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A Molecular Interpretation of the Parameters of the van der Waals Equation of State for Real Networks

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SUMMARY

A molecular interpretation of the phenomenological van der Waals parameters of the equation of state for real molecular networks is presented. The theoretical treatment is eludicating the special role of the crosslinks.

INTRODUCTION

The hypothesis that mutual interactions between the chains of a molecular network do not influence the force of deformation is in contradiction to the concept of a van der Waals equation of state /1,2/. The great potency of explaining a set of different experiments with the aid of that empirical equation of state /1,2/ is stimulating the question if there might be developed a justification of the van der Waals approach.

The situation will be considered to be entirely equivalent to that which is known from the statistical treatment of a van der Waals gas /4/. The problem of understanding is twofold: It is necessary in the first place to provide appropriate means for eludicating the influence of the finite chain lengths ("co-volume") and for subjecting this to quantitative characterization. Secondly, suitable relationships must be established to express the dependence of the physical properties of the molecular network on the mutual interactions between its chains.

THE IDEAL NETWORK

Let us recall essential properties of a Gaussian chain:

- the chain occupies no volume, thus allowing total penetration
- the energy of the chain is kinetical only substantiated by micro-brownian motions of its segments
- with no interactions, the various conformations of the chain are isoenergetical in the statistical average.

For the ideal network the following properties are important /8/:

- the N chains in the network are Gaussian-chains

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- the junctions are assumed to be point-like without any orientational restrictions to the segments involved
- the mean square end-to-end distance for the whole assembly of chains in the unstrained state is the same as for a corresponding set of free chains
- the junctions points between the chains move on deformation as if there were embeded in an affine continuum
- autonomy of the chains is represented by the fact that the entropy of the network is the sum of the entropies of the individual chains.

The ideal network has only kinetical energy which is uniformly distributed over the chains in the statistical average. Letting the "translational volume" occupied by the centers of mass of the chains, be invariant, we may describe the deformation with the aid of the idealized network model the centers of mass of which are considered to be localized. Hence, the ideal network may be described as "an ideal gas" in the conformational space /2,3/. The chains are the "quasi-particles" of the system which have the well-known deformation potential /8/

$$W = NkT \ \psi(\lambda); \quad \lambda = L/L_o \tag{1}$$

with N as the number of chains, k BOLTZMAN's constant, T the absolute temperature. $\psi(\lambda)$ is the "deformation function" which has for simple elongation the form

$$\psi(\lambda) = (\lambda^2 + 2/\lambda - 3)/2 \tag{2}$$

Hence, we learn from

$$W_o \ (\lambda = 1) = N \ (3kT/2) \tag{3}$$

which is the total kinetical energy of the ideal network in the unstrained state, that the quasi-particles are characterized by three freedoms of the kinetical energy.

The elastic retractive force of the ideal rubber is then equal to

$$f = \partial W/ \partial L = NkT \ (\lambda - \lambda^{-2})/L_o = n_o kT \tag{4}$$

with

$$n_o = (N/L_o) \ (\lambda - \lambda^{-2}) = (N/L_o) \ D(\lambda) \tag{5}$$

The meaning of n_o is easily obtained from the comparison with the situation for an ideal gas. Starting with the "isothermal deformation potential"

$$W = NkT \ \ln \ (V/V_o) \tag{6}$$

with V and V_o as the volume in the "deformed" and in the fiducial state resp. we arrive at the equation of state

$$p = (\partial W/\partial V/_T = (N/V)kT = n_g kT \qquad (7)$$

$n_g = N/V$ is the density of the particles in the local part of the phase space /4/. By analogy we thus understand n_o as the density of the quasi-particles (the chains) in the conformational part of the phase space. On stretching the sample, n_O is seen to be increased at least to infinitely large values in the limits $\lambda \rightarrow \infty$. Such singular behaviour is also obtained for an ideal gas in the limits $V \rightarrow 0$. Both of these extrapolations are heuristical, eludicating the fundamental limitations of the models employed.

THE VAN DER WAALS APPROACH

An improved equation of state for an real rubber in tension has recently been presented /1,2/ by taking into account the finite length of the chains as well as interactions between the chains which are modifying the retractive force. Both of these effects are phenomenologically considered by means of two "van der Waals-parameters" b and a /1,2/, thus arriving at the equation of state

$$f = (NkT)/L_o \, \frac{1}{1/D(\lambda) - b} - a \, D(\lambda)^2 \qquad (8)$$

An interpretation of a and b is now intended taking into consideration essentials of the molecular structure of a real network.

