AN APPRECIATION AND CRITIQUE OF THE SUSPENSION RHEOLOGY RESEARCH OF VLADIMIR VAND (BORN 6TH FEB. 1911 - DIED 4TH APR. 1968)


Vladimir Vand in 1949

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INTRODUCTION

In my research on suspension rheology, I had often come across references to the work of a man with the memorable name of VLADIMIR VAND (apparently known as V² to his colleagues!). However it was quite a number of years before I found out - much to my surprise - that not only had he been employed by the same company as me, but that he had carried out his work on suspension rheology some 50 years previously in the very same laboratory in which I was myself working, but no one had mentioned it! As he was the first person in Unilever Research to be really interested in suspension rheology, I started delving into his career while he was here, and I found such an interesting story that I thought it worthwhile passing on to others.

VAND'S BACKGROUND

We know little about the detailed origins of Vladimir Vand, except that he was born on the 6th of February 1911, and lived in Czechoslovakia. The first documentary evidence that can be found shows that he worked in the 1930s at the Spectroscopic Institute at Charles University in Prague. One of the first repressive measures taken by the Nazis when they occupied Czechoslovakia was aimed at Czech sciences. On November 17th, 1939, the Charles University in Prague, like all other Czech institutions of higher education, was closed by force with a large number of students interned in a concentration camp or executed and their teachers persecuted. However, at that time Vand and a university colleague were working on an aircraft bomb-aimer, and Vand fled first to France by bicycle with details of his work, but as the war caught up with him again, he came to England (his friend made his way to Russia). Two of his papers relating to his earlier work in Prague were published quoting a London address in 1942. He worked with the War Office on his invention, but was then interned temporarily under the Enemy Aliens Act. However he was soon released to do war work in a steel works in the English Midlands and eventually came to Unilever Research (or as it was then the Research Laboratories, Lever Brothers and Unilever Limited) in Port Sunlight in about 1944 to set up a physics section in the newly built laboratory.

From his pre-war publications, it is clear that he was originally an atomic physicist, but there was little call for this in an industrial laboratory, so he turned his hand, as required, to the more useful new areas of X-ray crystallography and suspension rheology. In the former area, within a year or so of self-study, he had become quite an expert, and was constructing mechanical analogue computers to solve structures of various kinds of materials, including (of course) soap (sodium caprilate) using X-ray machines. During his time at Port Sunlight he published many scientific papers on X-ray analysis. He then took up an ICI fellowship and went to Glasgow University in 1950, and while there furthered his X-ray work. At that time he published one important paper with Francis Crick on the X-ray pattern from a helix-type molecule, the year before Crick and Watson published on the *double* helix for which they were later awarded the Nobel Prize. After three years at Glasgow Vand emigrated to the USA and worked at State College, Pennsylvania State University, in the X-ray and Crystal Analysis Laboratory, situated in the department of Physics, continuing his interest in X-ray crystallography, and in the late 1960s was publishing a Fortran program to solve X-ray scattering. He died while still working at Penn State on the fourth of April 1968.

The other subject that Vand picked up quickly while here in this laboratory was suspension rheology. Apparently interest in this subject arose because of problems encountered with detergent slurries and the continuous extrusion of Sunlight Soap, that had superseded the traditional casting process. As Vand was not happy with the existing theories for the viscosity of concentrated suspensions, he developed his own, and finding '*no accurate data available for concentrated suspensions*' (his own words from a

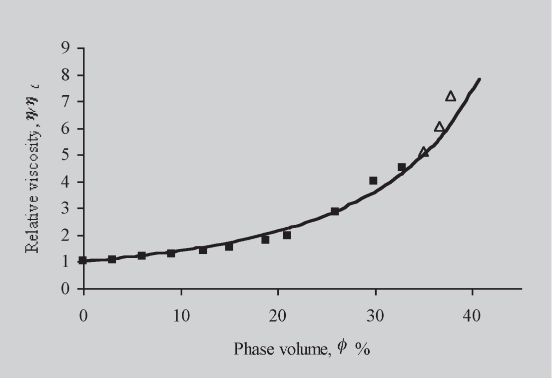

Figure 1: Relative viscosity as a function of phase volume for a 65mm glass-bead suspension in capillary tubes (solid squares) adjusted using a Mooney-type correction; in a concentric-cylinder viscometer (open triangles) with no correction and a plot of the Maron-Pierce-Quemada-Kitano equation with fm = 0.635 (solid line).

