

GASES AND RUBBERS

by

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1. Thermodynamics

1.1 The Gibbs Equation for Fluids and Solids

The Gibbs equation combines the first and second law

$$d\varepsilon = q + w \quad q = Td\eta .$$

These laws hold equally for fluids and solids. Moreover,

$$w = \frac{1}{\rho} t_{ij} \frac{\partial v_j}{\partial x_j} dt$$

is the same in fluids and solids. Combining these equations, we obtain

$$Td\eta = d\varepsilon - \frac{1}{\rho} t_{ij} \frac{\partial v_j}{\partial x_j} dt .$$

η, ε and t_{ij} depend on temperature T and on the deformation gradient F_{iA} ; and with $\frac{\partial v_j}{\partial x_j} = F_{Aj}^{-1} F_{iA}$, we may write

$$Td\eta = d\varepsilon - \frac{1}{\rho} t_{ij} F_{Aj}^{-1} dF_{iA} . \quad (1.1)$$

This is the Gibbs equation. It represents a restriction upon the dependence of η, ε and t_{ij} on F_{iA} .

What makes a fluid different from a solid is its isotropy and the fact that the dependence of η, ε and t_{ij} on F_{iA} reduces to a dependence on $\det F = \frac{\rho_R}{\rho}$ in a fluid, i.e. on the density ρ or the specific volume $v = \frac{1}{\rho}$. Therefore, t_{ij} assumes the form

$$t_{ij} = -p \delta_{ij} .$$

We note that $d(\det F) = (\det F) F_{Ai}^{-1} dF_{iA}$ and find that the Gibbs equation (1.1) in a fluid becomes

$$Td\eta = d\epsilon + pdv . \quad (1.2)$$

Thus, we may call (1.1) the Gibbs equation for a solid, since it cannot be simplified in general for solids and (1.2) we may call the Gibbs equation for fluids. We see that (1.1) is considerably more complex than (1.2) and this reflects the greater complexity of the stresses of solids over those of fluids. That greater complexity of stresses makes elasticity theory so much more complex than hydrodynamics. Here, however, we shall be interested in similarities between solids and fluids and not in their differences. Therefore, we restrict the attention to uniaxial stresses in isotropic, incompressible solids, i.e. we set

$$t_{ij} = \begin{bmatrix} t_{11} & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} ,$$

and obtain

$$F_{iA} = \begin{bmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{bmatrix} = \begin{bmatrix} \lambda & 0 & 0 \\ 0 & 1/\sqrt{\lambda} & 0 \\ 0 & 0 & 1/\sqrt{\lambda} \end{bmatrix} .$$

Thus, (1.1) becomes

$$Td\eta = d\epsilon - \frac{1}{\rho_R} \lambda_1 \lambda_2 t_{11} d\lambda_1$$

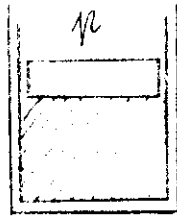
$$Td\eta = d\epsilon - S d\lambda, \quad (1.3)$$

where S is proportional to the force applied to the body.

1.2 Integrability Conditions

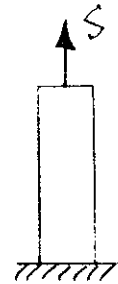
With (1.2) and (1.3) we have two nearly identical forms of the Gibbs equation. They only differ in notation and in the interpretation of the symbols. And they refer to

fluids



$$Td\eta = d\epsilon + p dv$$

solids



$$Td\eta = d\epsilon - S d\lambda$$

These equations imply restrictions upon the constitutive functions

$$\eta = \eta(T, v), \epsilon = \epsilon(T, v), p = p(T, v) \quad \parallel \quad \eta = \eta(T, \lambda), \epsilon = \epsilon(T, \lambda), S = S(T, \lambda)$$

We may write the Gibbs equation in the equivalent forms

$$\begin{aligned} Td\eta &= \left(\frac{\partial \epsilon}{\partial T} \right)_v dT + \left(\left(\frac{\partial \epsilon}{\partial v} \right)_T + p \right) dv & \parallel & Td\eta = \left(\frac{\partial \epsilon}{\partial T} \right)_\lambda dT + \left(\left(\frac{\partial \epsilon}{\partial \lambda} \right)_T - S \right) d\lambda \\ d(\epsilon - T\eta) &= -\eta dT - p dv & \parallel & d(\epsilon - T\eta) = -\eta dT + S d\lambda. \end{aligned} \quad (1.4)$$

The restrictions on the constitutive relations result from the integrability conditions implied by these equations:

$$\begin{aligned} \left(\frac{\partial \epsilon}{\partial v} \right)_T &= T \left(\frac{\partial p}{\partial T} \right)_v - p & \parallel & \left(\frac{\partial \epsilon}{\partial \lambda} \right)_T = -T \left(\frac{\partial S}{\partial T} \right)_\lambda + S \\ \left(\frac{\partial \eta}{\partial v} \right)_T &= \left(\frac{\partial p}{\partial T} \right)_v & \parallel & \left(\frac{\partial \eta}{\partial \lambda} \right)_T = - \left(\frac{\partial S}{\partial T} \right)_\lambda. \end{aligned} \quad (1.5)$$

Combination of the two equations gives

$$p = -\left(\frac{\partial \epsilon}{\partial v}\right)_T + T\left(\frac{\partial \eta}{\partial v}\right)_T \quad \left[\begin{array}{c} | \\ | \\ | \end{array} \right] \quad S = \left(\frac{\partial \epsilon}{\partial \lambda}\right)_T - T\left(\frac{\partial \eta}{\partial \lambda}\right)_T \quad (1.6)$$

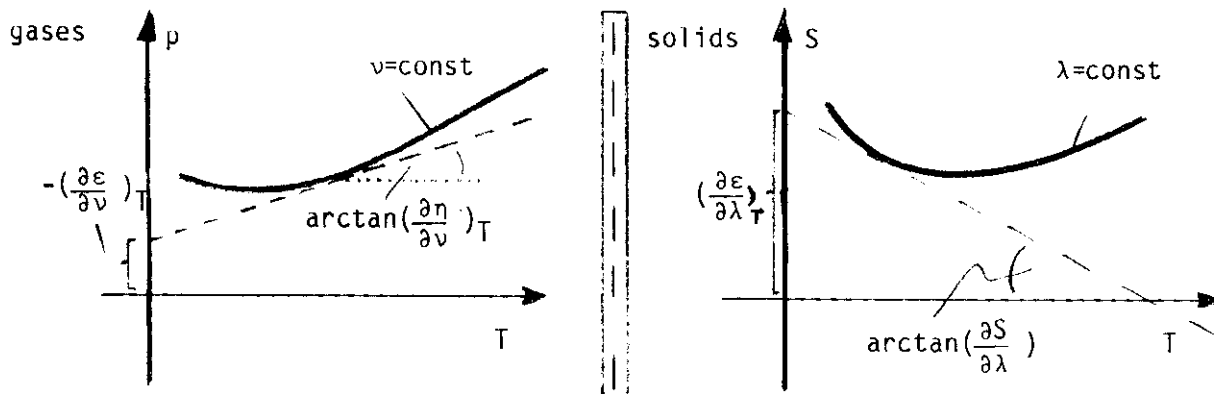
which states that the pressure, or force, are derivatives of the free energy $\epsilon - T\eta$ with respect to v or λ . Of course, this could have been read off from (1.4) directly.

