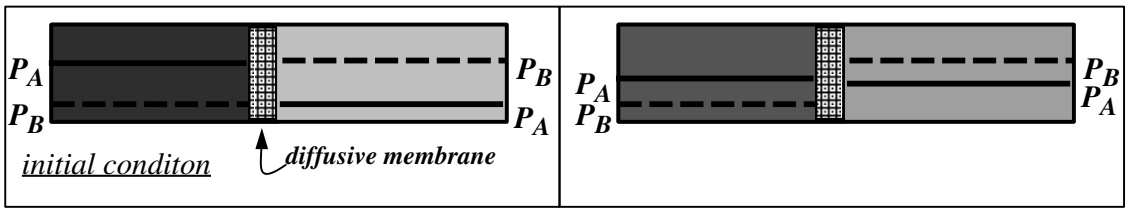


Figure 5-5: Illustration of the gas diffusion analogy to the Kirkendall effect. Suppose only the $A$ gas can diffuse across the membrane, then an initial system that is in mechanical equilibrium on the left will develop a spontaneous pressure difference as illustrated on the right.

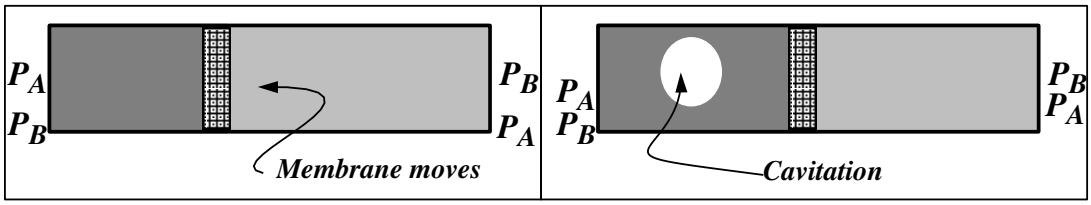


Figure 5-6: If the membrane can move (by analogy to the marker atoms) it will do so to equilibrate the pressure. If the membrane cannot move, then it is possible for the fluid on the left to cavitate.

It is clear from the figures that, in a lattice, there will be contribution of stress to the driving force for diffusion.

## Contribution of Stress to Diffusion

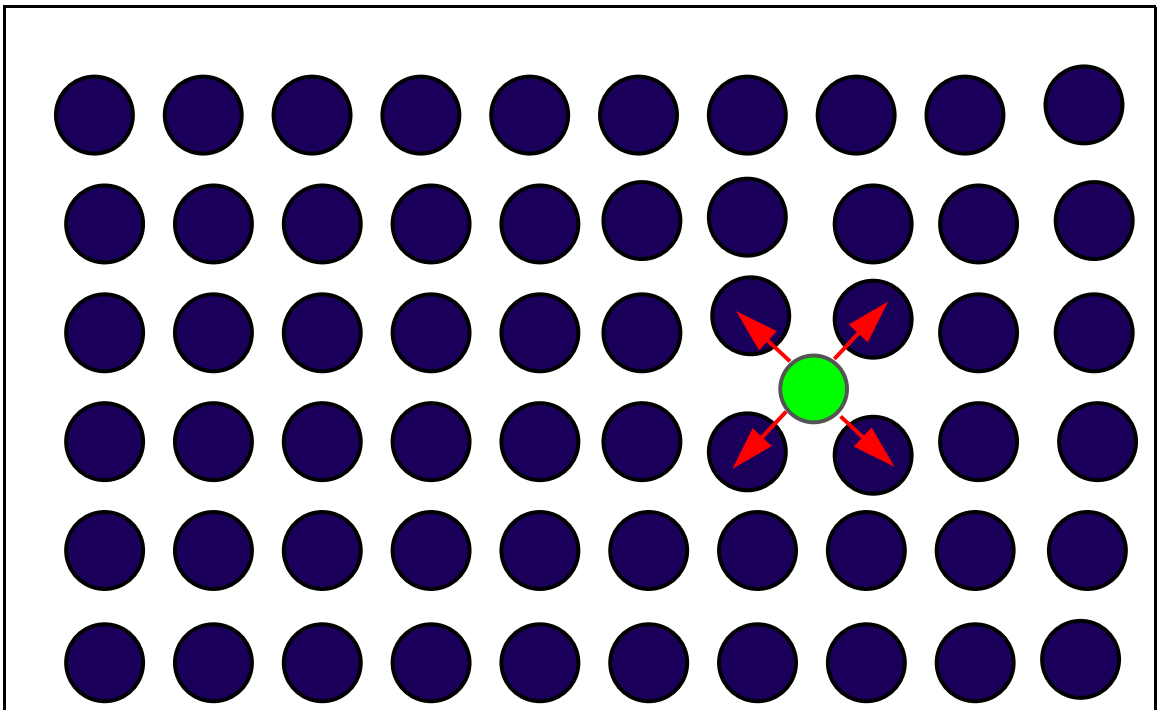

Figure 5-7: Origin of the the lattice stress contribution to diffusion.

