

Reduced van der Waals equation of state and critical properties of rubbers

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(Received 17 June 1982; revised 17 September 1982)

A reduced equation of state describing the deformation mode as simple elongation is derived for van der Waals networks, thus manifesting general relationships for molecular networks also embracing their stability characteristics and the occurrence of a phase transition.

Keywords Real networks; reduced equation of state; critical data; necking; phase transition

INTRODUCTION

The systems we are dealing with are molecular networks with crosslinked chains of finite lengths. They are indeed localized in physical space, nevertheless representing 'quasi-particles' in conformational space which may be considered as 'conformons' with weak interactions^{1,2}. The idea of considering such networks in their global properties as a van der Waals conformational gas^{1,3} raises questions as to whether there might exist a reduced representation of the equation of state in analogy to the well known formulation for real gases⁴.

THE VAN DER WAALS EQUATION OF STATE AND ITS CRITICAL DATA

In the mode of isothermal isobaric simple elongation a 'van der Waals' network has been shown to have the equation of state^{1,19}:

$$f' = \frac{f}{Nk} = DT \frac{D_m}{D_m - D} - aD^2 \quad (1)$$

with

$$D = \lambda - \lambda^{-2} \quad \lambda = l/l_0 \quad (2)$$

where l is the independent strain variable related to l_0 , the length in the unstrained state. According to equation (2) D_m is written correspondingly:

$$D_m = \lambda_m - \lambda_m^{-2} \quad \lambda_m = l_{\max}/l_0 \quad (3)$$

The maximum strain λ_m should be related to the number of statistical segments in the chains, n_{st} , for a Gaussian chain^{5,6} expressed by:

$$\lambda_m^2 = n_{st} \quad (4)$$

In equation (1) T is the absolute temperature and the parameter a is the second van der Waals coefficient which takes into consideration global interactions which are cooperative in nature.

For all rubbers that have been studied up to now, the van der Waals equation of state describes the elastic properties quite well within the total range of elongations^{7,8}. But we note immediately that this

equation of state does not everywhere satisfy the criteria of intrinsic stability¹. For one of these criteria is that:

$$(\partial f'/\partial \lambda)_T > 0 \quad (5)$$

and this condition is clearly violated for systems with appropriate values of (λ_m, a) over a definite range of strains. This is shown for a typical isotherm in *Figure 1*. A phase transition consequently must occur in this system.

We shall consider a rubber in the state A of *Figure 1* and in contact with a temperature and pressure reservoir. The force of the reservoir is quasistatically increased and leads to a corresponding quasistatic increase in the force of the system. The temperature is maintained strictly constant. The system proceeds along the isotherm in *Figure 1* from the point A in the direction of B. Under equilibrium conditions (leaving out the problems of phase nucleation) a new phase with the intrinsic strain λ'' should appear at B coexisting with the original system elongated only to λ' . The total length of the system thus suffers a discontinuous change at the force of the phase transition.

The general characteristics of stability of such systems of the van der Waals type can then best be expressed by the use of the 'critical coordinates' which can be derived from the conditions⁴:

$$\partial f'/\partial \lambda = \partial^2 f'/\partial \lambda^2 = 0 \quad (6)$$

With $\partial D/\partial \lambda > 0$ the identity:

$$\partial f'/\partial \lambda = (\partial f'/\partial D)(\partial D/\partial \lambda) \quad (7)$$

leads to:

$$\frac{\partial f'}{\partial D} = \frac{\partial^2 f'}{\partial D^2} = 0 \quad (8)$$

With equation (1) we thus find:

$$\frac{\partial f'}{\partial D} = \frac{D_m T}{D_m - D} + \frac{D D_m T}{(D_m - D)^2} - 2aD \quad (9)$$

as well as:

$$\partial^2 f'/\partial D^2 = 2 \left(\frac{D_m T}{(D_m - D)^2} + \frac{D D_m T}{(D_m - D)^3} - a \right) \quad (10)$$