[In passing, I note that the equations (1.5)₁ are of paramount importance in thermodynamics, since they provide a relation between the "caloric state function" $\epsilon(T, v)$, or $\epsilon(T, \lambda)$ and the "thermal state function" $p(T, v)$, or $S(T, \lambda)$. Since the latter is easily measured, while the former is not, the relations (1.5), save a lot of effort that would have to be spent on caloric measurements.]

1.3 Role of Energy and Entropy in Elasticity

There is some insight to be gained by expressing the equations (1.6) in words as follows: The pressure, or force, consists of two parts; one is due to a change of internal energy ϵ with a change of volume, or deformation, while the other one is due to a change of entropy with changing v or λ . We call these parts the energetic and entropic parts of p , or S , respectively. Obviously the entropic part becomes more important when the temperature rises.

The relations (1.5) provide an instructive possibility to measure the energetic and entropic parts of pressure, or force, by the easy measurement of p , or S , as a function of T for given v , or λ . Let the outcome of such a measurement be given by the following curves.



We see that the tangent to these curves in the state (T, v) , or (T, λ) determine the energetic and entropic parts of p , or S . The entropic part is indicated by the slope of the tangent while the energetic part is determined by the value of p , or S , in which the tangent cuts the ordinate. Note that p , or S , as functions of T are very easy to measure.

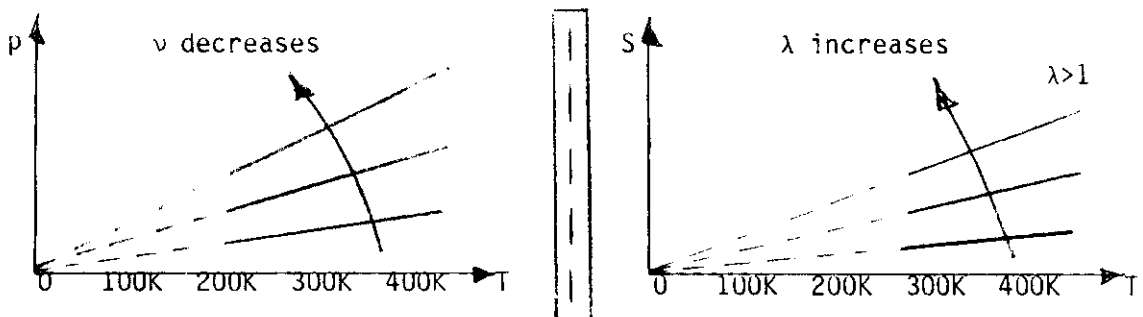
2. Experimental Results in Ideal Gases and Ideal Rubber

2.1 Experiments

The measurement of the pressure of an ideal gas as a function of temperature for a fixed volume was done by Gay-Lussac. The outcome, if plotted in a (p, T) -diagram gives a straight line of positive slope which, if extrapolated to small temperatures gives $p = 0$ at $T = 0$. [Of course, Gay-Lussac did not have the absolute temperature scale, but it was with his work that speculation of an absolute zero of temperature started, precisely because of the above-mentioned result].

Ideal rubber, far removed in appearance as it is from an ideal gas, exhibits much the same behaviour. The force S is an increasing linear homogeneous function of T . Also ideal rubber is isotropic and nearly incompressible so that the calculations of the previous section should apply to it.

We combine these findings in the following schematic plots



Note that for a solid the (S,T)-diagram is a little extraordinary as it implies that, upon an increase of T, S must be increased, if λ is to be held fixed. This indicates that rubber wishes to contract as T increases in contrast to most solids that show a thermal expansion (nb!) [Actually rubber is not quite incompressible; therefore it may, and does show a certain thermal expansion, i.e. it requires an increasing compressive force, if $\lambda = 1$ is to be maintained at rising temperature. That effect has been ignored in the (S,T)-diagram shown above].

2.2 Elasticity of Ideal Gases and Ideal Rubber is Entropy Induced

We compare the experimental (p,T)-curves, or (S,T)-curves, for ideal gases, or ideal rubbers, with the corresponding general curves drawn and interpreted in Section 1.3. Clearly, the conclusion is that

$$\left(\frac{\partial \epsilon}{\partial v} \right)_T = 0 \quad \left[\right] \quad \left(\frac{\partial \epsilon}{\partial \lambda} \right)_T = 0 \quad (2.1)$$

so that we may say that the only cause of pressure in an ideal gas, or force in ideal rubber, is a change of entropy with volume, or with extension. One expresses this finding by saying that the elasticity of ideal gases and of ideal rubber is entropy induced:

$$p = T \left(\frac{\partial \eta}{\partial v} \right)_T \quad \left[\right] \quad S = -T \left(\frac{\partial \eta}{\partial \lambda} \right)_T \quad (2.2)$$

In this thermodynamic aspect ideal gases and ideal rubbers are alike and people sometimes say that ideal rubber among the solids plays the same role that ideal gases play among the fluids.

3. KINETIC THEORY OF IDEAL GASES AND IDEAL RUBBER

3.1. Purpose

The purpose of the kinetic theory - as presented here - is the determination of the thermal equations of state $p = p(T, v)$ of ideal gases and of the thermal equation of state $S = S(T, \lambda)$ of ideal rubber by use of the relations (2.2).

Someone who works in mechanics has a fairly good grasp of the concept of energy, while his conception of entropy may be vague. Therefore a mechanician may give up the hope of understanding rubber elasticity when he hears that it is entropy induced rather than energy induced. Certainly he will expect the theory of rubber elasticity to be more esoteric and difficult than the theory of metal elasticity which is largely energy induced.

However, the opposite is true! It turns out that the calculation of entropy in ideal gases and ideal rubber involves no more than the counting of numbers of atomic arrangements. This is so, because in statistical mechanics the entropy is seen to be a measure for the number of possibilities in which a thermodynamic state can be realized.

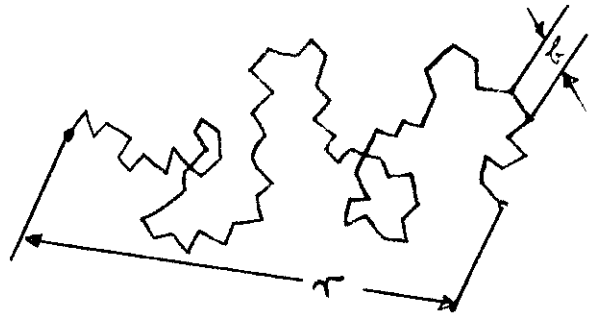
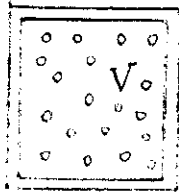
3.2 Statistical Definition of Entropy

Entropy is a property that refers to systems of many tiny elements such as

an ideal gas which consists of N atoms changing their positions independently.

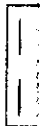


a rubber molecule which consists of a long chain of N links changing their orientation independently.



In equilibrium we describe such a system macroscopically by

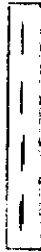
volume V



end-to-end distance r .