THE "EXCLUDED VOLUME"

For an ideal conformational gas the phase space may be separated into three parts, the part describing the positions of the centers of mass, the conformational space and the space of momentum. Hence, it is possible to relate the total differential of the deformation function $d\psi$ to the relative change of the volume of the conformational part of the phase space dV_c/V_c according to /1/

$$dV_c/V_c = - d\psi = - d\lambda \, /(1/D(\lambda)\,) \qquad (9)$$

For real networks with chains the lengths of which are finite but sufficiently large, the above relations must properly be modified in respect to the influence of finite chain lengths. The volume of the chains themselves may be neglected in this case. In turning to equation (8), letting a be equal to zero, we arrive at

$$f = \frac{NkT}{L_o} \, /(1/D - b) \qquad (10)$$

For an permanent network, full stretching is possible only if an "infinite" force is applied. Hence, in these limits we have the condition

$$b = 1(\lambda_{max} - \lambda_{max}^{-2}) = 1/D_m \qquad (11)$$

with $\lambda_{max} = L_{max}/L_o$, which can directly be related to the chain length y for Gaussian chains according to

$$\lambda_{max} = y/y^{1/2} = y^{1/2} \qquad (12)$$

Introducing this correction into equation (9), we obtain

$$(dV_c/V_c) \frac{1}{1-V_{ec}/V_c} = -d\psi \frac{1}{1 - D/D_m} \qquad (13)$$

Hence, the fraction of excluded volume in the conformational space, V_{ec}/V_c is continously increased with increasing values of the elongation

$$V_{ec}/V_c = D/D_m \qquad (14)$$

occupying finally at $\lambda = \lambda_{max}$ the total conformational volume.

Thus, the van der Waals-parameter b is clearly defined by structural properties of the network chains. The situation is more complex for real networks with a chain-length distribution as well as for short-chain networks where the volume of the chains should equally well influence the magnitude of the excluded volume.

THE "INTERACTION PARAMETER a"

Exchange of energy and momentum in the ideal network is only possible at the junctions. Hence, the macroscopically measurable retractive force is in the static limits due to the exchange of momentums. The sum of these momentums is negative in contrast to well known calculations of the static pressure of the ideal gas /9/. In real networks interactions may modify the exchange of momentums.

In order to arrive at a general interpretation of the van der Waals-parameter a, we introduce a local potential along the chains $\phi(z)$ with z running from z = 0 at the junction point up to z = y/2, the center of the chain. Two effects may determine the course of $\phi(z)$:

a) With the formation of the junctions the actual structure properties of the crosslinks are restricting the conformational freedoms in its next neighborhood. On account of the solid angles between the chemically bounded units, for example, the formation of a great number of non-isoenergetical conformations is expected.

b) The mutual interactions between neighboring chain segments may locally be different because of the sterical situation at the junctions themselves.

We now assume that all these complex conformational restrictions are in the statistical average defining the following differential equation

$$-\partial\phi/\partial z = n_o < \gamma(z)> \tag{15}$$

with $<\gamma(z)>$ characterizing locally the energetical situation. $<\gamma(z)> = 0$ results in the ideal network. For real networks, on the other hand, the gradient $\partial\phi/\partial z$ is assumed to vary locally such that the average potential is increased when getting nearer to the junctions. It must be considered as a first approximation if n_o is assumed to be independent on z.
In this particular situation we derive from equation (15) by integration

$$\phi(0) = n_o E \tag{16}$$

where

$$E = 2 \int_0^{y/2} < \gamma(z) > dz \tag{17}$$

If the probability of occupation is then given by BOLTZMANN'S law, we find

$$f = nkT = n_o(\exp(-n_o E/kT))kT \tag{18}$$

With $n_o E \ll kT$ we derive then the approximative equation of state

$$f = n_o kT - n_o^2 E \tag{19}$$

With equation (5) this may be cast into the form

$$f = (NkT/L_o)\cdot D - (N/L_o)^2 E (D)^2 \tag{20}$$

By comparison with equation (8) (letting here b be equal to zero) the statistical equivalent of the phenomenological parameter a is given by

$$a = (N/L_o)^2 E \tag{21}$$

Relation (20) is particularly noteworthy: The equilibrium retractive force of a real molecular network is predicted to be deminished on account of conformational constraints in the next neighbourhood of the junctions: Due to the local potential $\phi(z)$ which is assumed to take its maximum value at the junctions, the exchange of momentum over the crosslinks is reduced, thus, yielding a "pressure component" in the static force f.