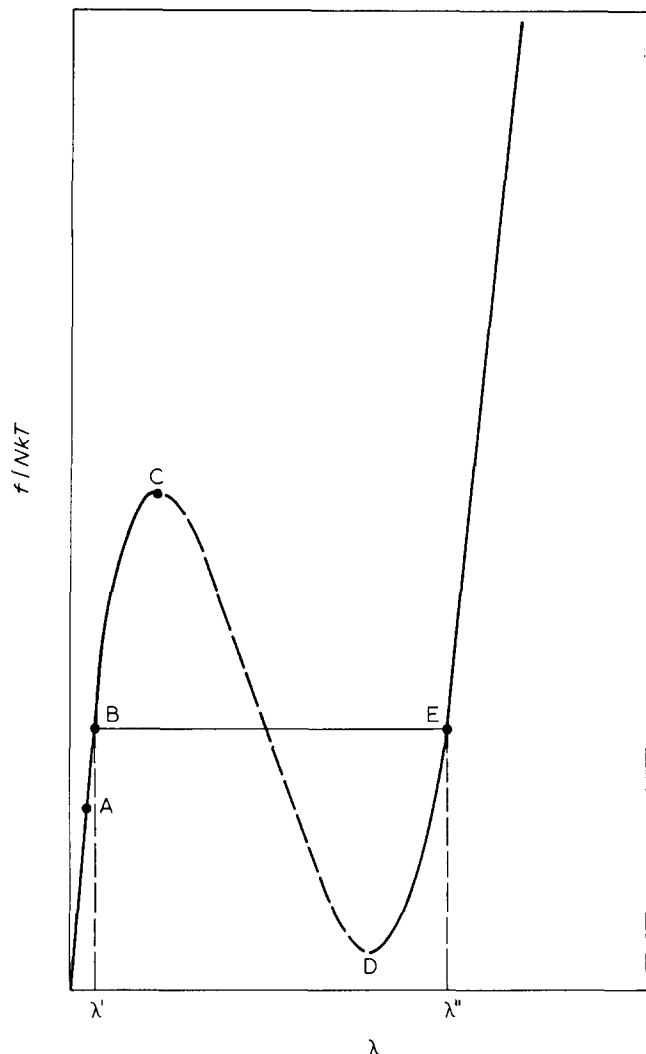


Figure 1 Stress-strain curve with absolute boundaries of stability given by C and D. A phase transition has to occur along the Maxwell line BE transforming the system from the homogeneous orientation state λ' into that one as represented by λ'' by macroscopical necking

The critical coordinates of the van der Waals conformational gas are thus obtained as:

$$\begin{aligned} T_c &= 8aD_m/27 \\ D_c &= D_m/3 \\ f'_c &= aD_m^2/27 \end{aligned} \quad (11)$$

It is evident that the thermoelastic stability of real networks is uniquely determined by the van der Waals parameters, λ_m and a . It is to be noted that these parameters modify the global properties of real networks only, letting the transformation of all intrinsic properties, such as for example the short-range order which is 'liquid-like', be regulated by the thermodynamical conditions of internal equilibrium⁹.

It may be of interest to remark here on the consequences that might become important for understanding irreversibly processed extensions of polymers with network structures, also embracing solid-state deformation. The treatments must of course be

extended by appropriate means^{10,11}. Because of the necessity to relate such considerations in principle to equilibrium states^{10,12}, we immediately recognize the significance of a generalized van der Waals approach without discussing details as to how this approach has to be formulated. Hope is engendered to derive stability criteria for probably heuristical equilibrium states in deformed networks which must of course also govern all of the irreversible phenomena. Hence, 'necking', for example, often observed in solid-state extension experiments of polymers¹³, might become understandable from analogous reasons as in the van der Waals approach presented.

