The van der Waals-network – a phenomenological approach to dense networks

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An entangled network model developed by S. F. Edwards is used to identify, in more concrete terms, one of the parameters appearing in a phenomenological van der Waals equation of state.

Keywords Rubber; dense networks; van der Waals equation of state; molecular interpretation

INTRODUCTION

A quantitative treatment in the total range of deformation of rubbers is possible with the aid of the van der Waals equation of state of molecular networks[1-3]. This approach can be related to the picture of a conformational gas with weak interactions. Both of the van der Waals parameters, one of them characterizing finite chain extensibility, the other global interactions between the chains, are required to achieve a satisfactory fit to the data[3,4].

It is natural to ask as to whether there is any interpretation of the van der Waals parameters on the basis of an appropriate network model. As a first step in that direction, we present an identification of the chain extensibility parameter with parameters characterizing very entangled networks in the theory by S. F. Edwards recently published[5]. Some interesting conclusions are then discussed.

THE EDWARDS' MODEL FOR DENSE NETWORKS

A randomly crosslinked network is considered, taking into account conformational restraints that are caused by entanglements of interpenetrating chains. These restraints are directly related to the 'primitive path' as shown by the broken line in *Figure 1*. 'Excursions' of chain segments are only allowed to occur if there is a surplus of length over the primitive path. Whereas the total length of the chains is unaltered by deformation, the length of the primitive path is increased when approaching at least the limiting case where the chains are in the state of maximum extension. The primitive path 'system' is assumed to be always deformed according to the law of an affine transformation.

Using this model, Edwards is led to the entropy of deformation $\left(\frac{S}{k}\right)$ as given by

$$\frac{S}{k}=\frac{1}{2}\left\{J^2\left(\frac{1-\alpha}{1-\alpha J}\right)+\log\left(\frac{1-\alpha J}{1-\alpha}\right)\right\}+ +J^2+\beta(J-1) \tag{1}$$

where k is Boltzman's constant. J^2 is defined as

$$J^2=\frac{I}{3}=\frac{1}{3}\sum_{i=1}^{3}\lambda_i^2 \tag{2}$$

where λ_i describes the strain in direction i. In this regime of very entangled networks we have the following relations for the system parameters α and β

$$\alpha=\frac{L_0}{L} \tag{3}$$

and

$$\beta=\alpha q_0\frac{Ll}{6} \tag{4}$$

L_0 is the total length of the primitive path in the unstrained state which is in general less than L, the invariant total length of the chains. l is the size of the

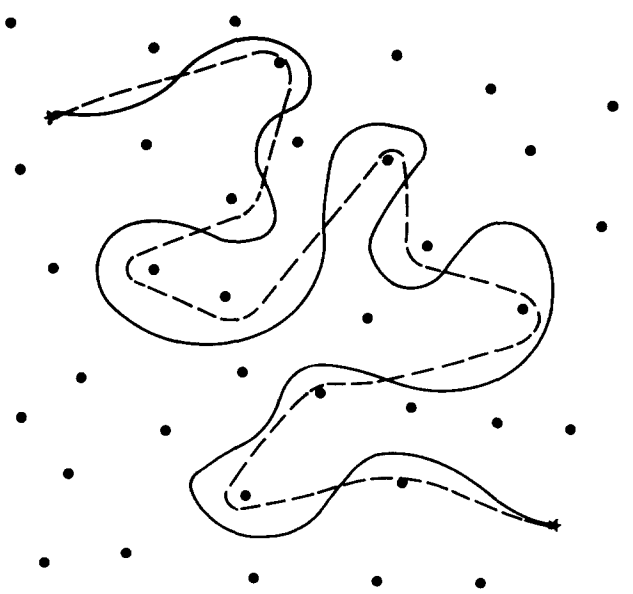

Figure 1 Network model of Edwards. The points illustrate the chains perpendicular to a reference chain represented by the solid line. The broken line would be the primitive path (according to Edwards[5])

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average Kuhn length. To a first approach q_0 may be estimated in terms of the density of entanglements in the dense network, leaving this parameter then independent upon deformation. This parameter defines at least the strength of a local harmonic potential 'pipe' which is imposing typical conformational restraints upon excursing chain sequences within the densely entangled network.