Thomas's influential, often-quoted compilation of relative viscosity versus phase volume marks the '*state of the art*' up to the mid 1960s [11]. He too remarks about Vand's work that his analysis was an improvement on the previous analysis of Guth and Simha [10] (Vand's starting point) by his taking [transient] doublet formation into account, but Thomas also notes that his coefficient was increased by Manley and Mason [12] who showed that the period of doublet rotation was larger than assumed by Vand, resulting in a ϕ^2 pre-multiplier of 10.05 instead of 7.349. With regard to Vand's experimental values, Thomas shows that the relative viscosities are on the high side. They are among a collection of data that he suggested should be corrected because of a particle inertial contribution that would increase with particle size.

Did Vand *overcorrect* for the wall effect? As well as assuming that there is an effective lubricating layer at the wall, he also assumed that particles are displaced from this region, and added to the bulk, so that his final tabulation of corrected viscosity was as a function of corrected concentration. Typical corrections at higher concentrations are 42.75 to 45.65% and 46.8 to 50%, which are relatively large corrections. In reality, the local distribution near the wall is changed to a damped oscillatory function, see Barnes [7]. Later work has shown that both the rearrangement and depletion of particles near the wall are accommodated by assuming an effective particle-free layer of continuous phase near the wall. In fact Whitmore stated as early as 1959 that '*Vand considered that a disperse suspension should appear to slip at any solid boundary but measurements in co-axial rotating-cylinder viscometers show the viscosity to be independent of the width of the annulus and do not confirm Vand's conclusion*' [13]. However, he does show that anomalies occur in tube flow, and agreed with Vand with respect to his analysis of suspensions in tube flow. He changes Vand's value of *D* to 0.5*a*, and quotes others who had recently found equally smaller values of *D*, i.e. 0.67*a* and 0.69*a* respectively. (The most recent work in this area suggests even smaller values of around 0.25*a* are appropriate for concentrated suspensions [14]). He also stated that '*Vand's used slowly settling spheres and [his] experimental technique can be criticised ... [he] obtained a value of D varying from 0.34a at 5% to 1.36 at 30% volume concentration, with a [recalculated?] mean value of 0.89a*'. He points out that the variation of shear stress is far more uniform in a concentric-cylinder situation than in tube flow, thus leading to a greater movement of particles due to the resulting shear-rate gradient away from the wall (see an extended discussion in Barnes [15]).

If a simpler correction of Vand's original data is made, then the picture simplifies. First, we carry out a simple Mooney-type analysis of Vand's original uncorrected concentration versus viscosity data, extrapolating the capillary data - as viscosity at any concentration versus the inverse of the tube diameter - to zero. Then plotting these values against the uncorrected Couette data, we see good agreement (Fig. 1). The reason for leaving the Couette data uncorrected is that as well as Whitmore's statement quoted above, we see that given the relative sizes of the spheres and the gap, and the concentrations used by Vand, we would not expect any need for a correction since the ratio of gap to particle diameter is nearly 100:1, see reference 15. The data is a reasonable fit to the well-known Maron-Pierce/Quemada/Kitano equation

$$\frac{\eta}{\eta_o} = \left(1 - \frac{\phi}{0.635}\right)^{-2}$$

as shown in Fig. 1. We should say that the usual accepted value of the maximum phase volume parameter for the simple suspensions we are discussing is higher at values around 0.68 for such large particles, see for instance Thomas's compilation [11].

CONCLUSION

Vand was obviously a man who was clever enough to pick up quickly any area of science that he needed to, and within a short time, rise to world class in that subject. He was himself a

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small, slim, slightly reserved man, who was very enthusiastic about his work. He had a wide range of other scientific interests, and published on such diverse topics as the evolution of the universe, meteorites and the structure of the moon. Just like one of the meteorites that he was interested in, Vladimir Vand came and went, but left behind him a brilliant, luminous trail which has persisted in the night sky of Rheology until today. Had he continued his interest in rheology, we can only guess at the consequences. Certainly of all his published papers (over 50), his suspension viscosity papers [1, 6] are the most cited by far, with over 450 referrals in the last 25 years or so (Science Citation Index of the Institute for Scientific Information), which is nearly twice the number of his other famous paper published with Crick of later Nobel Prize fame [16]. Whenever suspension rheology is written about, Vand will continue to be quoted as the instigator of new ideas in the subject. Those few erstwhile colleagues of his who are still alive remember the brilliant applied mathematician and experimentalist, who became lost to Rheology, but was a great gain to Crystallography.

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