THE REDUCED EQUATION OF STATE

The presence of relationships in the deformation behaviour of rubbers in the mode of isothermal-isobaric simple elongation, which is recognized from the typical bending of the stress-strain curves⁵, is best investigated by formulating a reduced equation of state. This can easily be done by referring to the critical coordinates of the van der Waals network. Hence, defining:

$$\tilde{f}' = f'/f'_c \quad d = D/D_c \quad t = T/T_c \quad (12)$$

we are immediately led to the reduced equation of state:

$$\tilde{f}' = d \left(\frac{8t}{3-d} - 3d \right) \quad (13)$$

The quality of the quantitative representation of the experimental data on various rubbers is demonstrated in Figure 2.

With the limits of stability defined by:

$$\partial \tilde{f}' / \partial d = 0 \quad (14)$$

we arrive at the analytical representation:

$$\tilde{f}'(d) = d^2(3-2d) \quad (15)$$

In this way we obtain the broken curve drawn in Figure 3, separating the homogeneous from the heterogeneous regions in the state diagram. It may be stressed here that the above representation is possible with knowledge of the two van der Waals parameters only, thus clearly bringing out the fact that the relative course of the stress-strain curves of rubbers is determined solely by 'global' properties of the networks. The similarity in shape of the reduced experimental stress-strain data^{1,3,5,7,8} underlines topological symmetry in the deformation behaviour of rubbers irrespective of the actual number of chains present. This number, defined in the simplest case by N and in more complicated situations by an adequately formulated 'prefactor' in the equation of state¹⁴⁻¹⁷, comes into play of course if the discussion of absolute forces is wanted.

In view of the phenomena which are expected to arise close to the limits of stability^{10,12}, it appears very satisfactory to observe that the parameters, a and λ_m , obtained by an optimum fit to the experimental data^{1,7,8}, are found to have always the same order of magnitude (see legend of Figure 2 as well as refs. 1, 7 and 8).

By knowing the limits of stability (broken curve in Figure 2), it is indeed shown by the isotherms of actual

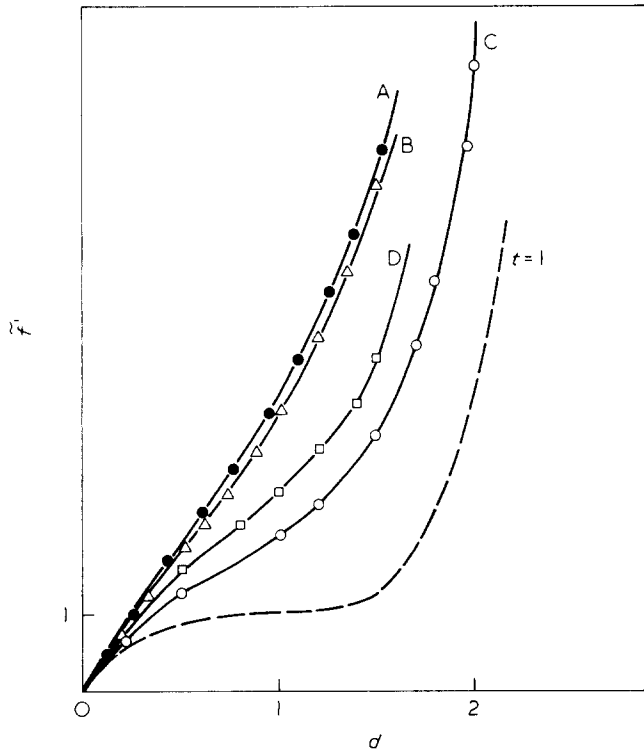


Figure 2 Experimental representation of the stress-strain curves in the reduced representation. Curve A: $D_m=10$, $a=0.2$, $t=1.685$, with $D_c=3.33$, $T_c=177.8$ K and $f_c/Nk=0.74$ (natural rubber and polychloroprene). Curve B: $D_m=8.5$, $a=0.24$, $t=1.66$, with $D_c=2.83$, $T_c=181.3$ K and $f_c/Nk=0.64$ (polybutadiene). Curve C: $D_m=7.5$, $a=0.36$, $t=1.25$, with $D_c=2.5$, $T_c=240$ K and $f_c/Nk=0.75$ (styrene-butadiene rubber). Curve D: $D_m=13.5$, $a=0.18$, $T=1.39$, with $D_c=4.5$, $T_c=216$ K and $F_c/Nk=1.2$ (styrene-butadiene rubber). Full curves: calculated with equation (13); points: experimental values according to refs 1, 3, 5, 7, 8 and 9

systems that rubbers in practical use are altogether constituted so as to be a marked distance from their limits of stability (see also later).