Microscopically we describe the system by saying that

$N_{\tilde{x}}$ atoms lie at the point \tilde{x} with $\sum_{\tilde{x} \in V} N_{\tilde{x}} = N$



$N_{\theta\phi}$ links point into the direction θ, ϕ with $\sum_{\theta, \phi} N_{\theta\phi} = N$, $\sum_{\theta, \phi} b \cos \theta N_{\theta\phi} = r$

There are

$$W = \frac{N!}{\prod_{\tilde{x} \in V} N_{\tilde{x}}!}$$



$$W = \frac{N!}{\prod_{\theta, \phi} N_{\theta\phi}!} \quad (3.1)$$

possible realizations of the microscopic state, and the entropy measures this number by giving

$$H = k \ln W.$$

If the system is left alone so that equilibrium can be established, we shall see the microscopic state most often that has the greatest number W . If the maximum is sharp enough, we shall see that state exclusively. Equilibrium entropy therefore comes out as

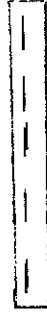
$$H|_E = k \ln W_{\max} \quad (3.2)$$

3.3 Calculation of $H|_E$ for Ideal Gases and Rubber Molecules.

We maximize

$$H = k \ln \frac{N!}{\prod_{x \in V} N_x!}$$

$$= k [N \ln N - \sum_x N_x \ln N_x]$$

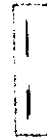


$$H = k \ln \frac{N!}{\prod_{\theta, \phi} N_{\theta\phi}!}$$

$$= k [N \ln N - \sum_{\theta, \phi} N_{\theta\phi} \ln N_{\theta\phi}]$$

under the constraints

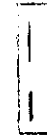
$$\sum_x N_x = N$$



$$\sum_{\theta\phi} N_{\theta\phi} = N, \quad \sum_{\theta\phi} b \cos \theta N_{\theta\phi} = r. \quad (3.3)$$

There results

$$N_x = e^{-(1 + \frac{\alpha}{k})}$$



$$N_{\theta\phi} = e^{-(1 + \frac{\alpha}{k}) - \frac{\beta}{k} b \cos \theta}$$

For the determination of the Lagrange multipliers α and β , we insert these distributions into the constraints and assume that

the number of points between \underline{x} and $\underline{x} + d\underline{x}$ is equal to $\gamma d\underline{x}$



the number of orientations between θ, ϕ and $\theta + d\theta, \phi + d\phi$ is equal to $\gamma \sin \theta d\theta d\phi$.

Thus one obtains

$$N_x = \frac{1}{Y} N \frac{1}{V}$$

$$N_{\theta\phi} = \frac{1}{2\pi Y} N \frac{e^{-\frac{\beta}{k} b \cos \theta}}{\int_0^\pi e^{-\frac{\beta}{k} b \cos \theta} \sin \theta d\theta} \quad (3.4)$$

with β to be determined from

$$\begin{aligned} \frac{r}{Nb} &= \frac{\int_0^\pi \cos \theta e^{-\frac{\beta}{k} b \cos \theta} \sin \theta d\theta}{\int_0^\pi e^{-\frac{\beta}{k} b \cos \theta} \sin \theta d\theta} \\ &= -\frac{d}{d(\frac{\beta}{k} b)} \ln \left(\int_0^\pi e^{-\frac{\beta}{k} b \cos \theta} \sin \theta d\theta \right) \\ &= -\frac{d}{d(\frac{\beta}{k} b)} \ln \left(2 \frac{\sinh \frac{\beta}{k} b}{\frac{\beta}{k} b} \right) \\ &= -\left(\coth \frac{\beta}{k} b - \frac{1}{\frac{\beta}{k} b} \right) \\ &\approx -\left(\frac{1}{3} \frac{\beta}{k} b \right) \text{ for } \frac{r}{Nb} \ll 1. \end{aligned}$$

$$\Rightarrow \frac{\beta}{k} \approx -\frac{r}{Nb^2} \quad (3.5)$$

Insertion into the entropy formula gives $H|_E$, and we get

$$\begin{aligned} H|_E &= k(N \ln N + \sum_x (\ln Y + \ln V - \ln N) N_x) \\ &= Nk (\ln Y + \ln V) \\ &= Nm \left[\frac{k}{m} \ln (Nm Y) + \frac{k}{m} \ln v \right] \end{aligned}$$

$$\begin{aligned} H|_E &= k[N \ln N + \sum_{\theta, \phi} (\ln 2\pi Y + \\ &\quad \ln \int_0^\pi e^{-\frac{\beta}{k} b \cos \theta} \sin \theta d\theta - \\ &\quad \ln N + \frac{\beta}{k} b \cos \theta) N_{\theta\phi}] \\ &= k[N \ln (2\pi Y) + N \ln \left(2 \frac{\sinh \frac{\beta}{k} b}{\frac{\beta}{k} b} \right) + \frac{\beta}{k} r] \\ &\approx k[N \ln (4\pi Y) - \frac{2}{3} \frac{r^2}{Nb^2}] \quad (3.6) \end{aligned}$$

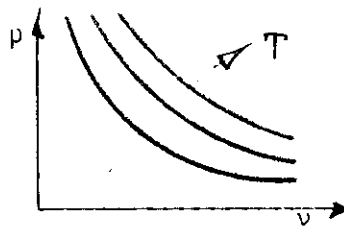
Note that the entropy of a gas is biggest when v is infinite so that there is an equidistribution in space. Also the entropy of a rubber molecule is biggest for $r = 0$ when there is an equidistribution of orientation. There are many other examples of this type and one expresses this by saying that the tendency for entropy to grow reflects the tendency of systems to an equidistribution or to maximum disorder.

3.4 Thermal Equation of State for an ideal gas

As far as the gas is concerned, the story is readily concluded. We have $\eta = \frac{k}{m} \ln v + \alpha$ and insertion of this expression into (2.2)₁ gives

$$p = \frac{k}{m} \frac{1}{v} T \quad (3.7)$$

which is the thermal equation of state of an ideal gas. Its v -dependence is illustrated by the figure



3.5 Suggestive considerations concerning one rubber molecule.

With respect to ideal rubber we are not finished. Indeed, while we have calculated the entropy of a rubber molecule we are far from having calculated the specific entropy of a piece of bulk rubber. Nevertheless, before we embark on this it is instructive to comment on some features of (3.6).

Indeed, we may consider a rubber molecule in itself as a system with entropy induced elasticity, whose load L results from a differentiation of

entropy with respect to the length in the manner indicated by (2.2):

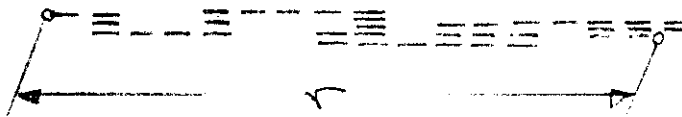
$$L = -T \frac{\partial H|_E}{\partial r} .$$

Thus one obtains

$$L = \frac{4}{3} \frac{kT}{Nb^2} r. \quad (3.8)$$

In this manner the rubber molecule is understood to have the same load-length characteristic as an elastic spring, but with a temperature dependent spring constant. Indeed this is how the dynamic behaviour of long chain molecules in polymer solutions is modelled in the kinetic theory of such solutions.

