

PRESSURE DEPENDENCE OF VISCOSITY: A NEW GENERAL RELATION

Jörn W.P. Schmelzer^{1,*} & Alexander S. Abyzov²

¹Institut für Physik der Universität Rostock, Albert-Einstein-Strasse 23-25, Rostock, 18059, Germany

²National Science Center Kharkov Institute of Physics and Technology, Academician Street 1, Kharkov, 61108, Ukraine

*Address all correspondence to: Jörn W.P. Schmelzer, Institut für Physik der Universität Rostock, Albert-Einstein-Strasse 23-25, Rostock, 18059, Germany; Tel.: +49 381 498 6889; Fax: +49 381 498 6882, E-mail: juern-w.schmelzer@uni-rostock.de

Original Manuscript Submitted: 1/16/2018; Final Draft Received: 2/27/2018

We reanalyze the pressure dependence of viscosity of liquids of constant composition under isothermal conditions. Based exclusively on very general considerations concerning the relationship between viscosity and free volume of the liquid, we show that viscosity increases, as a rule, with increasing pressure. The conditions are specified at which such normal behavior is replaced by an anomalous decrease of viscosity with pressure. A variety of relations employed frequently in the description of the pressure dependence of viscosity are shown to be special cases of the general relation derived.

KEY WORDS: Nucleation, crystal growth, glasses, glass transition, fluid dynamics, viscosity, rheology

1. INTRODUCTION

In the analysis of crystallization and glass formation, caused by variations of either temperature or pressure, the knowledge of the dependence of viscosity on these thermodynamic parameters is an essential ingredient of the description. This dependence determines to a large degree whether a given liquid, in response to variations of temperature and/or pressure, will crystallize or be transferred to a glass (e.g., Fokin et al., 2006; Schmelzer, 2012).

Relations for the temperature dependence of the viscosity have been widely discussed in the past and the situation is here well-settled (Frenkel, 1946; Gutzow and Schmelzer, 2013; Mazurin, 1986; Skripov, 1974; Skripov and Koverda, 1984). As one general consequence it was found that the viscosity always increases with decreasing temperature. In contrast, the dependence of viscosity on pressure is in comparison to the first case much less analyzed and much more complex (Andersson and Johari, 2016; Brazhkin and Lyapin, 2000; Bridgman, 1946; Macedo and Litovitz, 1965; Syono and Manghnani, 1992). An increase of pressure may result both in an increase but also in an anomalous decrease of viscosity (see, e.g., Abramson, 2011, 2014; Scarge et al., 1987; Schmelzer et al., 2005). By this reason, intensive further research is required in order to arrive at a similarly satisfactory description as obtained for the dependence of viscosity on temperature. In particular, it is of interest to find out at what conditions mentioned anomalous behavior occurs and how it can be described.

Motivated by such considerations, in Schmelzer et al. (2005) a relation was derived correlating variations of viscosity with temperature with its changes with pressure. In this analysis, we employed free volume models as discussed in detail, e.g., by Frenkel (1946). Characterizing free volume concepts, Frenkel wrote in the Russian edition of his book: “A highly densely packed crowd of people cannot leave a room even if the doors are open” (in the English translation, this phrase has been modified to “A highly densely packed crowd of people cannot leave a room until the doors will be opened,” resulting in a slight but significant deviation of the content due to the personal view on this statement by the translator). The respective ideas have been developed later on by different authors advancing

particular models of free volume theories for the dependence of the viscosity on the thermodynamic state parameters (for an overview, see, e.g., Cohen and Grest, 1979; Doolittle, 1951; Gutzow and Schmelzer, 2013; Schmelzer and Gutzow, 2011; Skripov and Faizullin, 2006).

In particular, in their extended investigation of similarities and differences of liquid–vapor and liquid–solid phase transitions, Skripov and Faizullin (2006) analyzed the dependence of viscosity, η , on temperature, T , and pressure, p , along the liquid-crystal equilibrium coexistence curve for several classes of liquids. They restricted their analysis to the cases where the thermal expansion coefficient of the liquid is positive. The analysis of both literature data and their own results led those authors to conclude that the relations $(\partial\eta/\partial T)_p < 0$ and $(\partial\eta/\partial p)_T > 0$ must be fulfilled resulting in $(\partial p/\partial T)_\eta > 0$. These relations imply that the viscosity must decrease with increasing temperature for isobaric processes and must increase with increasing pressure at isothermal conditions.