Consider the additional discussion of elastic terms are included into a thermodynamic framework that appears at the end of lecture 3. It was shown that:

$$Tds = du - \mu_i dc_i + Pd\Delta_\epsilon - \tilde{\sigma_{ij}} d\tilde{\epsilon_{ij}} \tag{5-9}$$

where $P$ is (minus) three times the trace of the stress tensor (the hydrostatic pressure), $\Delta_\epsilon = dV/V$ is the dilation, and $\tilde{\epsilon}$ and $\tilde{\sigma}$ are the deviatoric strains and stresses.

If the entropy production in the absence of heat flow is considered:

$$T\dot{\sigma} = -J_1 \nabla \mu_1 + J_{vol} \nabla P - J_{shear} \nabla \tilde{\sigma_{ij}} \tag{5-10}$$

Considering the combined effect of the motion of an interstitial, one can associate the various flux terms with a single diffusing species, i.e.,

$$\begin{aligned} J_{vol} &= \Delta\Omega^{total} J_1 \\ J_{shear} &= \Delta\tilde{\epsilon}^{total} J_1 \end{aligned} \tag{5-11}$$

In other words, the diffusion atoms carries a dilation and a strain along with it. In this case, the entropy production in Eq. 5-12 can be factored:

$$T\dot{\sigma} = -(\nabla\mu_1 - c_1\Delta_1\Omega\nabla P + c_1\Delta\tilde{\epsilon_1}\nabla\tilde{\sigma_i}j)J_1 \tag{5-12}$$

The term inside the parenthesis becomes the generalized driving force for diffusion—it contains chemical plus elastic terms.

Often the deviatoric terms can be neglected, for instance for an interstitial in a cubic material, in this case (assuming ideal solution):

$$J_1 - -M_1(kT\nabla c_1 - \Delta\Omega c_1\nabla P) \tag{5-13}$$

## Addendum:
## Stresses, Thermodynamics and Number of Independent Variables in $\sigma_{ij}$

Sometime there is confusion associated with how to include stress properly into the driving force. the stress tensor $\sigma_{ij}$. This is not really part of kinetics but thermodynamics, but a good question nonetheless.

Stress is a generalized way to think of pressure in materials that can support shears—a fluid is an example of a material that cannot sustain a shear at equilibrium. As a matter of fact, there is a nice proof in Gibbs that shows that the lowest energy state of a material is one that is in pure hydrostatic stress (pure pressure).

We have been writing the thermodynamic relation that relates the quasi-static changes in the entropy and the internal energy and the various ways the system can perform work as:

$$TdS = dU - F_i dY_i \tag{5-14}$$

where the $F_i dY_i$ are the various ways a system can store work. From the thermodynamics of fixed composition fluids–which is usually taught, this is written as:

$$TdS = dU + PdV \tag{5-15}$$

i.e. the pressure comes in with a funny minus sign compared to the other work terms as in a more general case:

$$TdS = dU - V\sigma_{ij}d\epsilon ij - V\phi dq - V H_i dB_i - \mu_i dN_i \tag{5-16}$$

In the above equation,[9] it would be a mistake to add the $PdV$ term.

We are considering the appearance of the stress term in this question. Consider the term representing stress:

$$\sigma_{ij} = \frac{F_i}{A_j} \qquad (\text{i.e., } \sigma_{xz} = \frac{F_x}{A_z} = \sigma_{xz} = \frac{\vec{F}\cdot\hat{i}}{\vec{A}\cdot\hat{k}}) \tag{5-17}$$