Also, the consideration of rubber molecules is particularly apt for a suggestive explanation of entropy induced elasticity. Indeed, from the picture of the rubber molecule as an entangled chain, we understand immediately the large extensibility of rubber. But why does it go back? The formal answer to that is, of course, that the entropy wants to grow and therefore r tends to zero. But this can also be understood suggestively. Indeed, under the thermal motion the molecular chain assumes a different configuration every 10^{-12} sec(say) and each configuration occurs with the same probability. But there are many more configurations pertaining to a short end-to-end distance than to a long one. Therefore a small value of r is much more probable than a large one and we expect (nb!) to see a contraction. To give an idea about numbers, let us check out the "one-dimensional" tangle" consisting of N_{\pm} links in the positive and negative direction respectively.



In this case we have

$$\begin{aligned} N_+ + N_- &= N \\ N_+ - N_- &= \frac{r}{b} \end{aligned} \quad N_{\pm} = \frac{N}{2} \left(1 \pm \frac{r}{Nb} \right) \quad (3.9)$$

and the number of possibilities to realize r is given by

$$W = \frac{N!}{N_+! N_-!} = \frac{N!}{\left[\frac{N}{2} \left(1 + \frac{r}{Nb} \right) \right]! \left[\frac{N}{2} \left(1 - \frac{r}{Nb} \right) \right]!} \quad (3.10)$$

If $r = Nb$, we obviously have $W = 1$, but for $N_+ = N_- = 50$ (say) we have

$$W \approx e^{69} \approx 9 \cdot 10^{29}.$$

The contraction can only occur when there are thermal fluctuations and it is clear that it is made easier by more vigorous fluctuations, i.e. by a higher temperature. Therefore it is more difficult to maintain a given deformation at a high temperature than at a low one and the force needed is bigger.

3.6 Entropy of Bulk Rubber

We focus attention upon a small volume element of rubber which has n molecules as indicated in the figure:



If the volume element is cubic at first, it will go into a orthorhombic shape under the deformation

$$F_{iA} = \begin{bmatrix} \lambda & 0 & 0 \\ 0 & 1/\sqrt{\lambda} & 0 \\ 0 & 0 & 1/\sqrt{\lambda} \end{bmatrix}$$

and the molecules will be combed in the direction of the applied force.

To fix the ideas, we shall assume the molecules are shifted parallel with the end down to the center of the cube into the origin of a rectangular Cartesian coordinate frame. The axes are denoted by θ_i before the deformation and by ϑ_i afterwards.



The entropy of the element is given by the sum of the entropies of the molecules and we have ⁺)

$$H_U|_E = \iiint_{-\infty}^{\infty} k[N \ln(4\pi Y) - \frac{2}{3} \frac{\theta_1^2 + \theta_2^2 + \theta_3^2}{Nb^2}] Z(\theta_1 \theta_2 \theta_3) d\theta_1 d\theta_2 d\theta_3$$

$$H|_E = \iiint_{-\infty}^{\infty} k[N \ln(4\pi Y) - \frac{2}{3} \frac{\vartheta_1^2 + \vartheta_2^2 + \vartheta_3^2}{Nb^2}] z(\vartheta_1 \vartheta_2 \vartheta_3) d\vartheta_1 d\vartheta_2 d\vartheta_3 \quad (3.11)$$

before and after the deformation. $Z(\theta_A)$ and $z(\vartheta_i)$ are the respective number densities of end points of the chains and these functions must now be determined.

$Z(\theta_A)$ is easily determined from the plausible assumption that the number of ends between θ_A and $\theta_A + d\theta_A$ be proportional to the maximal number of possibilities to realize that end to end distance. Thus

⁺) Integration may be taken from $-\infty$ to $+\infty$, instead of from $-Nb$ to $+Nb$, because the difference in the integral is small, since Z and z are falling off rapidly for large arguments, as we shall see.

$$Z(\theta_A) \sim W = e^{H|E/k} \quad \text{or by (3.6)}$$

$$Z(\theta_A) = Ce^{-\frac{2}{3} \frac{\theta_1^2 + \theta_2^2 + \theta_3^2}{Nb^2}}$$

The constant of proportionality may be determined from the requirement that the total number of points equals n . thus

$$n = \iiint_{-\infty}^{\infty} Z(\theta_A) d\theta_1 d\theta_2 d\theta_3 + C = \frac{n}{[\frac{3}{2} \pi Nb^2]^{3/2}}$$

We have therefore found

$$Z(\theta_1) = \frac{n}{[\frac{3}{2} \pi Nb^2]^{3/2}} e^{-\frac{2}{3} \frac{\theta_1^2 + \theta_2^2 + \theta_3^2}{Nb^2}} \quad (3.12)$$

The determination of $z(\theta_i)$ makes use of the "assumption of an affine deformation". By this we mean that the end-to-end distance r of the molecules deform in the same manner as the element as a whole. This means that we must have

$$\theta_i = \begin{bmatrix} \lambda & 0 & 0 \\ 0 & 1/\sqrt{\lambda} & \\ 0 & 0 & 1/\sqrt{\lambda} \end{bmatrix} \theta_A \quad (3.13)$$

This assumption allows us to determine $z(\theta_i)$ because the number of molecules is conserved in the deformation so that we have

$$z(F_{iA} \theta_A) d\theta_1 d\theta_2 d\theta_3 = Z(\theta_A) d\theta_1 d\theta_2 d\theta_3 \quad (3.14)$$

Now, because of incompressibility $d\theta_1 d\theta_2 d\theta_3$ equals $d\theta_1 d\theta_2 d\theta_3$ and we obtain from (14)

$$z(\theta_1, \theta_2, \theta_3) = Z(\frac{1}{\lambda} \theta_1, \sqrt{\lambda} \theta_2, \sqrt{\lambda} \theta_3)$$

$$z(\theta_1, \theta_2, \theta_3) = \frac{n}{[\frac{3}{2} k N b^2]^{3/2}} e^{-\frac{2}{3} \frac{\lambda^{-2} \theta_1^2 + \lambda(\theta_2^2 + \theta_3^2)}{N b^2}} \quad (3.15)$$

Insertion of $Z(\theta_A)$ and $z(\theta_i)$ from (3.12) and (3.15) into (3.11) allows us to calculate $H_U|_E$ and $H|_E$:

$$H_U|_E = k N n \ln(4\pi Y) - nk \frac{3}{2}, \quad H|_E = k N n \ln(4\pi Y) - nk \left(\frac{\lambda^2}{2} + \frac{1}{\lambda} \right) \quad (3.16)$$

We divide by nm , where m is the mass of a molecule, and obtain

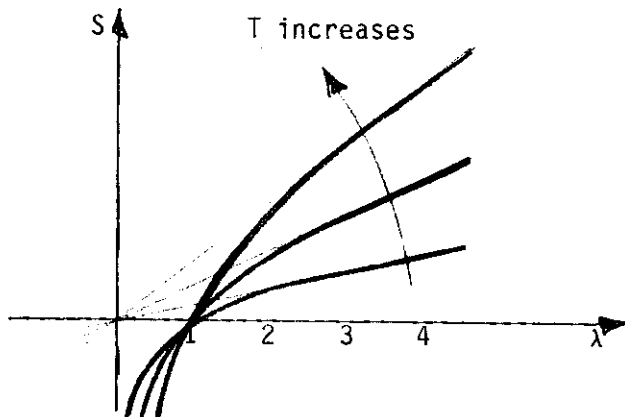
$$\eta_U = \frac{k}{m} N \ln(4\pi Y) - \frac{k}{m} \frac{3}{2}, \quad \eta = \frac{k}{m} N \ln(4\pi Y) - \frac{k}{m} \left(\frac{\lambda^2}{2} + \frac{1}{\lambda} \right) \quad (3.17)$$

