

BULLETIN



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FLOW THROUGH POROUS MATERIALS, Part II

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In Part I (Vol. 24, No. 3, pages 43 - 49) simple models of a porous material and relevant regimes of flow were described. In this Part II some experimental results and some current problems are outlined. References to Part I are in the form "equation I.(1)" and references of the form "equation II.(1)" will refer to content of this article. Symbols defined in I are not re-defined here.

About one quarter of the article is taken up with the flow of gases or vapours. Arguably this is inappropriate for a rheological Bulletin. On the other hand, many rheological situations involve a mixture of phases (e.g. displacement of oil by carbon dioxide) and to understand them the flow of each separately is a relevant beginning. (When different phases are present complicated situations can arise, for example, a shock front can develop, Romero and Nilson (1981.)

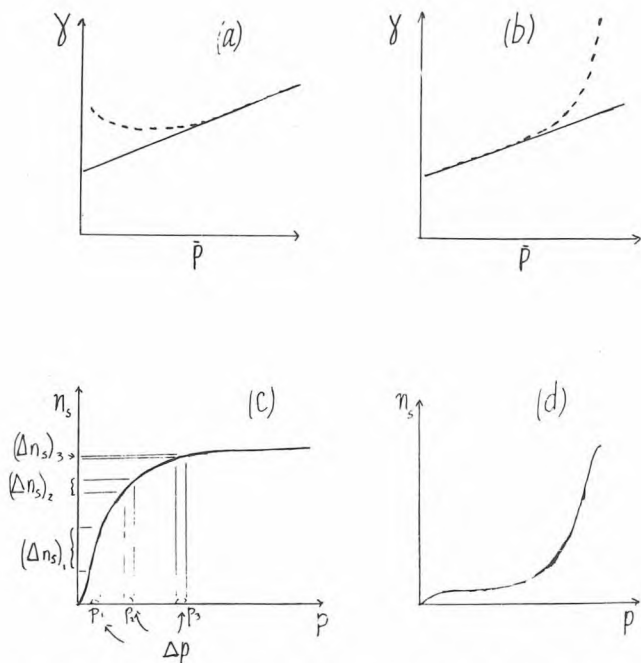
Flow of Adsorbable Vapours

Experiment shows that gas flow through a porous material can be described by

$$\gamma = Q \left(\frac{T}{M} \right)^{\frac{1}{2}} / \left(\frac{dp}{dx} \right) = \frac{b\bar{n}}{\mu} \left(\frac{M}{T} \right)^{\frac{1}{2}} \pm c \quad (1)$$

in which b and c are constants of the porous material. (For the capillary model $b = nBr^4$ and $c = nCr^3$, see equation I (4)). When b and c have been determined experimentally using one gas at one temperature, results for other gases and other temperatures can be predicted. Measured flow of gases agree with those predicted but the flow of vapours is frequently different. Departures follow one of two patterns: (1) the observed and expected flows agree at the higher pressures but observed flow is bigger at lower pressures (Fig. 1 (a)); (2) the observed and expected flows agree at lower pressures and the observed flow is larger at higher pressures (Fig. 1 (b)). In the figure the full line represents predicted flow and the dashed line the observed flow. The difference can be accounted for by different adsorption patterns. Consider the number of molecules n_s adsorbed per unit area as a function of pressure as sketched in Fig. 1 (c) (Langmuir adsorption). Consider equilibrium flow experiments being done at constant pressure difference Δp but at different mean pressures $p_1, p_2, \dots$. At p_1 the concentration gradient in the surface is proportional to $(\Delta n_s)_1$, and at p_3 to $(\Delta n_s)_3$. As $(\Delta n_s)_1 > (\Delta n_s)_3$ so flow in the adsorbed phase is greater at p_1 than at p_3 . Similarly, adsorption isotherms as in 1(d) can be correlated with flow depicted in 1(b).

Fig. 1



It is instructive to consider the influence of pore radius on the proportion of adsorbed flow in the total flow. In a practical example of 1(a) at $\bar{p} = 20$ Torr and for $\bar{r} = 0.1 \mu\text{m}$, flow in the vapour phase was predominantly slip flow Q_s and the flow Q_a in the adsorbed phase was equal to Q_s , so that in,

$$Q = Q_s + Q_a = K_s \cdot r^3 + K_a \cdot r$$

K_s/K_a could be determined. [Q_a is expected to be proportional to the circumference of the pore]. Hence the proportion of different regimes of flow at $\bar{p} = 20$ Torr, for different $\bar{r}$, can be calculated, see Table. (Q_μ is a viscous flow)

Table

$\bar{r} (\mu\text{m})$	100	10	1	0.1	0.01
Q_μ	100%	67%	20%	2%	0%
Q_s	0%	33%	80%	49%	1%
Q_a	0%	0%	0%	49%	99%

From the table it is seen that adsorbed flow does not become relevant until $\bar{r}$ is as small as $0.1 \mu\text{m}$ and then for smaller pores it

predominates. Stomata in leaves are typically $0.1\mu\text{m}$ in size and variable by the plant depending on conditions (amount of CO_2 required) and variation in size would vary the ratio of adsorbable materials to non-adsorbable materials entering from the atmosphere (or leaving from the inner leaf). No doubt in nature, these various mechanisms of flow are of considerable importance. Also, in the fabricated charcoal air cleanser the impurities would not penetrate the fine pores of the charcoal sufficiently rapidly by diffusion in the gas phase, to cleanse the air, but flow in the adsorbed phase is sufficiently rapid to clean the air quickly.

