

Free Volume Concept in Rheology

Leszek A. Utracki

National Research Council Canada, Industrial Materials Institute, 75 de Mortagne,
Boucherville, QC, Canada J4B 6Y4

ABSTRACT

Free volume in liquids and glasses is often computed from the Simha-Somcynsky (S-S) hole-lattice theory. The well defined hole fraction (h) is a measure of free volume fraction (f). In the presentation the relation between viscosity (η – either zero-shear or constant stress) and h will be discussed. Since h changes in a well predicted manner with temperature (T), pressure (P) and composition (ϕ), these influences on η collapse onto a “master curve” $\eta = \eta(h)$. Flow behavior of solvents, solutions, melts will be discussed. As an example of industrial application extrusion foaming of polystyrene will be presented.

INTRODUCTION

In 1873 van der Waals¹ introduced the free volume concept in the configurational thermodynamics. Accordingly, molecules move in “cells” made of surrounding molecules with a uniform potential. The original idea was to simulate a pseudo-crystalline structure of liquids by placing each rigid molecule of diameter a in a cell of diameter b made of the surrounding molecules. Thus, the observed specific volume of a given liquid, V , is seen as a sum of the occupied volume, V_{occ} , and free volume, V_f . Instead of the latter parameter it is more convenient to use a relative measure, the free volume fraction $f = (V - V_{occ})/V$. The model has been used by Eyring and many others in developing thermodynamic and rheological theories of liquids and their mixtures.

In 1913 Batschinski² demonstrated utility of the free volume model to rheology. He measured the temperature and pressure dependencies of density and viscosity for low molecular weight liquids (solvents). Operationally he defined V_{occ} as the specific volume, at which the liquid viscosity was immeasurably high, $\eta \rightarrow \infty$. This value was found to be slightly larger than the specific volume in the crystalline state. A good correlation was found between V_{occ} and critical volume or the van der Waals constant: $3V_{occ}V_{crit} = V_{occ}^3/b = 0.921 \pm 0.018$. Batschinski showed that for solvents the pressure and temperature dependence of viscosity is given by the proportionality: $\eta \propto 1/f$.

Nearly forty years later, Doolittle's analysis of viscosity and specific volume for a series of paraffins with molecular weight MW = 72 to 1000 g/mol resulted in derivation of a similar dependence³:

$$\ln \eta = a_o + a_1 / f = a_o + a_1 V / (V - V_o) \quad (1)$$

where V_o is the value of V extrapolated to 0 Kelvin.

A measure of free volume is an integral part of the most successful equation of state (EoS) derived in 1969 by Simha and Somcynsky⁴ for liquids and glasses. The authors assumed that V_f exists in two forms: (i) as expanded lattice cell volume (the "solid-like" contribution), and (ii) as a fraction of unoccupied lattice "holes" (the "gas-like" contribution that makes it possible to correctly describe the system entropy). An important advantage of the theory is the directly calculable volume and temperature dependent hole fraction, $h = h(V, T)$, a measure of f .

Since the mid-1960's the positron annihilation lifetime spectroscopy (PALS) has been used to study polymers. The connection of h with the results of PALS has been demonstrated^{5,6}.

The EoS was shown to precisely describe the PVT behavior of single component liquids and their mixtures⁷, solutions, blends, composites⁸ and nanocomposites⁹. The theory has been found useful in addressing several problems in polymer physics, e.g., surface tension^{10,11}, gas-liquid solubility^{12,13}, viscoelasticity¹⁴, kinetics of volume relaxation¹⁵, etc. Its extension into the glassy state has led to a theory of elastic moduli¹⁶.

SIMHA-SOMCYNKY EQUATION OF STATE (EoS)

The theory is formulated in scaled form, with scaling parameters defined by the intersegmental potential and a flexibility factor, in two coupled equations. The scaled variables of state are:

$$\bar{P} = P/P^*; \quad \bar{V} = V/V^*; \quad \bar{T} = T/T^*,$$

where the scaling parameters are given by:

$$P^* = zq\varepsilon^*/sv^*; \quad T^* = zq\varepsilon^*/Rc; \quad V^* = v^*/M_o \quad (2)$$

$$P^*V^*/RT^* = (1/M_o)\chi c/s$$

The coupled equations are:

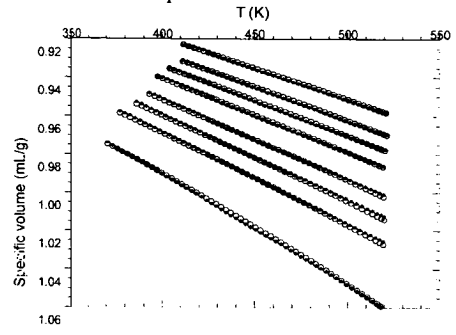
$$\bar{P}\bar{V}_i/\bar{T}_i = (1-\eta_i)^{-1} + 2y_iQ_i^2(AQ_i^2 - B)/\bar{T}_i \quad (3)$$

and

$$3c_i[(\eta_i - 1/3)/(1-\eta_i) - y_iQ_i^2(3AQ_i^2 - 2B)/6\bar{T}_i] + (1-s_i) - s_i \ln[(1-y_i)/y_i] = 0 \quad (4)$$

The elimination of $y = 1 - h$ then yields the scaled EoS: $\bar{V}_i = \bar{V}(\bar{P}_i, \bar{T}_i)$.

In the above relations (for an i -th component): y_i is fraction of occupied lattice sites; s_i is number of segments per chain of molar mass M_i ; $3c_i$ is number of external degrees of freedom per chain; M_{oi} is segmental molar mass M_i/s_i ; v_{ii}^* is molar repulsion volume between segment pair of constituent liquid i ; ε_{ii}^* is molar attraction energy between segment pair of constituent liquid i ; $qiz = s_i(z-2) + 2$ is intermolecular contacts number; A , B , and z are constants equal 1.011, 1.2045, and 12, respectively; $Q_i = 1/(y_i\bar{V}_i)$ and $\eta_i = 2^{-1/6}y_iQ_i^{1/3}$ are dimensionless quantities.



PVT of PS-667; T = 100-250°C, P = 10-190 MPa

Figure 1. Specific volume vs. T for PS-667 at P (from top): 10, 40, 70, 100, 130, 160 and 190 MPa. Points are experimental, circles are computed from EoS.

The procedure is to fit the experimental PVT data to Eqs. 3-4 to obtain the five characteristic parameters: P^* , V^* , T^* , c and s . For linear molecules the external degrees of freedom are expressed as: $3c = s + 3$. Thus, for macromolecules: $s \gg 1$, $3c/s \cong 1$ and only three parameters (P^* , V^* , T^*) are required¹⁷. Within the whole range of liquid state the hole fraction, h , depends on two reduced variables: $h = h(\bar{V}, \bar{T})$ or $h = h(\bar{V}, \bar{P})$.

As an illustration, the PVT dependence of injection molding grade of polystyrene, PS-667 from Dow, is presented in Fig. 1. In Fig. 2 the corresponding h vs. \bar{V} relation is shown¹⁸.

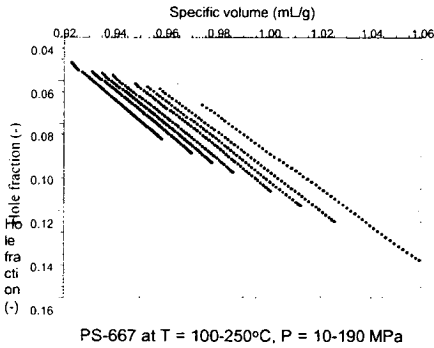


Figure 2. Hole fraction vs. specific volume for PS-667 at P (from right): 10, 40, 70, 100, 130, 160 and 190 MPa.

RELATIONSHIPS BETWEEN η AND h

The EoS provides a measure of the free volume via directly calculable hole fraction, $h = h(T, P)$. Thus, replacing f in Doolittle's Eq. 1 by computed values of h was an obvious thing to do.

In 1982 zero-shear viscosity of low molecular weight n-paraffins C_5 to C_{18} within the T-gap of about 100°C and P up to 1000 MPa were calculated^{19, 20} as η vs. $1/h(T, P)$. Good superposition was obtained. Furthermore, it was observed that all data points fall on a single straight line when plotted as:

$$\ln \eta = a_0 + a_1 Y_s ; \quad Y_s = 1/(a_2 + h) \quad (5)$$

where a_i 's ($i = 1-3$) are equation parameters. The dependence worked equally well (see Fig. 3) for neat liquids as for their solutions²¹. The concentration effect was incorporated via the component volume fraction, ϕ :

$$\ln \eta = b_0 + b_1 Y_c ; \quad Y_c = 1/(b_2 + \phi) \quad (6)$$

Next, the T , P , and concentration effects on η for molten polymers (e.g., PDMS, PS,

PE, PMMA, PP, PB) were examined^{22, 23}. For melts the zero shear viscosity is rarely available, hence instead a constant-stress viscosity was used. For the specific T and P the values of $h = h(\bar{V}, \bar{T})$ were computed from S-S EoS using the literature values of P^* , V^* and T^* . In spite that different grades (of the same resin) were used to measure η and PVT, the superposition on a single master curve was quite good (e.g., see Fig. 4).