DISCUSSION

We find from the above representation that the chains in rubbers are on average thermodynamically equivalent; for f' is the average force imposed on a 'single chain' as a basically autonomous subsystem of deformation (see equation (11)). Taking these subsystems as fully autonomous we are led to the ideal network in respect to its global properties^{1,3}. Limitations of stability are shown to be related to global interactions and restrictions in the real network. Here, it is important to notice that the parameter, a , in the form as used is basically expressing energetic interactions affecting the average potential energy of the substituents while λ_m modifies the changes of density of the average kinetic energy of the chains which have finite lengths. Both of these parameters, λ_m and a , are necessary to limit the stability of the system, thus predicting the occurrence of a phase transition at temperatures below the critical temperature²⁰.

An interesting conclusion follows from the fact that every ideal isotropic elastic body has an equation of state which for large elongations shows the same dependence on the strain function $D=\lambda-\lambda^{-2}$ as derived for ideal

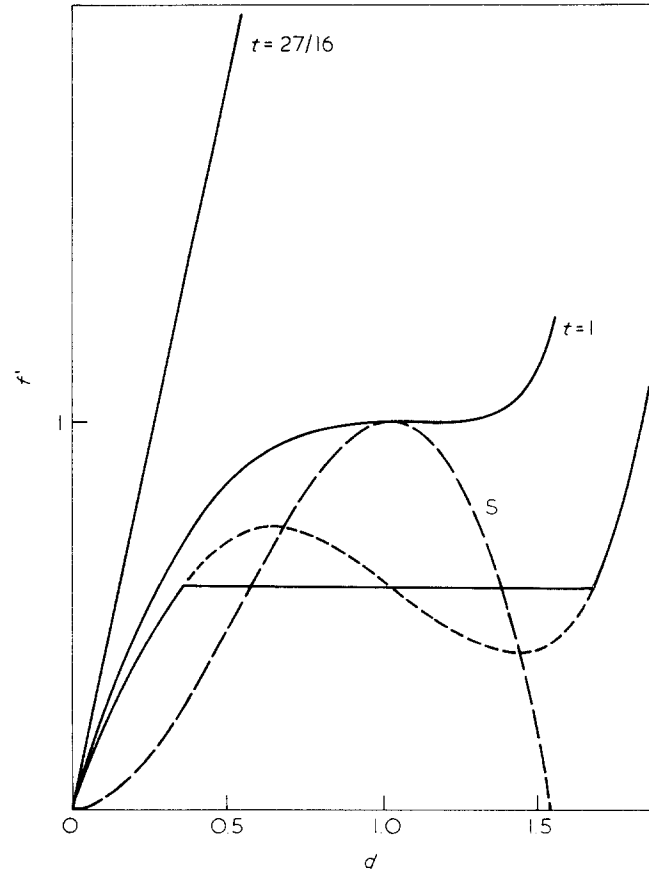


Figure 3 Various deformation curves in the reduced representation. The parameter t represents the ratio $t = T/T_c$ and describes the distance from the boundary of stability marked S. Technical unfilled rubbers are characterized by $t \approx 27/16$

networks¹⁸. The modulus of these systems is naturally related to different origins. Nevertheless, the limits of stability should in principle be related to global interactions between appropriate subsystems of deformation. In the simplest approach they are represented by an adequate van der Waals equation of state. There seems especially to be no doubt about the necessity of considering global entropy and energy changes upon deformation, if the limiting factors of stability, in isotropic or quasi-isotropic elastic systems at sufficiently high strain, are to be identified in general.

ACKNOWLEDGEMENT

The authors are indebted to the Deutsche Forschungsgemeinschaft for supporting this work.

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