Advancing these considerations, in Schmelzer et al. (2005) we derived an equation first for $(\partial p/\partial T)_\eta$. In this analysis, we employed free volume concepts in a very general form (Frenkel, 1946). These basic ideas may be expressed as: (i) free volume uniquely determines the value of the viscosity; (ii) free volume is uniquely determined by the total volume, $V(p, T)$, of the liquid and not by pressure and temperature, separately. Based on this essence of free volume concepts, $(\partial p/\partial T)_\eta$ may be replaced by $(\partial p/\partial T)_V$ leading after some transformations to the desired relation (for details, see Schmelzer et al., 2005, and Section 2.1). The resulting equation we will employ here in order to arrive at a general new expression for the pressure dependence of the viscosity employing well-established equations for the temperature dependence of viscosity. This new relation for the pressure dependence of the viscosity, its main features, and possible applications will be established in Section 2. Conclusions and possible further developments of the presented here analysis are discussed in Section 3 completing the present paper.

2. THEORY

2.1 Derivation of the Basic Equation

Based on the above formulated essence of free volume models of viscosity, in Schmelzer et al. (2005) a relation was derived for the description of the interrelation between variations of the viscosity, η , in dependence on temperature, T , and on pressure, p . This relation reads

$$\left(\frac{\partial\eta}{\partial p}\right)_T = -\frac{\kappa_T(p, T)}{\alpha_p(p, T)} \left(\frac{\partial\eta}{\partial T}\right)_p, \quad (1)$$

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_T, \quad \alpha_p = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p. \quad (2)$$

Here $\kappa_T(p, T)$ is the isothermal compressibility and $\alpha_p(p, T)$ the isobaric thermal expansion coefficient (Kubo, 1986). Both thermodynamic coefficients depend on pressure and temperature; the composition of the liquid is considered here as constant.

Generally, the thermodynamic equilibrium conditions result in $\kappa_T > 0$ (Kubo, 1986). At normal conditions, the isobaric thermal expansion coefficient, α_p , is also a positive quantity (see Schmelzer et al., 2005). Typical values of κ_T are found in the range 10^{-6} – 10^{-11} Pa⁻¹ and, in this case, of α_p in the range 10^{-4} – 10^{-6} K⁻¹, its ratio is, consequently, as the rule a small quantity utilizing the standard variables employed here. In the framework of the here described free volume approach, the anomalous decrease of viscosity with increasing pressure is uniquely correlated with negative values of the thermal expansion coefficient.

Based on the above relation, we can determine the pressure dependence of viscosity provided the respective dependence on temperature is known. In general, we may express the viscosity as (Fokin et al., 2006; Gutzow and Schmelzer, 2013; Skripov and Faizullin, 2006; Skripov and Koverda, 1984)

$$\eta = \eta_0 \exp\left(\frac{E_\eta(p, T)}{RT}\right). \quad (3)$$

Here R is the universal gas constant and E_η is the activation energy for the viscous flow depending, in general, both on pressure and temperature. However, once Eq. (1) was derived based on free volume concepts, it is obviously reasonable to select a particular equation for the description of the dependence $\eta = \eta(T)$ which also can be interpreted in such terms.

For such purposes, here we will employ the Vogel–Fulcher–Tammann (VFT) equation

$$\eta = \eta_0 \exp\left(\frac{A(p)}{T - T_0}\right) \quad (4)$$

for an illustration of the method and for the derivation of some representative results. Such choice we consider as most appropriate (i) from the point of view that, for a variety of systems, the temperature dependence of the viscosity is well-described by this relation (e.g., Gutzow and Schmelzer, 2013; Herlach et al., 2007; Mazurin, 1986; Ngai, 2011; Priven, 2011). From a theoretical point of view, (ii) the VFT-equation can be considered also as a consequence of free volume approaches (Herlach et al., 2007; Macedo and Litovitz, 1965). By this reason, a combination of Eqs. (1) and (4) can be expected to allow one a derivation of a hopefully similarly appropriate relation for the pressure dependence of the viscosity as the VFT equation yields for the temperature dependence of the viscosity. A substitution of Eq. (4) into Eq. (1) yields

$$\left. \frac{\partial \ln \eta(p, T)}{\partial p} \right|_T = \frac{1}{\Pi(p, T)}, \quad \frac{1}{\Pi(p, T)} = \left(\frac{\kappa_T(p, T)}{\alpha_p(p, T)} \right) \frac{A(p)}{(T - T_0)^2}. \quad (5)$$

The parameter Π has hereby the dimension of pressure.