THE MECHANICAL EQUATION OF THE STATE OF THE EDWARDS NETWORK

In making a comparison with the van der Waals equation of state, we need to know the mechanical equation of state for simple extension belonging to the potential defined in equation (1) with the strain invariant formulated as

$$I=\lambda^2+\frac{2}{\lambda} \tag{5}$$

This potential can be rewritten in the special form

$$-\frac{S}{k}=\frac{1}{2}\left\{\frac{1}{3}\left(\lambda^2+\frac{2}{\lambda}\right)\frac{1-\alpha}{1-\frac{\alpha}{\sqrt{3}}\left(\lambda^2+\frac{2}{\lambda}\right)^{1/2}}\right.$$

$$\left.+\log\left[\frac{1-\frac{\alpha}{\sqrt{3}}\left(\lambda^2+\frac{2}{\lambda}\right)^{1/2}}{1-\alpha}\right]\right\}+\frac{1}{3}\left(\lambda^2+\frac{2}{\lambda}\right)+$$

$$+\frac{\beta}{\sqrt{3}}\left[\left(\lambda^2+\frac{2}{\lambda}\right)^{1/2}-1\right] \tag{6}$$

For isothermal extensions we thus derive from

$$\mathrm{d}F=-T\mathrm{d}S\ (\mathrm{d}U=0) \tag{7}$$

with strain independent parameters α and β, the mechanical equation of state of the very entangled network is

$$\frac{f}{k_BT}=D\left\{\frac{1}{3}\frac{1-\alpha}{1-\frac{\alpha}{\sqrt{3}}\left(\lambda^2+\frac{2}{\lambda}\right)^{1/2}}\right.$$

$$+\frac{1}{2}\left(\lambda^2+\frac{2}{\lambda}\right)\frac{(1-\alpha)\frac{\alpha}{\sqrt{3}}}{\left(1-\frac{\alpha}{\sqrt{3}}\left(\lambda^2+\frac{2}{\lambda}\right)^{1/2}\right)^2}+$$

$$\left.+\frac{2}{3}+\frac{\beta}{\sqrt{3}}\frac{1}{\left(\lambda^2+\frac{2}{\lambda}\right)^{1/2}}\right\} \tag{8}$$

with

$$D=\lambda-\frac{1}{\lambda^2} \tag{9}$$

This equation of state is indeed a modification of the ideal network defined in the 'diluted regime'[6] which is easily demonstrated by putting α and β equal to zero, then, arriving at

$$\frac{f}{k_BT}=D \tag{10}$$

The same form of the mechanical equation of state as derived here, is obtained in the van der Waals approach, thus, allowing a direct comparison of both of these approaches.

THE VAN DER WAALS EQUATION OF STATE

Accepting finite chain extensibility, there should exist a maximum macroscopic strain defined by

$$\lambda=\frac{L_{max}}{L_u} \tag{11}$$

where L_{max} and L_u denote the macroscopic lengths of the system in the state of maximum extension and in the unstrained state respectively. Defining then

$$D_m=\lambda_m-\lambda_m^{-2} \tag{12}$$

the van der Waals equation of state can be written as[3]

$$\frac{f}{kT}=D\left\{\frac{D_m}{D_m-D}-aD\right\} \tag{13}$$

with a as the second van der Waals parameter (besides that of λ_m) which is phenomenologically taking into account global interactions between the chains[1,3].

It is possible to derive a reduced equation of state by the use of the critical coordinates of the van der 'Waals-network'[7]. Due to being of sufficiently large distances from the limits of stability, it is then quite easy to defend the picture of considering actual molecular networks as *van der Waals conformational gases with weak interactions only*[1,8]. From this point of view it would be very interesting to ask what the relationships are to the parameters of the entanglement model network of Edwards.