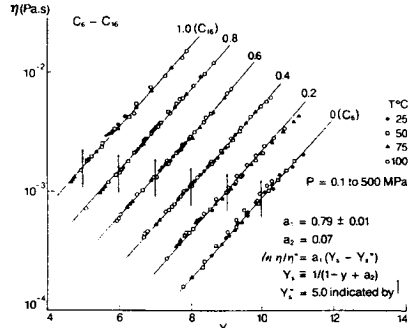


Figure 3. Viscosity of C_6 - C_{16} solutions²¹ at $T = 25$ - 100°C and $P = 0.1$ - 500 MPa.

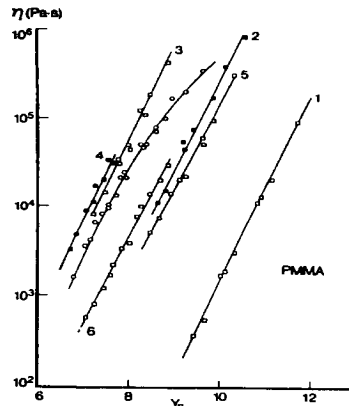


Figure 4. PMMA melt viscosity^{22, 23} at $T = 140$ to 255°C and P up to 173 MPa. Data for resins with $M_w/M_n \approx 2-3$ and $M_w = 13$ to 184 kg/mol.

For n-paraffins the numerical values of two principal parameters in Eq. 5 ($a_0 = \ln \eta_0$ has a reference value significance) was common: $a_1 = 0.79 \pm 0.01$ and $a_2 = 0.07$. For polymer melts it was found that the parameter a_1 depends on the polydispersity

index, M_w/M_n (see Fig. 4), and the extra free volume parameter, $a_2 \cong 0$.

EXTRUSION OF POLYMER FOAMS

Recently PS was extrusion foamed²⁴ with three physical foaming agents (PFA): CO₂, 1,1,1,2-tetrafluoroethane (HFC-134a), and 1-chloro-1,1-difluoroethane (HCFC-142b). A co-rotating, fully intermeshing twin-screw extruder was used. The concentration of injected PFA was $W = 0$ to 5 wt% for CO₂, and $W = 0$ to 15 wt% for the other agents. The constant stress viscosity at $\sigma_{12} \cong 40$ kPa, was measured "on-line" at $T \cong 110$ -210°C and pressures $P \cong 5$ -13 MPa. From the PVT data of PS and PFA's the hole fraction, $h = h(\bar{V}, \bar{T})$ was computed²⁵ by least-squares fit to Eqs. 2-4. It was noted that while for polymer the usual values of h extend up to 0.1, for PFA $h \leq 0.6$.

Since EoS of PS/PFA and thus its h is not known some assumptions had to be made regarding the compositional variation of h in the mixtures. Several mixing rules were tried to relate the measured values of η to the computed from EoS components h -values. The best and the simplest to use is the one based on two assumptions:

1. For liquid mixtures the weight-averaging log additivity rule is obeyed.
2. The $\log \eta$ vs. Y_S dependence for PS and its mixtures with PFA is the same (i.e., the a_i parameters of Eq. 5 are identical).

These assumptions lead to the following relations:

$$\begin{aligned} \log_{10} \eta_{PS} &= a_0 + a_1 Y_{PS}; \quad Y_{PS} = 1/(a_2 + h_{PS}) \\ \log_{10} \eta_{PS/PFA} &= \sum \log_{10} W_i \log_{10} \eta_i = a_0 + a_1 Y_S \quad (7) \\ 100 Y_S &= W/(a_2 + h_{PFA}) + (100 - W)/(a_2 + h_{PS}) \end{aligned}$$

The computations are made in two stages: (1) determination of a_i parameters for PS melt (see top line in Eq. 7), and (2) calculation of Y_S (see bottom line in Eq. 7) for all the PS/PFA compositions. The calculations resulted in a reasonable superposition of data for PS/CO₂ and PS/HCFC-142b, but rather poor for PS/HFC-134a.