3.7 Thermal Equation of State for Ideal Rubber.

Insertion of (3.17) into the equation (2.2)₂ gives

$$S = \frac{kT}{m} \left(\lambda - \frac{1}{\lambda^2} \right). \quad (3.18)$$

This is the thermal equation of state for ideal rubber. As observed - see Section 2.1 - S increases linearly with T and its λ -dependence is illustrated by the following figure:



3.8 The Strain Energy Function

Actually, as we have seen, the strain energy function in the present case is $-T\eta$ so that in reality it is an entropy. We have from (3.17)

$$-T(\eta - \eta_0) = + \frac{kT}{2m} [(\lambda^2 + \frac{2}{\lambda}) - 3]; \quad (3.19)$$

and we should like to write this in a form that is more familiar to people who work in mechanics. In that field the strain energy of an isotropic solid is given as a function of $\underline{C} = \underline{F}^T \underline{F}$, or rather of the three principal invariants of \underline{C} , viz.

$$I_1 = \epsilon_1 + \epsilon_2 + \epsilon_3, \quad I_2 = \epsilon_1\epsilon_2 + \epsilon_1\epsilon_3 + \epsilon_2\epsilon_3, \quad I_3 = \epsilon_1\epsilon_2\epsilon_3$$

where ϵ_i are the eigenvalues of \underline{C} . In the present case we have

$$C = \begin{bmatrix} \lambda^2 & 0 & 0 \\ 0 & 1/\lambda & 0 \\ 0 & 0 & 1/\lambda \end{bmatrix}$$

and therefore

$$I_1 = \lambda^2 + \frac{2}{\lambda}, \quad I_2 = 2\lambda + \frac{1}{\lambda^2}, \quad I_3 = 1.$$

Thus it turns out that the strain energy function (3.19) can be written as

$$-T(\eta - \eta_0) = \frac{kT}{2m} (I_1 - 3). \quad (3.20)$$

This is independent of I_2 ; and, of course, I_3 is not a variable in an incompressible body for which $I_3 \equiv 1$.

The form (3.20) of the strain energy function is said to characterize a Neo-Hookean elastic solid. This is the form that comes out from the kinetic theory.

3.9. Strain Energy Functions of Ideal Gases and Rubbers.

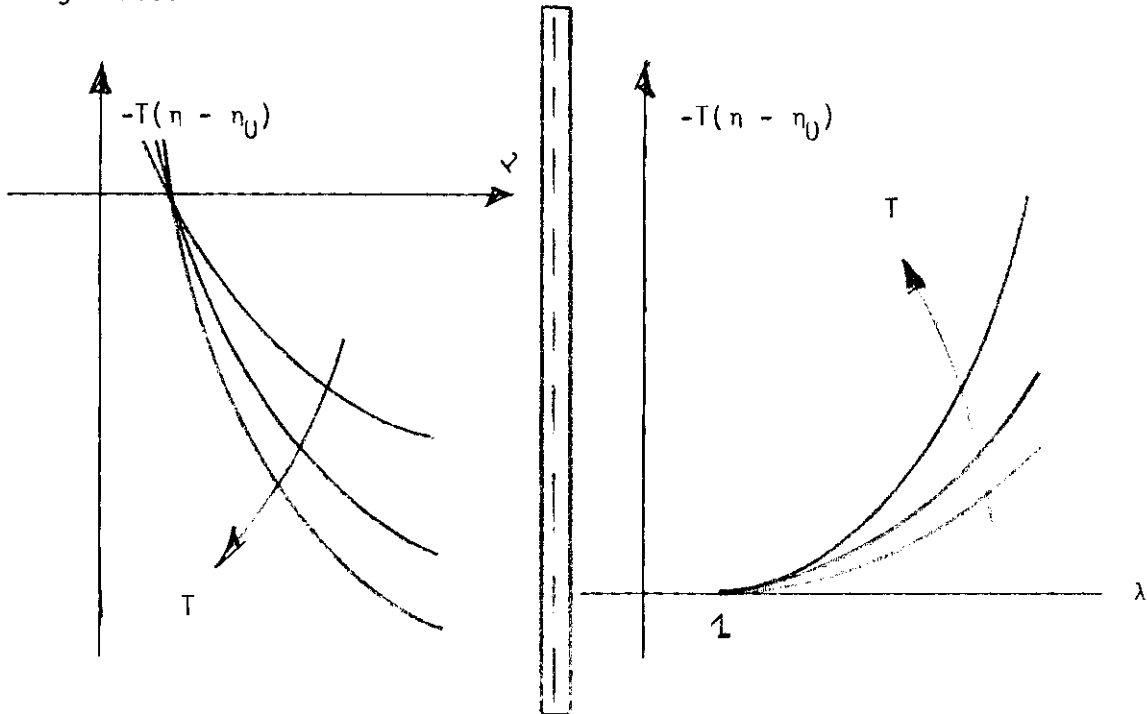
The strain energy function of the ideal gas is equal to $-Tn$ just as for the rubber, but of course the form of that function is different. Indeed, from (1.5) and (3.7) we conclude

$$\left(\frac{\partial n}{\partial v} \right)_T = \frac{k}{m} \frac{1}{v}$$

and hence follows by integration

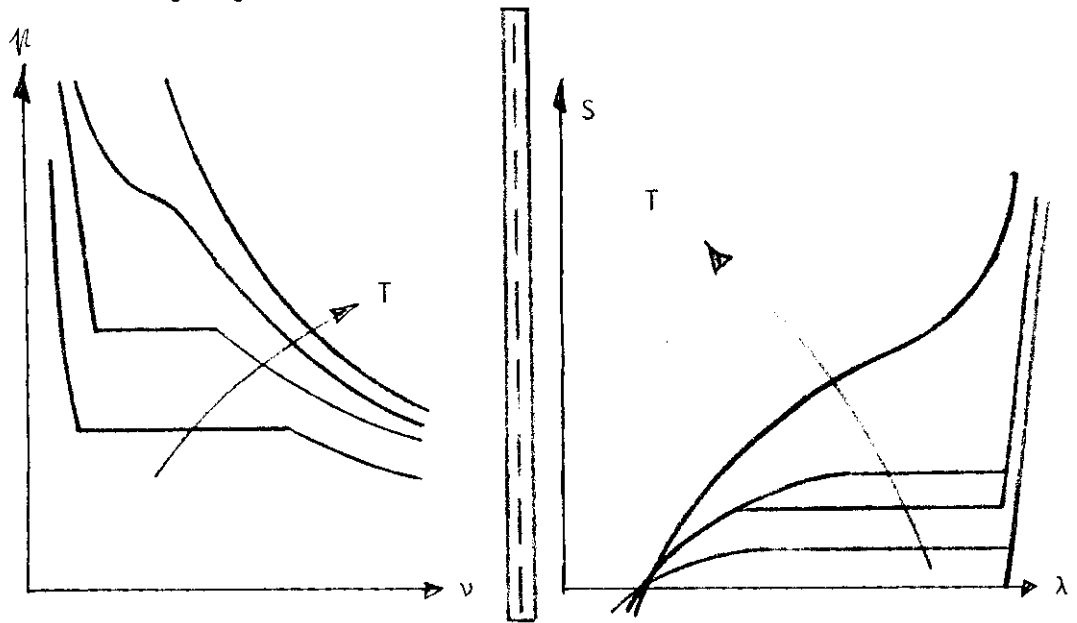
$$-T(n - n_0) = -\frac{k}{m} T \ln \frac{v}{v_0} \tag{3.21}$$