THE COMPARISON

The parameters can easily be related by using the heuristical state of maximum elongation. Here, in both cases a 'catastrophe' occurs, predicting infinitely large forces. We are led to the condition:

$$\alpha J_m=\frac{\alpha}{\sqrt{3}}I_m=\frac{\alpha}{\sqrt{3}}\left(\lambda_m^2+\frac{2}{\lambda_m}\right)^{1/2} \tag{14}$$

Having $\lambda_m \gg 1$ in networks comprising chains which are sufficiently long, the approximate relationship results in

$$\alpha=\frac{\sqrt{3}}{\lambda_m} \tag{15}$$

It is evident in this case that the van der Waals parameter λ_m in very entangled networks is related to effective network functions, also embracing entanglement effects. Moreover, it is a very important observation that both of

these equations of state indeed deliver the same stress–strain behaviour over the total range of strains, provided that in the van der Waals equation of state a is taken to be zero. This is demonstrated in *Figure 2*.

Yet when comparing calculated stress–strain curves with experimental data a satisfactory total fit can only be achieved by the use of both of the van der Waals parameters a and λ_m. When compared with the purely entropyelastic calculation (curve A in *Figure 3*) the modification in the stress–strain behaviour caused by additional global interactions ($a>0$), is illustrated by curve B in *Figure 3*.

DIFFERENT DEFORMATION MODES

For equibiaxial extension the strain invariant of an initially isotropic rubber is defined as[1,6]

$$I^{(2)}=2\lambda^2+\lambda^{-2} \tag{16}$$

Hence, in this deformational mode, we arrive at the relationship

$$\frac{\sqrt{3}}{\alpha}=\sqrt{2}\lambda_m^{(2)}\left(1+\frac{1}{2\lambda_m^{(2)3}}\right)^{1/2} \tag{17}$$

which for $\lambda_m \gg 1$ can be simplified to

$$\lambda_m^{(2)}=\left(\frac{3}{2}\right)^{1/2}\alpha^{-1} \tag{18}$$

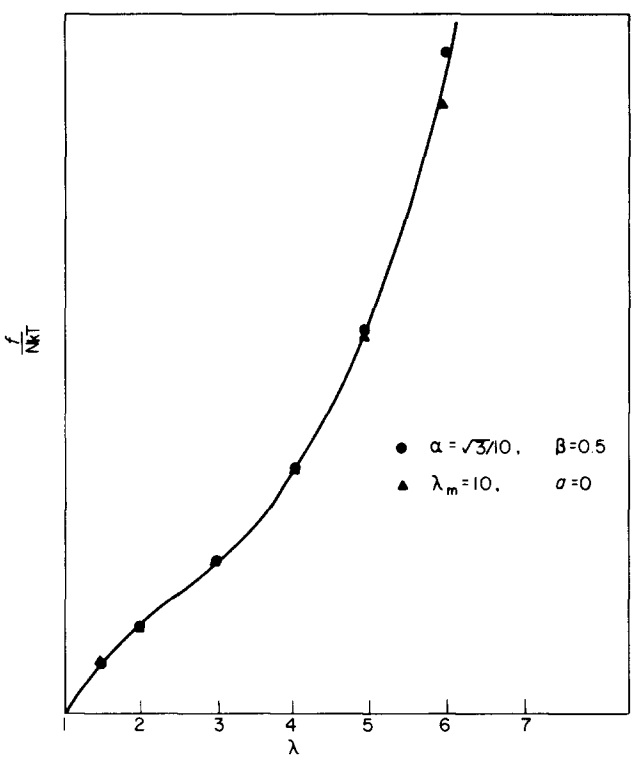

Figure 2 Calculations with the Edwards and van der Waals model deliver good agreement over the total elongation range. Parameter used in the Edwards calculation $\alpha=\frac{\sqrt{3}}{10}$, $\beta=0.5$ (●) and in the van der Waals calculation $\lambda_m=10$, $a=0$ (▲)