Another mechanism of adsorbed flow is flow of "condensate". As the pressure p_v of a vapour approaches its saturation vapour pressure p_o , condensation can take place in a fine pore when $p_v < p_o$. How much less depends on r as given by the Kelvin equation. When $r = 0.01\mu\text{m}$ condensation of water vapour will occur at $p_v/p_o = 0.9$. If now $p_o > p_2 > p_1 \geq p_v$ then the wetting angles θ_2 and θ_1 at the ends of the capillary will be different from each other and a net surface tension force of $2\pi r\omega(\cos \theta_1 - \cos \theta_2)$ will pull the condensate through the pore. The force is equivalent to a pressure difference

$$\Delta p_c = \frac{p_2 RT}{M} \ln \left(\frac{p_2}{p_1} \right)$$

which for the case being considered is about 80 atm. ($p_2 - p_1$) is of order 10^{-3} atm. and therefore despite the fact the viscosity of the condensate is 100X that of the vapour the flow is 100X larger than it would be in the absence of condensation.

Dimensionless Numbers

Define a Reynolds Number $\text{Re} = \bar{u}r/\mu$ where $\bar{u} = V/\text{An}\pi r^2$ (the mean speed in the porous material) then using 1(7) and 1(8) but corrected for the tortuosity factor, Jones (1956) and Jones and Mills (1961), give $\bar{u} = \pi U/2E$, in which $U = V/A$, so that

$$\text{Re} = \pi U p / S \mu \quad (2)$$

Similarly the friction factor

$$\lambda = \left(2r \left(\frac{dp}{dx} \right) / p u^2 \right) = \frac{32 E^3 \Delta p}{\pi^3 S p U^2 l} \quad (3)$$

The Dean number involves the radius of curvature a of the pores and for a bed made up of spherical particles the curvature would be the path around a particle so that $a = D/2$. Hence from I(12) and I(13) $a = 3(1-E)/S$ and

$$L = \frac{8(\text{Re})^2 r}{a} = \frac{8(\text{Re})^2 2E}{3(1-E)} \quad (4)$$

For beds of spherical particles S , $(1-E)$ and E are determined knowing the mass of particles per unit volume and their individual size. Flow is used to determine S when particle sizes and shape are not known; E

can always be found by straightforward weighing methods, possibly using liquid uptake.

Various other relations exist to define Re and λ depending on the model used for the porous material. In some works the mean diameter of the particles making up the porous material, rather than $\bar{r}$, is substituted for the linear dimension in Re . They may be related to II(2) and II(3), Jones (1976).

For non-newtonian fluids the apparent viscosity μ_a appropriate to the rate of shear $\dot{\gamma}$ must be substituted in eqn II(2). For a power-law fluid, constitutive equation

$$T = k^1 \dot{\gamma}^{n^1}$$

where k^1 and n^1 are constants, one finds for the capillary model

$$\mu_a = \frac{3n^1 + 1}{8n^1} \left(2k^1 \right)^{\frac{1}{n^1}} \left(\frac{17\pi s}{4E\Delta p} \right)^{\frac{1}{1-n^1}} \quad (5)$$

Kemblowski and Michmiewicz (1979) have considered the effect of the distribution of pore sizes and Franzen (1979) the effect of variations in the packing of spheres, on μ_a .

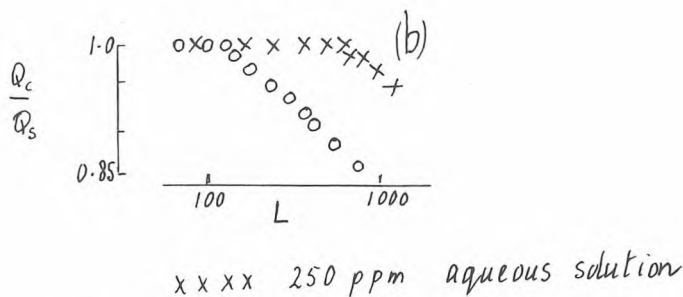
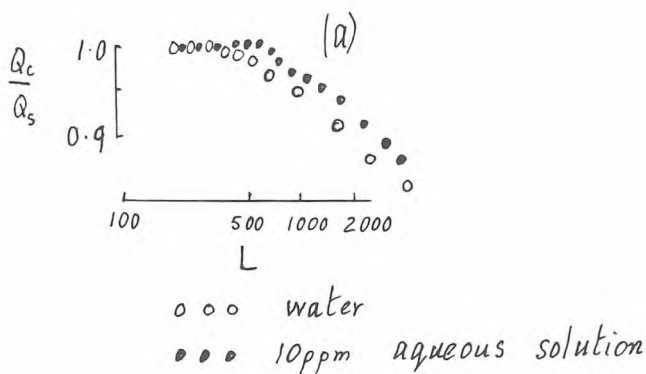
For elastic fluids normal stresses affect the flow and the Deborah number becomes relevant.