Graphically this function and the function (3.19) are represented by the following curves



4. Observations in Real Gases and Crystallising Rubber

At small temperatures and specific volumes the isotherms of a gas in the (p,v) -diagram do not have the form shown in Section 3.4 anymore. Nor are the isotherms of rubber in the (S,λ) -diagram given by the graphs in Section (3.7) at small temperatures and large values of λ . Instead we observe a behaviour as shown in the following figures



We attribute the departure from the ideal behaviour to a liquid-vapor phase transition in case of the gas and to a crystallisation in the case of rubber.

Let us discuss! In the case of the gas as the temperature is lowered the isotherms first fall below the hyperbolic curve of the ideal gas and then they go steeply up. But they are still smooth until the temperature is too low. From a certain critical temperature on downwards the isotherm develops a straight horizontal branch which grows in width as the temperature drops. Along this horizontal branch it is known that we have the body in an unhomogeneous state; it is partly saturated vapour and partly boiling liquid.

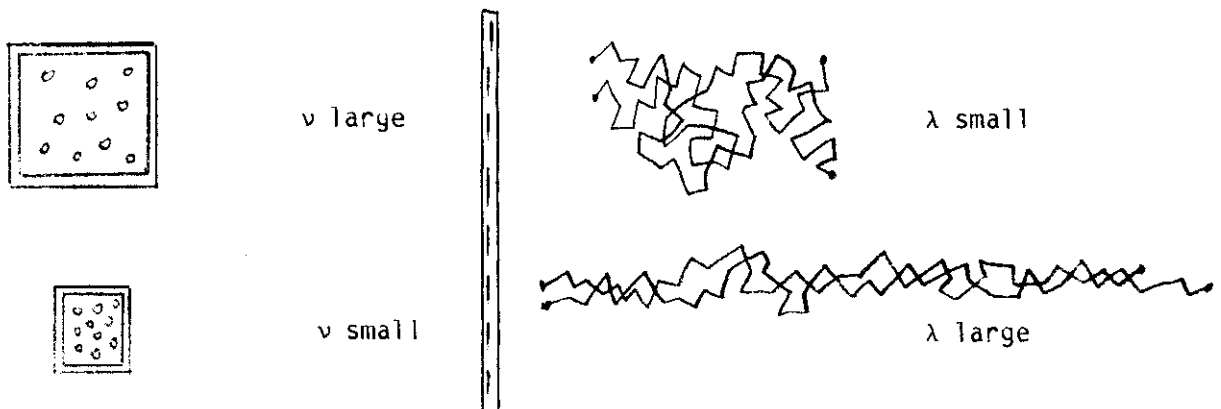
The behaviour of rubber is rather different. At first as the temperature sinks the isotherm falls below the straight asymptote that we have calculated in Section 3.7 and then it turns sharply up. There is again a critical temperature at which the isotherms begin to develop a horizontal branch both in loading and in unloading but now the loading curve is higher than the unloading curve. In other words we now have a hysteresis loop in the (S, λ) -diagram. We may say that the height of the upper branch corresponds to a yield limit and that the height of the lower one is the recovery limit. At small temperatures the recovery limit has fallen below the λ -axis and we observe a residual deformation after unloading.

The phenomena discussed above are indeed observed but the figures for rubber are somewhat idealized.

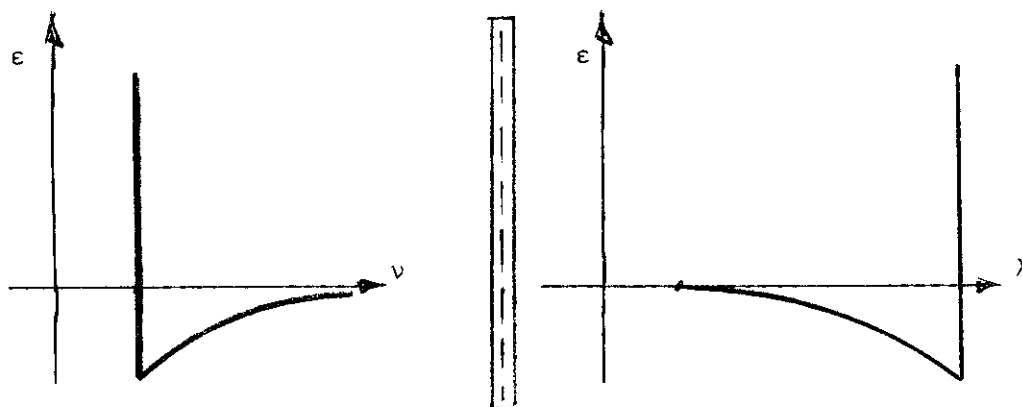
5. Free Energy in Real Gases and Crystallising Rubber

5.1 Qualitative Determination of Internal Energy

It is the growing importance of energetic intermolecular interaction with decreasing volume or increasing load that is behind the deviation of the thermal equations of state for gases and rubber from the ideal behaviour. From simple molecular considerations we can obtain a qualitative determination of the dependence of the internal energy upon volume or deformations.



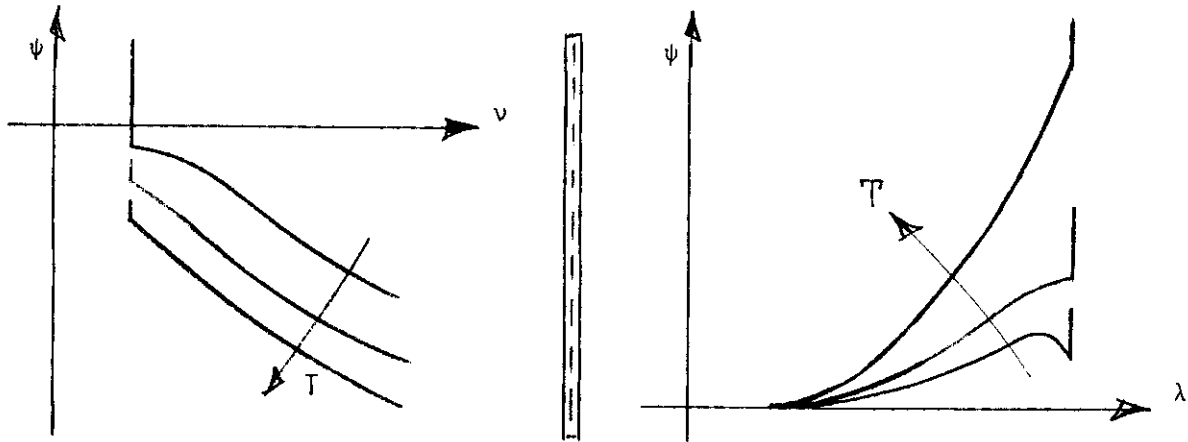
In the case of the gas the molecules are pushed into the range of their attractive van der Waals forces as the volume decreases. One may say that one molecule falls into the potential well of its neighbour and more and more molecules will suffer that fate as the volume keeps decreasing. Therefore the potential energy of the gas decreases with decreasing volume. Of course this cannot go on indefinitely, because eventually the volume will be so small that the molecules touch each other and a further decrease of volume will be resisted by a strong repulsive force. Therefore we expect the energy ϵ to depend on v as shown in the following graph on the left.