The pressure dependence of the viscosity is in such approach determined by the pressure dependence of the three thermodynamic quantities κ_T , α_p , and A for some appropriate temperature, T . Having at one's disposal these dependencies for a given system, the pressure dependence of the viscosity can be determined then easily via an integration of Eq. (5). Since such detailed knowledge is, as a rule, not available, in the next section we will consider several approximate solutions of Eq. (5).

2.2 Approximations

Assuming that the three thermodynamic quantities κ_T , α_p , and A are independent of pressure, Eq. (5) can be solved immediately, resulting in

$$\eta(p, T) = \eta(p_0, T) \exp\left(\frac{p - p_0}{\Pi(p_0, T)}\right), \quad \frac{1}{\Pi(p_0, T)} = \left(\frac{\kappa_T(p_0, T)}{\alpha_p(p_0, T)} \right) \frac{A(p_0)}{(T - T_0)^2}. \quad (6)$$

Here p_0 is some (arbitrary) reference pressure for which the viscosity, $\eta(p_0, T)$, is known.

In a more accurate approximation, we account for the pressure dependence of the thermodynamic coefficients and the activation energy parameter employing a Taylor expansion of the three thermodynamic quantities κ_T , α_p , and A truncated at linear in $(p - p_0)$ terms. The function $\Pi(p, T)$ can be written then either as

$$\frac{1}{\Pi(p, T)} = \left[\kappa_T A + \left(A \frac{\partial \kappa_T}{\partial p} + \kappa_T \frac{\partial A}{\partial p} \right) (p - p_0) + \frac{\partial \kappa_T}{\partial p} \frac{\partial A}{\partial p} (p - p_0)^2 \right] / \left[\left(\alpha_p + \frac{\partial \alpha_p}{\partial p} (p - p_0) \right) (T - T_0) \right] \quad (7)$$

or in the form

$$\frac{1}{\Pi(p, T)} = \frac{1}{\Pi(p_0, T)} \times \left\{ \left[1 + \left(\frac{\partial \ln \kappa_T}{\partial p} + \frac{\partial \ln A}{\partial p} \right) (p - p_0) + \frac{\partial \ln \kappa_T}{\partial p} \frac{\partial \ln A}{\partial p} (p - p_0)^2 \right] / \left[1 + \frac{\partial \ln \alpha_p}{\partial p} (p - p_0) \right] \right\}. \quad (8)$$

In both relations, Eqs. (7) and (8), the quantities κ_T , α_p , and A and their derivatives have to be taken at $p = p_0$ and the selected temperature, T . Eqs. (5) and (8) can be reformulated as

$$\frac{d \ln \eta(p, T)}{dp} = \frac{1}{\Pi(p_0, T)} \left\{ \frac{1 + a_1(p - p_0) + a_2(p - p_0)^2}{1 + a_3(p - p_0)} \right\}, \quad T = \text{constant}, \quad (9)$$

$$a_1 = \left(\frac{\partial \ln \kappa_T}{\partial p} + \frac{\partial \ln A}{\partial p} \right) \Big|_{p=p_0, T}, \quad a_2 = \left(\frac{\partial \ln \kappa_T}{\partial p} \frac{\partial \ln A}{\partial p} \right) \Big|_{p=p_0, T}, \quad a_3 = \frac{\partial \ln \alpha_p}{\partial p} \Big|_{p=p_0, T}. \quad (10)$$

The general solution of this equation is given by

$$\ln \left(\frac{\eta(p)}{\eta(p_0)} \right) = \frac{1}{\Pi(p_0)a_3} \left\{ \left(1 - \frac{a_1}{a_3} + \frac{a_2}{a_3^2} \right) \ln [1 + a_3(p - p_0)] + \left(a_1 - \frac{a_2}{a_3} \right) (p - p_0) + \frac{a_2^2}{2} (p - p_0)^2 \right\} \quad (11)$$

for $a_3 \neq 0$ and by

$$\ln \left(\frac{\eta(p)}{\eta(p_0)} \right) = \frac{p - p_0}{\Pi(p_0)} \left[1 + \frac{a_1}{2} (p - p_0) + \frac{a_2}{3} (p - p_0)^2 \right] \quad (12)$$

for $a_3 = 0$. Consequently, the type of behavior in the solution of Eq. (9) is determined in such approximation by the sign and magnitude of $\Pi(p_0, T)$ and of the three coefficients a_1 , a_2 , and a_3 .