To explain this discrepancy it was postulated that not all PFA supplied to the extruder participates in the melt flow. At the extrusion conditions, a part of the compressed gases may back-flow to hopper and escape from the system. Furthermore, at the extrusion conditions the injected PFA may not totally dissolve in the PS melt. If these postulates are true than, instead of the weight fraction of gas injected to the system, an effective part should be used: $W_{effective} = \kappa W$, where κ is the efficiency factor. Experimentally its values range from 0.6 for HFC-134a to 0.8 for CO₂, and 0.9 for HCFC-142b. Results of the calculations are shown in Fig. 5.

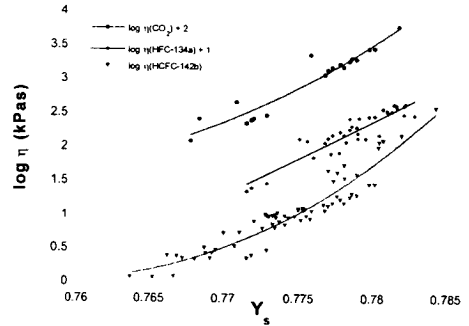


Figure 5. Viscosity of PS/PFA mixtures²⁵; points – experimental, line – least squares fit to Eq. 7. Data for PS/HFC-134a are multiplied by 10, these for PS/CO₂ by 100.

Validity of this postulate was confirmed using the literature data for PS/CO₂ system²⁵. These were collected dissolving ≤ 15 wt% of CO₂ in molten PS in a capillary rheometer at $T = 150$ -175°C and $P \leq 20$ MPa. Thus, the measurements of viscosity was carried out on an enclosed system, hence $W_{effective} = W$. Using Eq. 7 good superposition was obtained (see Fig. 6).

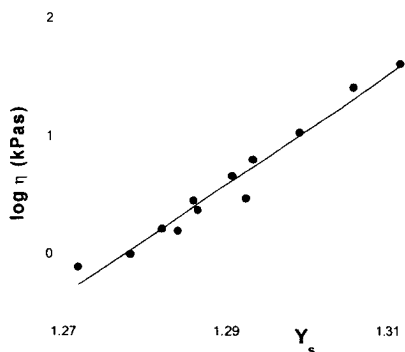


Figure 6. Zero-shear viscosity of PS/CO₂ system plotted according to Eq.7 ($\kappa = 1$). Data from ref. 26.

DISCUSSION

The hole fraction h in the Simha-Somcynsky theory is defined as a fraction of empty number of sites to the total. The occupied volume fraction $y = 1 - h$, is also allowed to expand. Analysis of EoS (Eqs. 2-4) led to the conclusion²⁷ that the theory inherently requires that $h = h(\bar{V}, \bar{T})$. This is in contrast with the definition of the free volume fraction that implies that f is a single parameter function: $f = f(\bar{V})$. However, knowing the characteristic parameters of the system makes it possible to convert h to f and *vice versa*. Only for highly volatile systems (e.g., PFA) $h \cong f$.

Distinction between h and f is important since better correlation was obtained between η and h than between η and f . This fact seems logical considering that for flow only the empty sites are pertinent – the expanded occupied ones remain inaccessible.

CONCLUSIONS

The 20-odd years long investigations of the η vs. h relations show that changes induced in liquid flow properties by T , P and/or composition (in a single phase) can be predicted knowing how these independent variables affect the EoS hole fraction, $h = h(\bar{V}, \bar{T})$.

Plotting $\log \eta$ vs. h for a single component system invariably results in superposition of data onto a “master curve”.

Furthermore, conversion of h into $Y_s = 1/(a_2 + h)$ linearizes the dependence.

For liquid mixtures the relationship is more complex since PVT data are not available. Here η cannot be predicted from the calculated (e.g., assuming volume additivity of components h -values) total hole fraction. In n-paraffin solutions the effective hole fraction was smaller than calculated from additivity. Thus, better packing of molecules of different size than a single size was postulated.

For polymer melt/compressed gas systems the best results were obtained assuming weight-average log additivity for η . Physical consequence of this observation is important: evidently the two components are not able to share the free space of each other! In spite that PFA contributes enormous quantities of h to the total hole content it is PS that dominates the mixture flow. One may speculate that the lattice cell size for the near-critical gas is so much larger that macromolecular segments cannot use it effectively. Similarly, the lattice size of PS melt is so small that its holes are of little use for PFA.

ACKNOWLEDGMENT

Thanks to Professor Robert Simha for many stimulating discussions on topics addressed in this paper. Collaboration of Richard Gendron is greatly appreciated.

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