Inertial Effects in the Flow of Liquids and Gases

The flow of all newtonian fluids including gases, can be represented on a single plot (usually logarithmic) of λ as a function of Re . Departure from a straight line occurs for $Re = O(10)$, Jones and Mills (1961) and Jones (1968). This occurs because curvature of the pores and/or cross-sectional shape, leads to secondary 'inertial' motion similar to Dean flow in pipes. It is interesting to see that equation II(4) with $L = 276$ (the 'critical' Dean number for secondary motion to be relevant, see I) and $E = 0.4$ leads to $Re = 9$, independently of the porous material.

The presence of traces of polymeric substances in a fluid (typically 10 ppm to 250 ppm by weight) affects the measurable onset of Dean flow in curved pipes. For example, the sketch in Fig. 2 (a) illustrates the fact that $Q_c/Q_s = 1$ for water up to $L = 276$ but for an aqueous Xanthan gum solution $Q_c/Q_s = 1$ up to $L = 520$. The effect would be larger at larger concentrations. For flow through a bed of glass beads a similar result is obtained (Fig. 2 (b)) suggesting the inertial effect in beds is similar to that in curved pipes.

Fig. 2



Relaxation Effects in the Flow of Liquids and Gases

For a given sample of porous material the flow of liquids and of gases begins to show inertial effects at exactly the same value Re of Re , in most cases. The exceptions are of some interest.

For the flow of carbon dioxide and of nitrogen at mean pressures of from 1 atm to 75 atm at temperatures ranging from room temperature to 35°C, Re is constant independently of pressure and of temperature provided the pore radius is "large". For "small" pores ($\approx 0.1 \mu m$), Re for the flow of nitrogen is constant independently of mean pressure but that for carbon dioxide varies with mean pressure. At 14.5 atm $(Re)_{CO_2} > (Re)_{N_2}$ whereas at 42 atm $(Re)_{CO_2} < (Re)_{N_2}$. This peculiar behaviour of CO_2 may be related to ideal Joule-Kelvin

cooling combined with real frictional heating, thus giving an energy sink (or source) which affects the onset of inertial flow. (Jones and Williams, 1963). The sink (or source) is identified with the vibrational mode of the CO_2 molecule, which takes $1.7\mu\text{s}$ to reach equilibrium with the translational mode. This relaxation time multiplied by the speed of flow of the gas, gives a 'relaxation length' of $0.1\mu\text{m}$ comparable with the pore radius. When this relaxation length differs significantly from the pore radius, the 'effects' do not occur.

For dilute solutions of macromolecules the longest relaxation time of an individual macromolecule is of order 1 ms, 1000 x that of the CO_2 molecule, so that effects on secondary motion and stability, might be expected in much larger pores. This is indeed the case and manifests itself as an increase in the resistance to flow as the relaxation length approaches the pore diameter. The resistance ultimately reaches a peak as flow rate increases, then falls off to near what is anticipated from newtonian viscous resistance. Savins (1969) described early experiments and their interpretation in terms of normal stresses and/or elongational viscosity. Jones and Davies (1976) and James and Soringer (1980) have pursued these ideas. Others interpret the results in terms of adsorption that is, molecules are attached to the surface thus reducing the pore space available for flow but at high rates of flow these are pulled off by shearing forces thus opening the pores out again. Jones and Ho (1979) elaborate on these concepts and they give references to relevant papers.

Current Problems

Several investigations now being undertaken on various aspects of flow in porous media arise from the one industrial problem of oil recovery, see for example Dreher and Gogarty (1979) and Johansen (1979). Oil occurs in the fine pores in sediments and is confined there under ambient pressure by an impermeable rock cap. When the cap is breached, oil (and gas) gushes out and may be piped to the surface. When the gusher ceases as much as 80% of the oil can remain underground. Water might now be forced down into the oil-bearing rock which will then push oil ahead of it and ultimately up a central pipe to the surface. (Secondary oil recovery.) Nevertheless, after this process 40% of the original oil can still remain stuck to the surface (or in constrictions) or in blocked pores. This oil might be 'washed off' and recovered (tertiary oil recovery) using a suitable surfactant. But surfactant is expensive and one proposal is to use a 'plug' of surfactant which is pushed along by water from behind. In some wells the oil might be too viscous to remove economically by this means and steam might be used as the displacing fluid as the oil would then be at a higher temperature and therefore less viscous. Carbon dioxide has also been considered as a displacement fluid rather than water, even for crude oils of low viscosity, provided the carbon dioxide can be brought up to the well conveniently. (Carbon dioxide dissolves in oil

thus lowering the viscosity.) Another option, is to burn the oil underground and use the energy in situ.