2.3 Analysis

As evident from the analysis of Eqs. (9)–(12), for small deviations of pressure from the initial state, p_0 , Eqs. (11) and (12) predict a linear change of $\ln(\eta)$ with $(p - p_0)$ in agreement with the approximation given by Eq. (6). For positive values of the thermal expansion coefficient, the viscosity increases; for negative values it decreases with increasing pressure. For larger values of the difference $(p - p_0)$, deviations from such linear behavior may occur. The directions of deviation from such linear law are determined by the values of the parameters a_1 , a_2 , and a_3 or, in other words, by the derivatives of the thermodynamic coefficients and the activation energy of viscous flow with respect to pressure. For some set of parameters, these results are illustrated in Fig. 1.

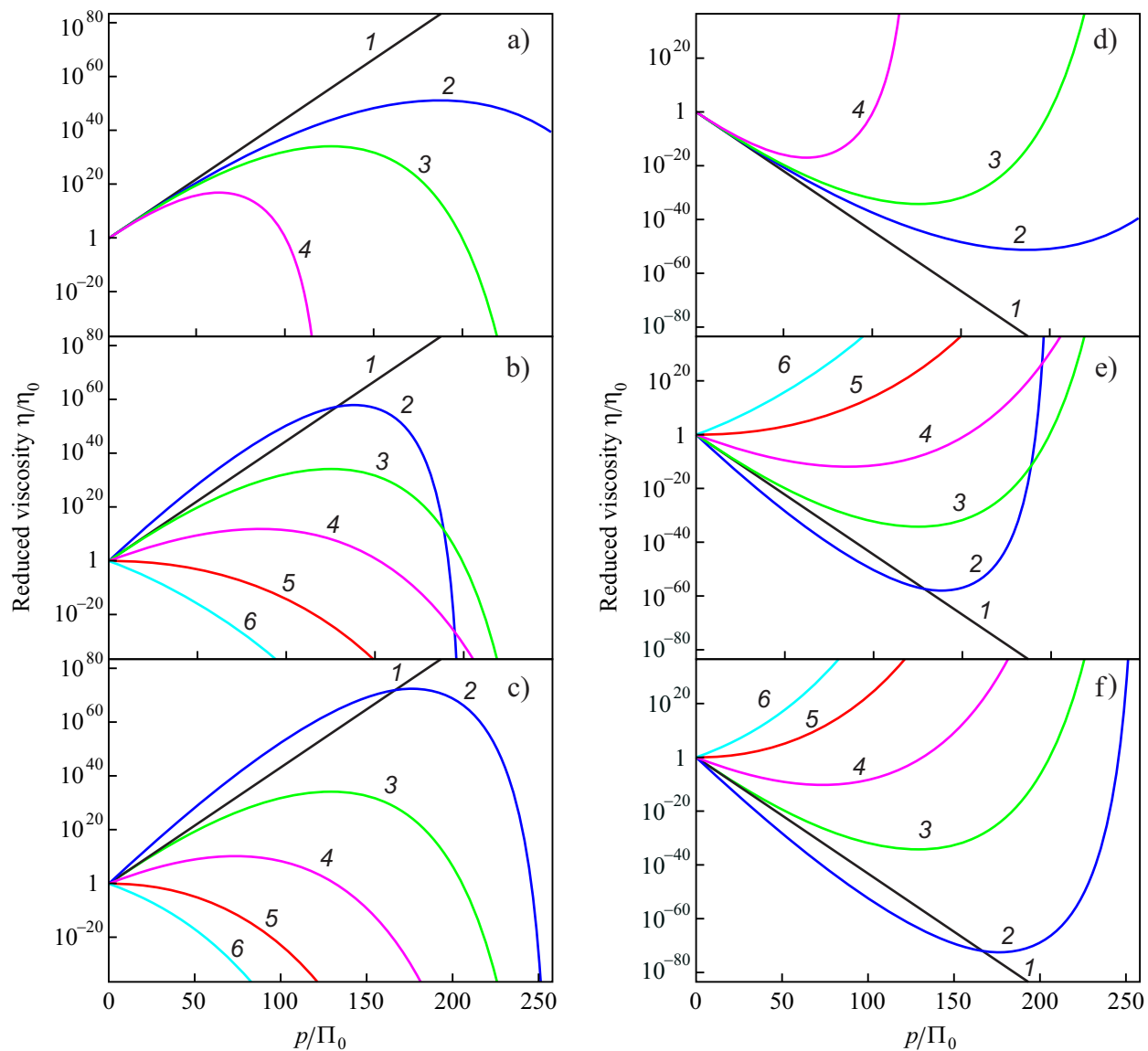
A comparison shows, moreover, that the relation derived by us contains as special cases a variety of relations derived earlier and employed widely. For example, it allows one to describe a linear increase of $\log \eta$ in dependence of $(p - p_0)$ as discussed, e.g., in Avramov et al. (2009); Brazhkin and Lyapin (2000), as well as deviations from such linear dependence (Avramov, 2000; Utracki, 1983). Note that also dependencies of the form $\log \eta \propto 1/(p - p_0)$ and similar relations as discussed by Paluch et al. (1998) can be described by the above equations. Indeed, a Taylor expansion of $1/(p - p_0)$ immediately leads in its simplest form to Eq. (6). Since density differences or volume changes as employed, e.g., in Abramson (2011, 2014); Brazhkin and Lyapin (2000); Doolittle (1951) can be easily converted into pressure differences, the latter statement holds also for such cases.