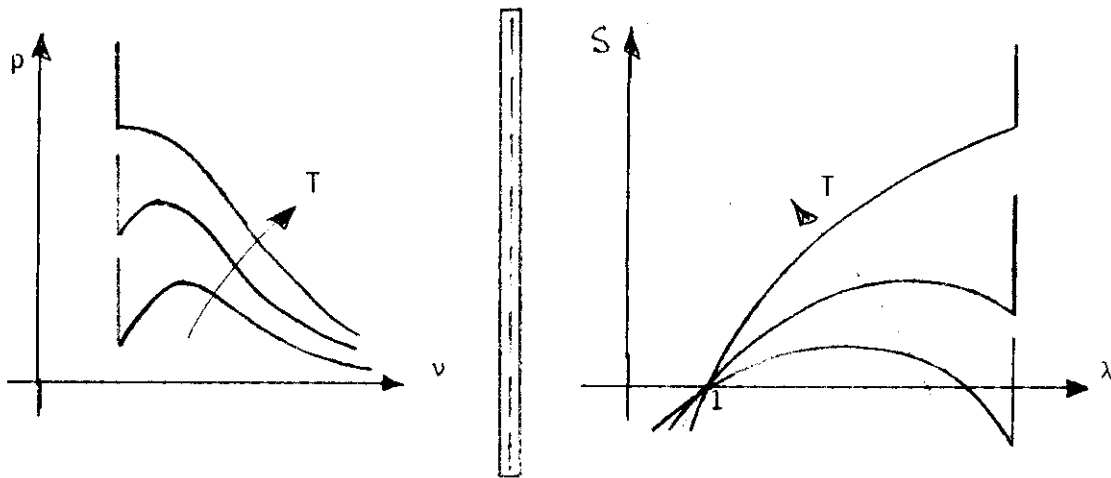
In the case of rubber the molecular picture is rather different. We have the entangled chains that were described in Chapter 3 and a partial disentanglement does not affect the energy appreciably. However, a large deformation will go a long way at disentangling the chains and at the same time the lateral contraction forces large parts of adjacent chains into the range of their mutual attractive van der Waals forces, so that the potential energy drops with increasing λ . This proceeds until the chains are fully extended and laterally squeezed tightly together. Then of course great forces would be needed to achieve a further extension. It would take a lot of energy to stretch the chains and to compress them further and therefore we expect to have a function ϵ versus λ as shown in the above qualitative plot.

5.2 Free Energy and Thermal Equations of State

The plot of free energy $\psi = \epsilon - T\eta$ of a fluid as a function of v results from adding the (ϵ, v) -curve of Section 5.1 to the curves $(-T\eta, v)$ of Section 3.9. Similarly for rubber we add the (ϵ, λ) -curve of Section 5.1 to the $(-T\eta, \lambda)$ -curves of Section (3.9). The following figures show the result



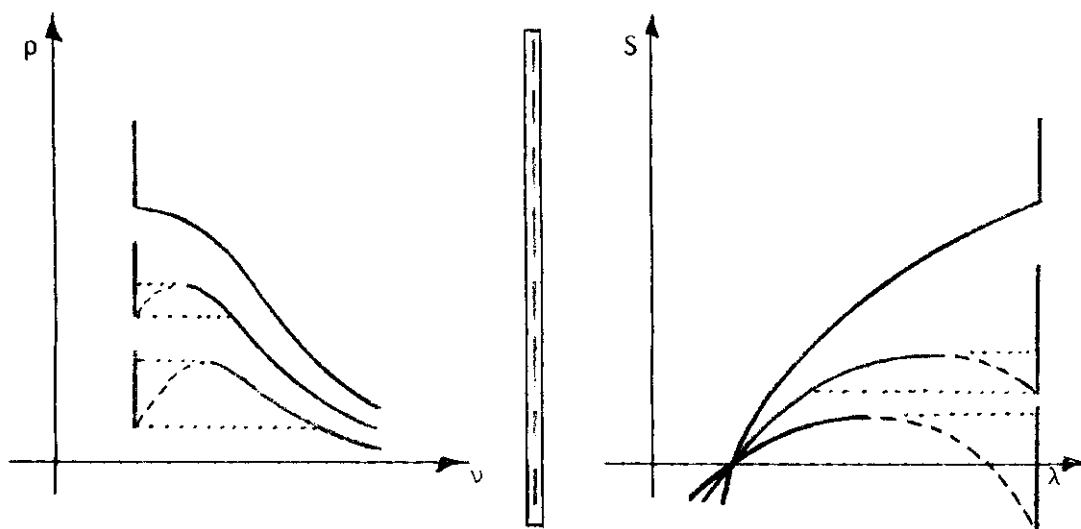
By (1.6) we obtain the thermal equations of state $p = p(v, T)$ and $S = S(\lambda, T)$ from the free energy by differentiation. Thus the isotherms of the fluid in the (p, v) -diagram and of rubber in the (S, λ) -diagram have the following forms.



5.3 Hystereses

The above plots of $p(v,T)$ and $S(\lambda,T)$ must be compared with the experimental results of Chapter 4 and on first sight there is little agreement. Indeed, where we had straight horizontal isotherms and hystereses in Chapter 4 we have non-monotone curves in Section 5.2.

However, with an additional argument we can at least obtain hystereses from the non-monotone curves. Let us consider the intermediate isotherm in the (S,λ) -diagram and let us apply an increasing force starting from $\lambda = 1$. The deformation grows as the force goes up but then there comes the point when the force reaches the maximum in the (S,λ) -curve. Upon a further increase of the force the deformation must increase dramatically until it reaches the right vertical branch. Further loading is now possible without an increase in deformation. Upon unloading the state will stay on the vertical line as long as that line exists and a further slight decrease of the force will make the body move back to the initial part of the isotherm. The behaviour thus described is indicated by the solid and dotted branches of the following curves