When the viscosity of the displacing liquid (water) is less than or similar to, the viscosity of the liquid being displaced then the front between the two fluids is unstable and some of the displacing liquid can penetrate into the displaced fluid, a phenomenon called 'fingering'. The interfacial tension is also relevant here as shown by Taylor and Saffman (1958). The characteristic number relevant to this fingering is $\mu\ddot{u}/\omega$. In the field, for quite viscous fluids, the 'mobility ratio'

$$M = \frac{k_{wo} \mu_o}{k_{ow} \mu_w}$$

is an important number to adjust where k_{wo} is the permeability of the rock to water in the presence of oil, k_{ow} is the permeability to oil in the presence of water, μ_o and μ_w are the shear viscosities of oil and water respectively. $M < 1$ reduces fingering and also cusping. One way of changing M is to increase the viscosity of the water and this is brought about by the addition of small quantities of high molecular weight polymers. Also of course the surfactant might carry oil along in it which is essentially the flow of an emulsion. Hence, the interest in the flow of polymer solutions and in the flow of emulsions, through porous media.

A related problem can arise when the rock is non-uniform and there are parallel strata of different permeabilities. Flow will tend to be faster through the more permeable and ways of slowing this down might be required. If the front is to move at the same speed $\ddot{u}$ through the finer pores as it does through the wider, then shear thinning of the pusher fluid might appear to be necessary since the average shear rate in a bore is $\ddot{u}/r$. However Jones (1980) showed the best that can be expected is some reduction of the larger flow through the more permeable material by using shear-thickening fluids as pushers. When two fluids are present, together with the front and associated capillarity, the relative slow-down in the larger pores is further enhanced as mentioned by Grist (1977). The use of foams as pusher fluids is also an advantage in these circumstances.

So the fundamentals of the flow of gases, vapours, and liquids (and various mixtures thereof) are relevant in this one industrial problem. Added to the possibilities of capillarity, adsorption, slip, and so on, there are the variables of clay platelets which adsorb materials, and salt which alters molecular shape. Furthermore, many oil wells are at high temperatures and high pressures so there must be no degradation of materials over several weeks, under such conditions. So not unexpectedly there is a demand for much development work (e.g. finding a suitable polymer) in the laboratory as well as in the field. There is still need for example for experiments on the flow of emulsions through corrugated pipes as a model of emulsion flow through porous materials.

I would like to acknowledge my indebtedness to B.P. Research (Sunbury-on-Thames) for support, thereby maintaining my interest in flow through porous materials.

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A REVIEW LECTURE

"A review lecture given on Max van den Tempel's contribution to the study of the rheology of dispersions and emulsions"

by DR. H. A. BARNES

Unilever Research Laboratory, Port Sunlight

Paper given at the
FAREWELL SYMPOSIUM

for

DR. M. VAN DEN TEMPEL

(Honorary Member of the B.S.R.)

on 4th June, 1981, at

Url Vlaardingen, Netherlands

Abstract of "Max van den Tempel's contribution to the study of the rheology of dispersions and emulsions" by Dr. H. A. Barnes — URL Port Sunlight

Van den Tempel's (hereafter vdT) interest in emulsion stability dates from his pre-Unilever days, and involved him in the calculation and measurement of the position and depth of the secondary minimum formed between neighbouring droplets. This work laid the foundation for his later interest in:

- (i) predicting the bulk rheological properties of emulsions and dispersions using theories containing the basic particle interaction terms or vice versa,
- (ii) using rheological measurements to evaluate otherwise unmeasurable colloid parameters, using a rheometer as a mechanical integrator.

This interest grew alongside the development of careful rheological measurements often performed in purpose built rheometers.

The first ever volume of *Rheologica Acta* saw the publication of his initial efforts in the field, being a qualitative description of a dispersion network model to interpret experimental results. This contained the germ of all the later work.

In seven papers following, the network model was:

- (i) made quantitative for attractive systems,
- (ii) used to measure bond strengths, interparticle distances and particle size,
- (iii) modified to include aggregate effects,
- (iv) extended to predict high stress effects (viscosity/shear rate),
- (v) lately to account for polyelectrolyte stabilised dispersions.

These efforts have been formalised into vdT's overall picture of weak gels and fit in well to the mathematical formulations of Marucci, Tanner and others.