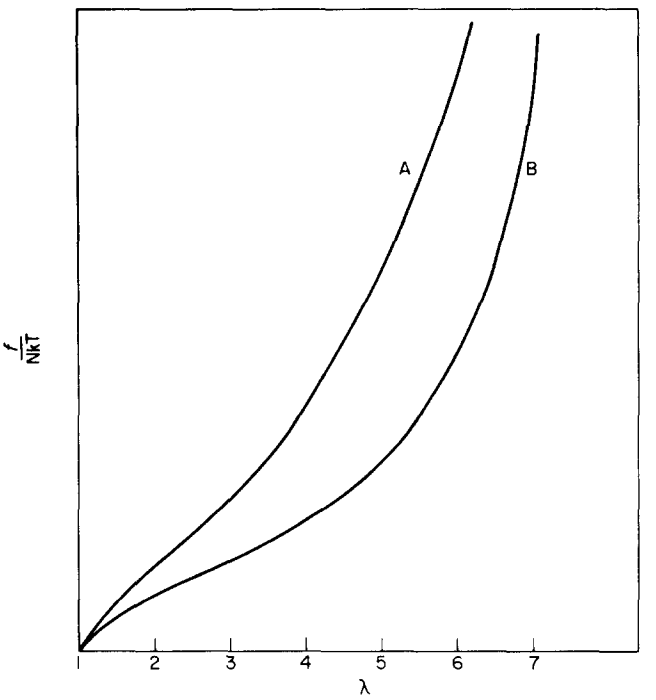

Figure 3 A, Edwards model *and* the van der Waals model without interactions $\lambda_M=10$, $a=0$. B, The van der Waals model with the same $\lambda_M=10$ but setting the interaction parameter to $a=0.2$. With this set of parameters the calculation can fully be fitted to Treloar's data[6], also given in *Figure 4*, curve A

For equitriaxial extension of the network (i.e. swelling) we are led to

$$\lambda_m^{(3)}=\alpha^{-1} \tag{19}$$

such that the following ratios should be in force

$$\lambda_m^{(1)}:\lambda_m^{(2)}:\lambda_m^{(3)}=1:\frac{1}{\sqrt{2}}:\frac{1}{\sqrt{3}} \tag{20}$$

with the mode of deformation indicated by the numbers in the brackets. We can now observe good accordance between the data and calculations as shown in *Figure 4*. The theoretical curves are computed with the $\lambda_m^{(i)}$'s as given in equation (20) also using the forms of the $D_{(i)}$ and $D_{m(i)}$[6] ($D_{(1)}=\lambda-\lambda^{-2}$; $D_{(2)}=\lambda-\lambda^{-5}$).

DISCUSSION

To understand the consequences of the above identifications let us first compute the stress–strain behaviour of a 'diluted' network with finite chain length (clearly representing a very heuristical system). According to the classical theory of Kuhn[9] we then have

$$\frac{f}{kT}=\frac{n^{\frac{1}{2}}}{3}\{\mathcal{L}^{-1}(n^{\frac{1}{2}}\lambda)-\lambda^{-\frac{1}{2}}\mathcal{L}^{-1}(n^{-\frac{1}{2}}\lambda^{-\frac{1}{2}})\} \tag{20a}$$

where $\mathcal{L}^{-1}(x)$ is the inverse Langevin function. n denotes the number of Kuhn segments in the chains. In the Gaussian 'single-chain' approach the maximum extensibility of the chain is approximately given by[6,10]