It is noteworthy to show that the stability of the network represented by equation (20) is limited.
Form

$$\partial f / \partial L > 0 \tag{22}$$

we derive

$$\lambda_c - \lambda_c^2 < NkT/2aL_o \tag{23}$$

Hence, stable deformed states are possible only in the range of $1 < \lambda < \lambda_c$. This situation is on principle comparable with the behaviour of gases: From the van der Waals equation of state it is predicted that a system with $b = 0$ (without any influence of the "Eigenvolume") are stable only for $V > V_c$. The occurence of condensation in this case is at least eludicating the fact that it is necessary to take into consideration both of the van der Waals parameters to get a reasonable fit to observations.

Hence, combining the above results we arrive at the equation of state of real molecular networks

$$\sigma = \frac{\rho RT}{L_o M_o y} D(\lambda) \frac{D_m(\lambda_m)}{D_m(\lambda_m) - D(\lambda)} - \frac{\rho N_L E}{L_o M_o y RT} D(\lambda) \tag{24}$$

with $\sigma = f/q_o$ where q_o is the initial crossection of the sample. ρ is the density of the system, M_o the molecular weight of the unit and y the number of periodic units of a chain. From this approach we arrive at the following conclusions which should at least be tested by experiments:

a) Molecular networks with sufficiently long chains and correspondingly small values of the parameter a are predicted to be thermodynamicly stable in the total deformation range.

b) E may be dependent on the chemical structure of the crosslinking untis.

c) A phase-transition should occur probably in short chain networks with a proper set of a and b's /1/.

The last statement is illustrated by the calculations shown in figure (1).

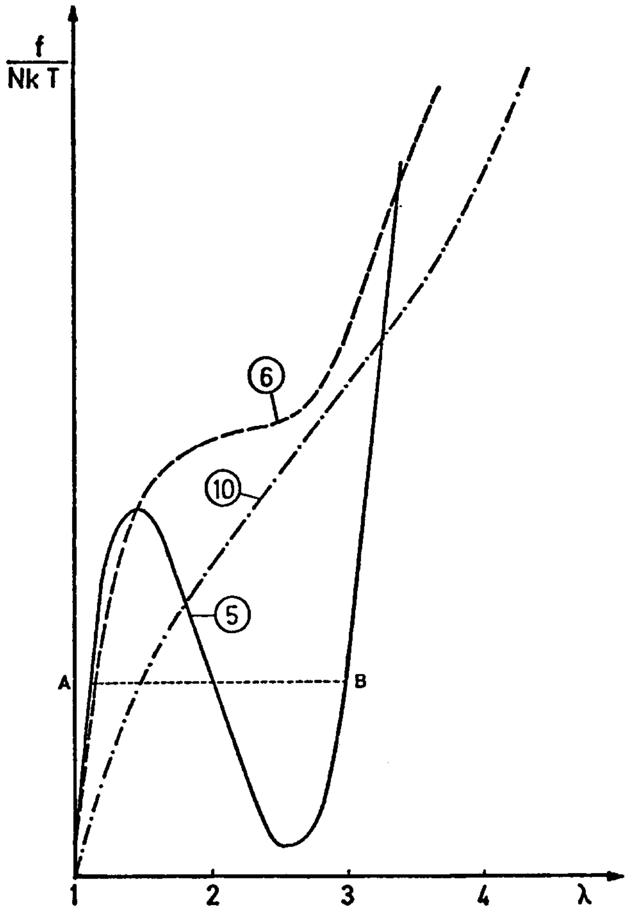

Figure 1: Stress-strain curves for van der Waals-networks with different chain lengths calculated with the aid of Eq.(19), using the parameter:

λ_m as indicated with each curve; $y = \lambda_m^2$; $a_o = \frac{\rho N_L E}{L_o M_o RT} = 20$

A ... B is MAXWELL's line for the transition from A↔B. It must be emphazised that the extrapolation to short-chain networks can only be taken for a qualitative information because of the limited validity of the van der Waals equation of state involved (representing a "conformational gas") /1/.

FINAL REMARKS

The above interpretation of the van der Waals coefficients of the phenomenological equation of state, is based on the assumption that the conformational and the dynamical situation in real molecular networks is characterized by the special role of the crosslinks. One of its manifestations may be seen in a "repulsive component of the retractive force" which should modify the end-to-end distance distribution compared to the Gaussian network.

This statement invites inquiry into the molecular structure of real networks. Significant in this connection are neutron-scattering experiments on model networks with labelled crosslinks published by BENOIT et al. /5/. W.WILKE /6/ has shown recently that the characteristical maximum of the scattering curves can easily be computed with the aid of a hard-core gas model. The hard core might be taken as the simplest representation of the repulsion between the crosslinks.

Using the above model we arrive at the final statement that the retractive force in strained molecular networks may not simply be related to the average segment orientation, thus, invoking a critical discussion of anisotropy properties in rubber elastic systems /7/.

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