VdT has kept interest alive in this otherwise neglected and unfashionable but important area of rheology.

TEXT

Van den Tempel's (hereafter vdT) interest in emulsion stability dates from his pre-Unilever days when he worked for the Dutch Rubber Foundation⁽¹⁻⁵⁾. This work involved him in the calculation and measurement of the position and depth of the secondary minimum formed between neighbouring emulsion droplets⁽⁶⁾. This work laid the foundation for his later interest in:

- (i) predicting the bulk rheological properties of emulsions and dispersions using theories containing the basic particle interaction terms or
- (ii) using rheological measurements to evaluate otherwise unmeasurable colloid parameters (this latter pursuit is still of major interest to colloid chemists).

This interest grew alongside the development of careful rheological measurements in purpose-built rheometers.

The first ever volume of *Rheologica Acta* contains a paper contributed by vdT on the rheology of plastic fats⁽⁷⁾ where he was already postulating the existence of a three-dimensional network. In his abstract of this paper in *Rheology Abstracts*, Lodge sums it up as "Data are interpreted qualitatively in terms of cracks produced in a network containing different kinds of junction points". (Abs. No. 141.)

In 1961 the first efforts were published of a quantitative approach⁽⁸⁾. Assuming attractive forces only (van der Waals) between particles of fat in an oil continuous phase, vdT suggested that "floculates will be formed in which the particles are arranged in such a way that their average mutual distance is as small as possible". They could be envisaged as chains of particles which were branched and interlinked to form the strong 3-dimensional networks seen at low strains ($G' \sim 10^5$ - 10^6 Nm⁻²).

If we have p particles/cm³, then

$$\pi D^3 p = 6\phi$$

where D is the particle diameter and ϕ the particle total phase volume. The total length of all chains/cm³

$$= pD = \frac{6\phi}{\pi D^2}$$

This gives an average $\frac{2\phi}{\pi D^2}$ chains per cm² in each direction to carry stress.

Assume small deformation i.e. that bonds can either:

- (i) stretch and remain unbroken or
- (ii) stretch, break and reform after suitable reorientation of particles.

This groups the bonds into primary (i.e. (i)) or secondary (i.e. (ii)); the latter causing continual deformation (i.e. flow).

Because the attractive forces are relatively short-ranged, interaction of particles with nearest neighbours only, need be considered.

The attractive forces were calculated (using Hamaker's equations) for particles with an averaged shape and orientation (fat crystals are not spherical) as:

$$F = -\frac{AD^{1.5}}{8H^{2.5}}$$

where A is the so-called Hamaker constant and H the average particle separation.

Differentiation and summing over all particles gives:

$$G' = \frac{5A\phi D^{0.5}}{24\pi H O^{3.5}}$$

The Eyring rate theory was used to calculate the breaking rate of the secondary bonds. This and the equation above yield a predicted creep curve of the form $\gamma = A' + B' \ln t$

where A' and B' are constants depending only on colloidal parameters.

Experiments using fat crystals suspended in oil were used to assess the theory. The creep curve was found to be linear when plotted as linear strain against log time provided that the total strain was less than approximately 1%. From this data the following colloidal parameters were evaluated:

- average bond energy approximately 40 kT units
- interparticle distance approximately 10 Å
- particle size — 2-4 μm

Knowing that γ_{crit} approx. 1%, and that

$$\gamma = 2 \frac{\delta H}{D}$$

where δH is the amount the bond can be stretched before non-linearity arises,

then $\delta H \sim 0.001\mu = 10.0\text{Å}$

In the 1963 J. Phys. Chem. paper⁽⁹⁾ vdT again used rheological measurements to obtain fundamental colloidal parameters. This time the viscosity at very low shear rates was used to assess the reduction in interaction energy between particles on the addition of surfactant.

At these low shear rates; the Eyring rate equation predicts that:

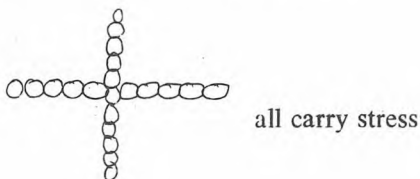
$$d \left(\frac{\Delta G}{kT} \right) = d \ln \eta$$

where $\frac{\Delta G}{kT}$ is the bond energy in kT units.

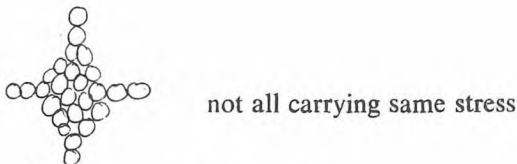
The results indicated values between 1 and 2 kT units reduction on the addition of various surfactants. This was assumed to result from an increased average interparticle distance of the order of a few Å compared with a value of approximately 10 Å for the average distance.