$$\lambda_m^*=n^{\frac{1}{2}} \tag{21}$$

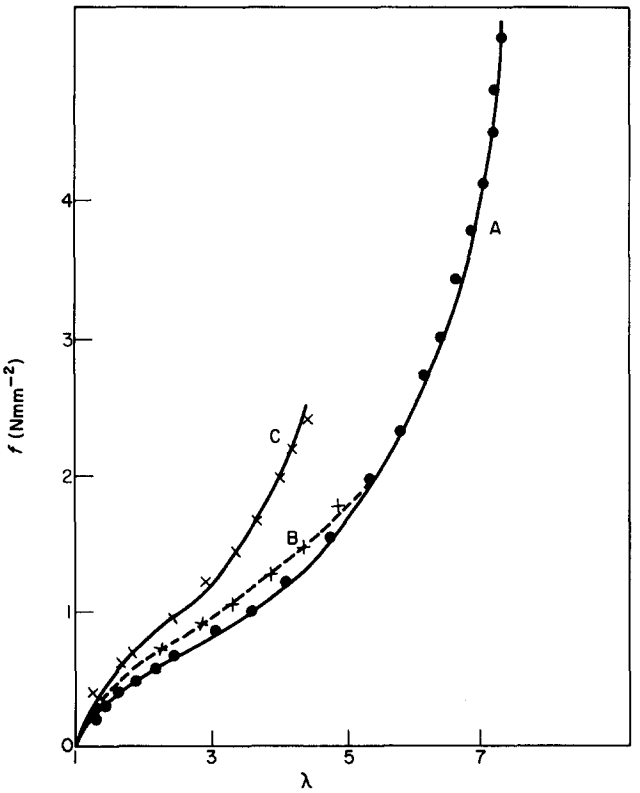

Figure 4 Different deformation modes of natural rubber according to Treloar[6]. A, Simple extension computed with the parameters $\lambda_m = 10$, $a = 0.2$, modulus = 35.8 Nmm^{-2} experimental values (●); B, pure shear calculated with $D = \lambda - \lambda^{-3}$, letting all parameters unaltered; C, equibiaxial extension obtained with the same parameters as used in A except $\lambda_m = \frac{10}{\sqrt{2}}$, $D_{(2)} = \lambda - \lambda^{-5}$

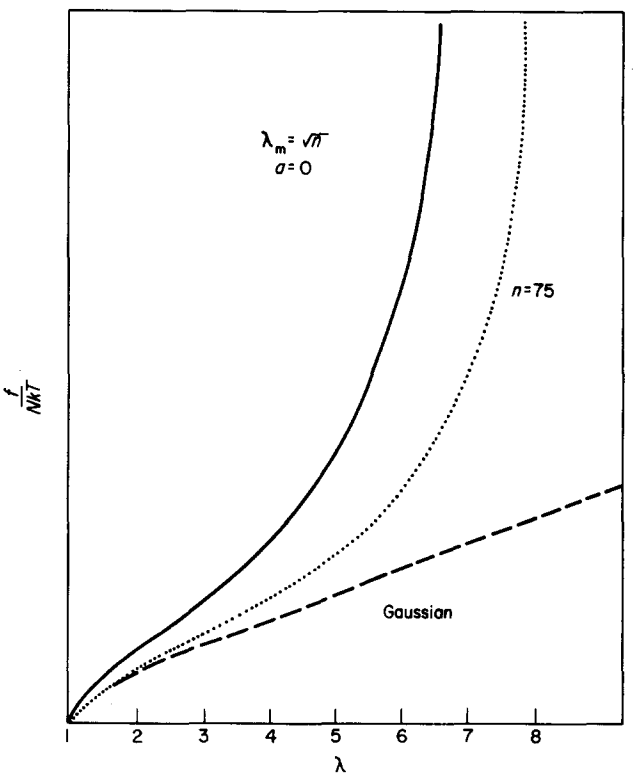

Figure 5 Calculated stress–strain curve of a dense network, represented by the solid line obtained for models employing the parameters: van der Waals $\lambda_m = \sqrt{n}$, $a = 0$; Edwards $\alpha = \sqrt{3/n}$, $\beta = 0.5$ ($n = 75$). The diluted network (Langevin) yields a stress–strain behaviour as given by the broken line with n equal to 75

Using this relation it can be seen from *Figure 5* that systematically increased stresses result for highly entangled networks due to typical constraints as formulated in the Edwards theory[5]. Hence, there is evidence that conformational abilities in highly entangled networks cannot be obtained correctly by a 'single-chain' approach: The conformational freedoms are clearly bound to limitations cooperatively developed by interpenetrating chains.

Taking it for granted that λ_m is uniquely related to the restraint-parameter α, we learn from our quantitative fits-to-data of a large set of rubbers with strain-independent van der Waals parameters in the total range of elongations[1-3,7], that the intrinsic parameters of the densely entangled system are indeed strain-independent. This is once more defending the idea of considering an actual network as a 'conformational gas' with weak global interactions having liquid-like local properties which always satisfy the conditions of internal equilibrium[3,11].

No doubts can be thrown upon the fact, that in the interesting theoretical approach presented by Edwards[5] the presence of global interactions as expressed phenomenologically by the van der Waals parameter a, has not yet been taken into consideration, thus not allowing a discussion of the limits of stability in molecular networks[7,8].

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