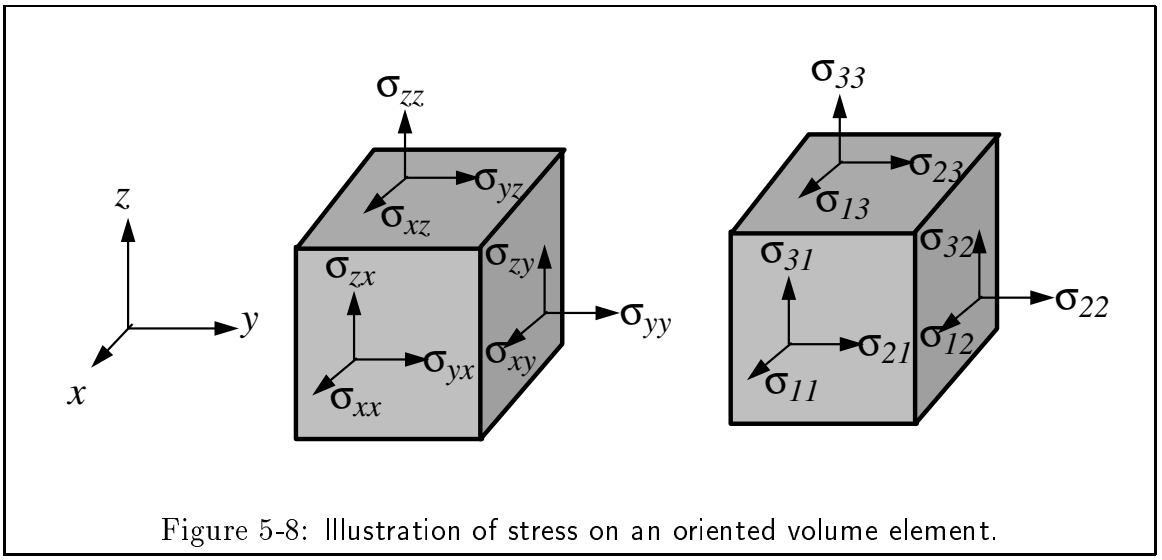


Figure 5-8: Illustration of stress on an oriented volume element.

$$\sigma_{ij} = \begin{bmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{bmatrix} \tag{5-18}$$

It is a requirement of mechanical equilibrium that the $\sigma_{ij}$ tensor is symmetric—it is also a guarantees that the quadratic form for energy at equilibrium will have real eigenvalues, which is a little like the Onsager symmetry hypothesis. The symmetry reduces the number of components from 9 to 6.

There is one special and very simple case of elastic stress, and that is called the hydrostatic stress. It is the case of pure pressure and there are no shear (off-diagonal) stresses. (i.e., all $\sigma_{ij} = 0$ for $i \neq j$, and $\sigma_{11} = \sigma_{22} = \sigma_{33}$). An equilibrium system composed of a body in a fluid environment is always in hydrostatic stress:

$$\sigma_{ij} = \begin{bmatrix} -P & 0 & 0 \\ 0 & -P & 0 \\ 0 & 0 & -P \end{bmatrix} \tag{5-19}$$

If the body that is being stressed hydrostatically is isotropic, then its response is pure dilation (in other words, it expands or shrinks uniformly and without shear):

[9] The extra volume terms come from the fact that we are writing the extensive entropy $S$ instead of the entropy density $s$.

$$\epsilon_{ij} = \begin{bmatrix} \Delta/3 & 0 & 0 \\ 0 & \Delta/3 & 0 \\ 0 & 0 & \Delta/3 \end{bmatrix} \tag{5-20}$$

where

$$\Delta = \frac{dV}{V} \tag{5-21}$$

So, for the case of hydrostatic stress, the work term has a particularly simple form:

$$\begin{gathered} V \sum_{i=1}^{3} \sum_{j=1}^{3} \sigma_{ij} d\epsilon_{ij} = -P dV \\ V \sigma_{ij} d\epsilon_{ij} = -P dV \qquad \text{summation convention} \end{gathered} \tag{5-22}$$

This expression is the same as the energy density for a compressible fluid, such as an ideal gas.

Sometime, people like to include the $PdV$ terms in thermodynamics of solids because it makes them feel comfortable. The way to do this is do define the "deviatoric stress:"

$$\tilde{\sigma}_{ij} = \begin{bmatrix} \sigma_{xx} - P & \sigma_{xy} & \sigma_{xz} \\ \sigma_{xy} & \sigma_{yy} - P & \sigma_{yz} \\ \sigma_{xz} & \sigma_{yz} & \sigma_{zz} - P \end{bmatrix} \tag{5-23}$$

where $P = \text{trace}\sigma_{ij}/3$. Now since, $\tilde{\sigma_{ij}}$ is a symmetric tensor with a zero trace, it only has five independent components, but the expression for the second law in terms of the deviatoric stress:

$$TdS = dU - V\sigma_{ij} d\epsilon_{ij} = TdS = dU + PdV - V\tilde{\sigma}_{ij} d\epsilon_{ij} \tag{5-24}$$

still has six independent terms for the elastic energy.