The 1979 J. Coll. Int. Sci. paper⁽¹⁰⁾ introduced a more realistic model for the conformation of particles in networks.

Instead of



we might have:



This would reduce the measured modulus by a factor

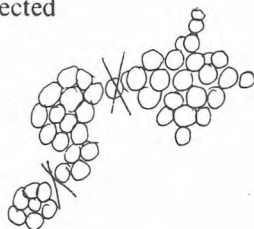
$$\frac{m}{n} \frac{Da}{D}$$

where m is the number of chains/unit volume,
 n the number of particles/aggregate and,
 D and DA the diameters of the particles and aggregates respectively.

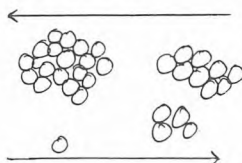
This was found to be correct, and only when the particle density is very large did the simpler theory appear to work. Then all particles are aggregated and also in chains.

This idea takes us to the interesting work on the viscosity of emulsions at higher shear rates where non-Newtonian effects appear⁽¹¹⁾.

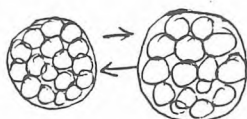
Starting from the connected



aggregate model just considered, we see that shearing will produce breaks in the connecting "chains" to leave a mixture of large aggregates and some single particles.



Any increase in shear rate will then decrease the size of the aggregates. This becomes the basis for the 1963 emulsion viscosity paper. The shear rates are now large and hydrodynamic forces predominate; the colloidal forces only operating *within* the aggregates.



The theory then depends on:

1. Knowing the *effective* volume of the non-interactive aggregates (particles + trapped liquid) (usually taken as $1.6 \times$ particle volumes).
2. Knowing the effect of ϕ_{eff} on η (vdT used Mooney).
3. Knowing how aggregation is affected by γ .

Elements of the work of Goodeve, Mooney, Albers and others were incorporated to give an overall theory: the predictions gave very good agreement with practice in:

- (i) Predicting electrolyte effect
- (ii) Particle size effects
- (iii) Concentration effects
- (iv) Viscosity/shear rate curves at high shear rate.

The theory was however limited in that a crucial interaction parameter B was found, not surprisingly, to be shear rate dependent.

Two later papers (12 and 13) in collaboration with workers from Wageningen (van Vliet and Lyklema) extended the low deformation/deformation rate work to emulsions stabilised by polyelectrolytes.

Here the original hypothetical concepts of permanent and temporary bonds were given reality when the permanent bonds were associated with inter-molecular interaction of the polyelectrolyte molecules which bridged between the emulsion droplets; while the temporary bonds were identified with the (weaker) van der Waals interactions between the emulsion droplets. These transient bonds caused the continuous deformation while the permanent bonds gave the initial elasticity. (This is not always necessary because a distribution of bond strengths can give weak/strong bonds.)

The theory again gave a creep curve of the form :

$$\gamma = A' + B' \ln t$$

from the experimental results, the activation energy of the transient bonds was calculated to be approximately 12 kT units. These bonds show non-linearity in strain above 0.001. Their relaxation time is 10's seconds. The particle separation was calculated as approximately 300 Å.

The primary bonds break/become non-linear at $\gamma > 0.02$ i.e. ΔH approx. 500 Å.

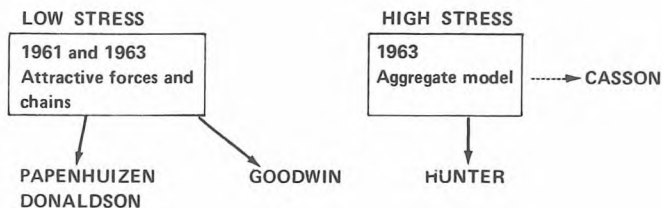
This implies that the polymer molecules are stretched by a factor of 1.7 on average before they become non-linear/break. The bond energy per particle is approximately 2000 kT which implies a single polymer chain bond energy of approximately 5-10 kT, this in turn suggests hydrophobic bonding.

In a similar work published in J. Coll. & Int. Sci. in 1978 ⁽¹³⁾ where dynamic measurements were performed on the polyelectrolyte stabilised emulsions, G' measurements showed that on average only one in three of the polyelectrolyte chains connected to the particles actually formed bonds with chains from adjacent particles.

In an unpublished conference paper in 1976 (abstract published in Rheol. Abs. 1976, Vol. 68) vdT showed that at sufficiently low frequency G'' is entirely determined by the breaking and reformation of interparticulate bonds. Results showed that calculated bond strengths are reasonable.

Those attending the 1979 BSR Conference on Applied Rheology heard vdT's ideas of networks extended in his now well-known "weak gels" ideas, referring to now not only dispersions and emulsions but also polymer solutions (and by implication mixtures). The bonds were identified with van der Waals attraction forces, dipole or ionic interactions or mechanical entanglements. This work was compared to the work of Marrucci, Tanner and others. The formalism described the overall rheological properties on a molecular or colloidal scale⁽¹⁴⁾.