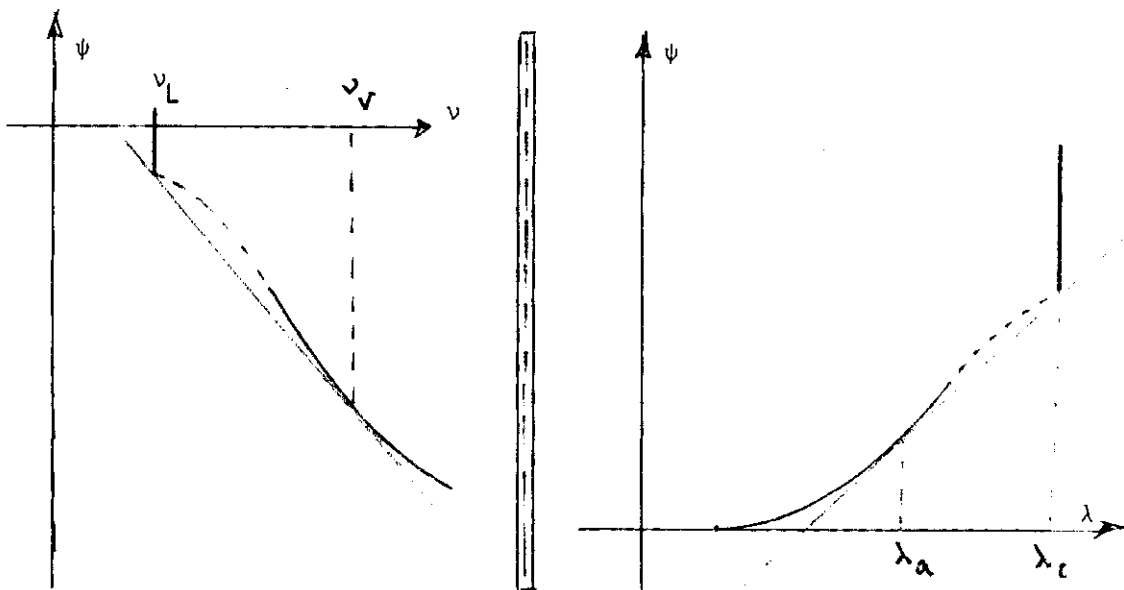
The downward sloping parts of the isotherm - now dotted - are bridged and we see that a loading-unloading cycle involves a hysteresis. Also of course we see

that there is a second force-free configuration at small temperatures in the case of rubber.

As far as the rubber is concerned we could now be satisfied with the agreement between the above curves and those of Chapter 4. However, what holds for rubber should also hold for the fluid and by the present argument we see hystereses in the (p,v) -diagram instead of the single horizontal line that is observed. Can we somehow make sense out of this line in terms of the simple theory presented here? We can indeed as I proceed to show.

5.4 Phase Equilibrium and the Maxwell Line

Non-convex free energy functions like the low-temperature ones in the ψ -diagrams of Section 5.2 allow the body to assume a lower free energy by becoming non-homogeneous. The following figures illustrate that. Indeed the fluid will fall apart into a vapour part of specific volume v_V and a liquid part with v_L . Similarly the rubber can decompose into an amorphous part with deformation λ_a and a crystalline part with λ_c . The overall volume or deformation will then be



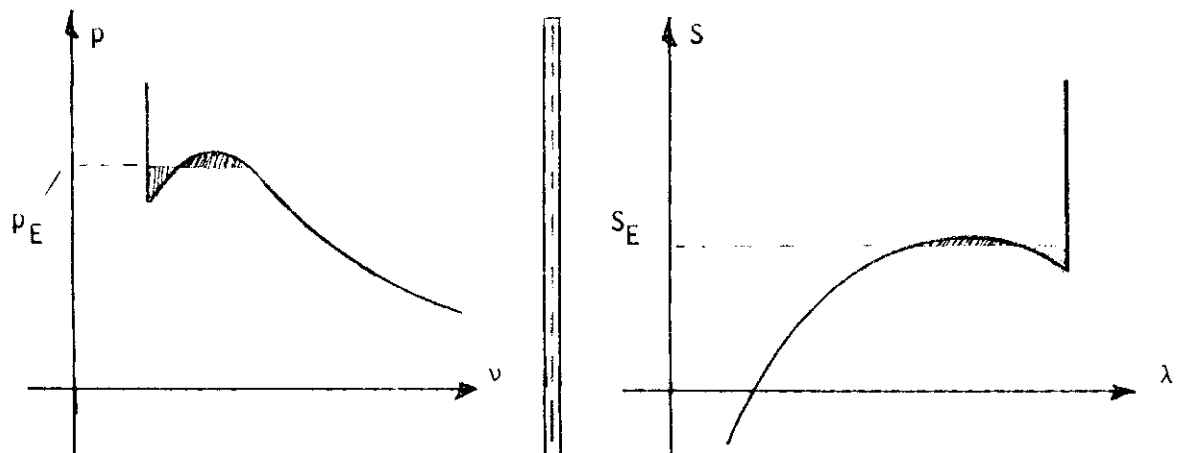
$$v = xv_V + (1 - x)v_L \quad \parallel \quad \lambda = x\lambda_C + (1 - x)\lambda_a \quad (5.1)$$

where x is the mass fraction of vapour or of crystallized rubber respectively. The free energies are

$$\psi = x\psi_V + (1 - x)\psi_L \quad \parallel \quad \psi = x\psi_C + (1 - x)\psi_a \quad (5.2)$$

and they are obviously lower than the actually calculated free energy. Therefore the bodies can establish a "phase equilibrium" on the convex envelope of the ψ -curves and change volume or deformation by changing the mass fractions x . The pressure p_E or force S_E in phase equilibrium is given by the slope of the straight lines.

A construction equivalent to the construction of the straight part of the convex envelope is the Maxwell construction in the (p,v) -diagram or the (S,λ) diagram that is shown in the following figures. The value of the pressure p_E



or force S_E for which the phase equilibrium exists is found by making the two shaded areas equal in size.

In order to prove that this construction is equivalent to the construction of the convex envelope of the ψ -curves, we write

$$\psi_V - \psi_L = -p_E(v_V - v_L) \quad \left| \begin{array}{c} \psi \\ \lambda \end{array} \right. \quad \psi_C - \psi_a = S_E(\lambda_C - \lambda_a) \quad (5.3)$$

which is read-off from the ψ -plots. On the other hand we have

$$p = -\frac{\partial \psi}{\partial v} \quad \left| \begin{array}{c} \psi \\ \lambda \end{array} \right. \quad S = \frac{\partial \psi}{\partial \lambda} \quad (5.4)$$

or by integration along the isotherm

$$\psi_V - \psi_L = -\int_{v_L}^{v_V} p dv \quad \left| \begin{array}{c} \psi \\ \lambda \end{array} \right. \quad \psi_C - \psi_a = \int_{\lambda_a}^{\lambda_C} S d\lambda \quad (5.5)$$

Comparison of (5.3) and (5.5) gives the equations

$$p_E(v_V - v_L) = \int_{v_L}^{v_V} p dv \quad \left| \begin{array}{c} \psi \\ \lambda \end{array} \right. \quad S_E(\lambda_C - \lambda_a) = \int_{\lambda_a}^{\lambda_C} S d\lambda \quad (5.6)$$

which proves that p_E must be such that the area under the isotherm in the (p, v) -diagram must be equal to the rectangle $p_E(v_V - v_L)$ and that confirms the method of determination of p_E in the above plot. An identical argument holds for the phase transition in rubber.

Thus we see that, if the phase separation occurred and if phase equilibrium were established the isotherms of both the fluids and rubber would contain a single horizontal line and no hysteresis. Since, according to Chapter 4, that is what is observed in fluids, while a hysteresis occurs in rubber, we must come to the conclusion that fluids do establish phase equilibrium, while rubber does not.