The following diagram shows who has used the ideas generated by vdT and where his work fits in with other workers (see Appendix for full citation list)



Papenhuizen^(15, 16) extended the chain idea to cover non-linear effects while Donaldson⁽¹⁷⁾ relaxed vdT's stipulation that at small strains emulsions and dispersions behave identically; Donaldson allowing the particle to be deformed and yet still having bond breakage.

Goodwin⁽¹⁸⁾ has recalculated the viscoelastic parameters for systems where only negative (repulsive) forces operate, using essentially the vdT approach, and he too has found excellent agreement between theory and practice.

The work on higher stresses has lead HUNTER to follow the aggregate idea via his "elastic floc" model. This predicts a Bingham type behaviour (i.e. $r=r_0 + \Sigma\gamma$) at high shear stresses, where the parameters can be predicted approximately from colloidal parameters. Casson's theory for chain-like aggregates also yields a flow equation, this time of the form

$$T^{\frac{1}{2}} = tce^{\frac{1}{2}} + k\gamma^{\frac{1}{2}}$$

The general principle of using rheology to probe the microstructure is now well accepted by colloid chemists particularly in the Bristol (Ottewill/Goodwin) and Wageningen (Lyklema/van Vliet) groups.

At a time when interest in the rheology of dispersions was very limited and "non-mainline"⁽²⁰⁾. Max van den Tempel worked on, and now when interest is again growing in this area, his work can be relied on by those who take up the interest to give a good start to their efforts.

Acknowledgement

Mrs. A. Bird for her help in information retrieval.

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Appendix

Using the Science Citation Index we find that the following references (see previous page to identify numbers) published by vdT have been cited: (other than vdT's own citations).

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PERSONAL NOTE

M. R. MACKLEY

After graduating in Physics at Leicester University Malcolm Mackley went in 1968 to the H. H. Wills Physics Laboratory and initially studied for an M.Sc. in Material Science. It was here that he had his first exposure from Professors Keller and Ward on the mysteries of polymers and from Professor Nye on the correct use of tensors. There then followed an extended period of research concerned with the effect that flow had on the crystallization of polymer solutions and melts. The work was carried out under the stimulating guidance of Professor Keller and Sir Charles Frank and in the post-doctoral period of this work attention was increasingly put on flow problems in the hope that these would be more tractable than the complex question of flow and crystallization.

Starting with the four roll mill that was invented by G. I. Taylor, a series of experimental roller devices were developed that could be used to explore well defined persistently extensional flows. This work culminated in a brief, amusing and instructive sojourn into the world of Catastrophe theory that at the time was being pioneered by Michael Berry at Bristol.

In 1976 a move to Lecturer in Material Science at Sussex University led to some changes in research interests. In particular collaboration with Dr. Graeme Knott, who at the time was working on wave energy devices, led to a series of experiments concerned with eddy motions and their associated energy losses. In 1979 a further move to Lecturer in Chemical Engineering at Cambridge University ensured a continuing interest in fluid flow problems and present interests include the flow properties of conventional melts and liquid crystal polymers. Work also continues on the understanding of eddy motions with a view to developing amongst other things a low Reynolds number mixing device.

Malcolm admits to a life-long addiction to dinghy sailing and currently races regularly on the river Orwell. At present he is completing the construction of his third National Twelve dinghy in the dining room of his home. His family consists of a very understanding wife, two daughters, an Irish setter and a cat.

MEMBERSHIP NEWS

The following applications for membership were approved at the December Council Meeting:

Moris Amon B S, PhD fetsa D	American Can Co. 433 N Northwest Hwy Barrington IL 60010 U.S.A.
Daryl Sheridan Kellingray BTech fetsa GK	Cement & Concrete Association Wexham Springs Slough Buckinghamshire SL3 6PL
Donald Gene Baird BS, MS, PhD fetsa DGLO	Virginia Polytechnic Institute and State University Department of Chemical Engineering Blacksburg VA 24061-6496 U.S.A.
Giuseppe Marrucci PhD	University of Naples Istituto de Principi di Ing. Chim. Piazzale Tecchio 80125 Napoli Italy
David K. Myers AMCostMaintAccountants pea DFGIJKLM	Sangamo Transducers Fairlands North Bersted Bognor Regis Sussex PO22 9BS
David John Groves BSc, PhD, MInstP fetsa CD	ICI Petrochemicals & Plastics Division PO Box 6 Bessemer Road Welwyn Garden City Hertfordshire AL7 1HD
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Resignations

R. W. Higman, Warren Spring Laboratory, Stevenage, Hertfordshire.

Dr. L. W. Morland, University of East Anglia, Norwich.

L. A. Wiseman, Bramhall, Stockport.

R. R. Blakey, BTP Tioxide Ltd., Stockton-on-Tees, Cleveland.

Dr. R. T. Fenner, Imperial College, London, SW7.

Dr. P. B. Smith, BP International Ltd., London, EC2.

V. W. Punton, Wiggins Teape R & D Ltd., Beaconsfield, Buckinghamshire.

Prof. B. W. Barry, University of Bradford.

Dr. B. J. Nangle, Loctite (Ireland) Ltd., Tallaght, Co. Dublin.

Prof. J. E. Carless, School of Pharmacy, London University, WC1.

A. D. Lott, Metal Box Ltd., Wantage.

T. P. Kelly, Gestetner Manufacturing Ltd., London, N17.

Dr. C. T. Cowan, The A.P.V. Co. Ltd., Crawley, West Sussex.

Dr. M. Hulatt, BP Chemicals Ltd., London, SW1.

J. C. Scott, University of Essex, Colchester.

Dr. D. M. Ford, Pedigree Petfoods Division, Mars Ltd., Melton Mowbray,
Leicestershire.

Dr. J. T. Holden, University of Nottingham.

M. Jensen, Kirk Kristiansen & Co., Baar, Switzerland.

D. Hodgson, British Sidac Ltd., Wigton, Cumbria.

S. D. Holdsworth, Campden Food Preservation RA, Chipping Campden,
Gloucestershire

Correction

D. M. Bancroft, Unilever Research Laboratory, Vlaardingen, Netherlands, did not resign his membership, as wrongly noted in the Bulletin, Vol. 24, No. 2.

Notification of Change in Address

Members are reminded to let the Membership Secretary know well in advance of changes in address so as not to miss out on receipt of journals.

If you experience missing copies of journals, please contact the Membership Secretary also.

Journals Back Numbers Available

R. R. Blakey has an almost complete set of Bulletins and Rheology Abstracts dating back to 1962 to dispose of. Anyone interested should contact him at BTP Tioxide Ltd., Central Laboratories, Stockton-on-Tees, Cleveland.

FUTURE CONFERENCES

DEFORMATION, YIELD AND FRACTURE OF POLYMERS

Cambridge — 29th March - 1st April

The Fifth International Conference on Deformation, Yield and Fracture of Polymers is being held at Churchill College, Cambridge, from 29th March - 1st April, 1982.

The conference will include seven sessions under the headings Deformation and Yield, Fracture, Crating, Fatigue, Composites, Time-Dependent Phenomena and the Effects of Processing.

A programme and further information on the conference can be obtained from The Plastics and Rubber Institute, 11 Hobart Place, London SW1N 0HL (01-245 9555).

NEW RHEOLOGICAL EQUIPMENT

The new Polymer Laboratories' Dynamic Mechanical Thermal Analyser was the subject of a first 'Users' Meeting' at the University of Warwick in September. Papers presented concerned measurements on solid polymer systems, polymer films and coatings. Synopses may be obtained, free on request, from Polymer Laboratories Ltd., Church Stretton, Shropshire, U.K.

EQUIPMENT REQUIRED

A second-hand Weissenberg Rheogoniometer or attachments for either R17 or R18.

Rheogoniometer is required by: Dr. T. E. R. Jones, Department of Mathematical Sciences, Plymouth Polytechnic, Drake Circus, Plymouth (0752-264657).

NEW BOOKS

RHEOMETERS FOR MOLTEN PLASTICS

A Practical Guide to Testing and Property Measurement

by John M. Dealy

272 pages, illus., \$37.00

Published by Van Nostrand Reinhold

New rheometrical techniques and commercially manufactured test instruments have made it possible to measure properties more closely related to processing behaviour. However, this proliferation of rheometrical techniques has also complicated the task of selecting the proper rheological test for a given application.

Over 50 currently available testers and scientific instruments made by 37 world-wide manufacturers for the study of molten polymers are described. Methods of selecting instruments and test procedures are discussed.

John M. Dealy teaches engineering and is an industrial consultant specialising in rheological measurement problems and polymer melt processing. He also supervises research in melt rheology and has developed numerous new techniques for characterising molten plastics. Dr. Dealy has degrees in chemical engineering and is a registered professional engineer. He is a member of the Society of Plastics Engineers, the American and British Societies of Rheology, the American Institute of Chemical Engineers and the Canadian Society for Chemical Engineering. For the past 17 years Dr. Dealy has been a professor at McGill University.

DIARY

1982

March 19. Council Meeting, London,

March 29 - April 1. Cambridge. Deformation, Yield and Fracture of Polymers (Plastics and Rubber Institute with the British Society of Rheology and other societies).

April 14 - 16. Meeting of European Rheologists — Graz.

May 18 - 20. Rheogoniometry Course.

September 21 - 24. Rheology and Microstructure. Trinity Hall, Cambridge.