3. CONCLUSIONS

In the present paper, a general relation for the pressure dependence of the viscosity is derived, allowing one to give an interpretation of the complex behavior one is confronted with in the analysis of this property. As shown, the pressure dependence of the viscosity is determined basically by the isobaric thermal expansion coefficient, the isothermal compressibility, and the activation energy for viscous flow of the VFT equation, i.e., via directly measurable experimental parameters. In principle, also a further development of the theoretical approach outlined is possible, extending the Taylor expansion in pressure differences of the thermodynamic coefficients and the activation energy in the VFT equation to higher-order terms. It is shown that already for the linear expansions considered here qualitatively the obtained general relation allows one to reproduce the behavior for the pressure dependence of the viscosity as determined experimentally. A detailed quantitative comparison for different systems can be considered therefore as highly promising. This task is attempted to be performed in a future study.

ACKNOWLEDGMENTS

The work described in Schmelzer et al. (2005) and in the present paper was significantly facilitated by discussions with Academician Vladimir P. Skripov and the acquaintance with his work. J.W.P.S. would like to express his sincere thanks also to Vadim V. Brazhkin (Troitsk, Russia) for stimulating suggestions. Financial support from the German Academic Exchange Service (DAAD, grant 91561917) is gratefully acknowledged.



curve num.	a) $\alpha_p > 0$, d) $\alpha_p < 0$			b) $\alpha_p > 0$, e) $\alpha_p < 0$			c) $\alpha_p > 0$, e) $\alpha_p < 0$		
	$a_1 \cdot 10^{11}$	$a_2 \cdot 10^{22}$	$a_3 \cdot 10^{11}$	$a_1 \cdot 10^{11}$	$a_2 \cdot 10^{22}$	$a_3 \cdot 10^{11}$	$a_1 \cdot 10^{11}$	$a_2 \cdot 10^{22}$	$a_3 \cdot 10^{11}$
1	0	0	0	0	0	0	0	0	0
2	-2.96	2.2	-1.48	-4.45	4.94	-2.78	-7.78	12.4	-2.22
3	-4.45	4.94	-2.22	-4.45	4.94	-2.22	-6.67	9.89	-2.22
4	-8.89	19.8	-4.45	-4.45	4.94	-1.85	-5.4	7.06	-2.22
5	-	-	-	-4.45	4.94	-1.58	-4.45	4.94	-2.22
6	-	-	-	-4.45	4.94	-1.39	-3.61	3.09	-2.22

FIG. 1: Possible dependencies of the viscosity on pressure. Plots (a)–(c) are made for positive values of the thermal expansion coefficient ($\alpha_p = 5 \cdot 10^{-5} \text{ K}^{-1}$), plots (d) and (e) for negative values ($\alpha_p = -5 \cdot 10^{-5} \text{ K}^{-1}$). The coefficients a_1, a_2, a_3 are given in the table (they are equal for positive and negative values of α_p)

REFERENCES

- Abramson, E.H., Viscosity of Argon to 5 GPa and 673 K, *High Pressure Res.*, vol. **31**, no. 4, pp. 544–548, 2011.
- Abramson, E.H., Viscosity of Fluid Nitrogen to Pressures of 10 GPa, *J. Phys. Chem.*, vol. **B 118**, no. 40, pp. 11792–11796, 2014.
- Andersson, O. and Johari, G.P., Thermal Conductivity of Glycerols Liquid, Glass, and Crystal States, Glass-Liquid-Glass Transition, and Crystallization at High Pressures, *J. Chem. Phys.*, vol. **144**, no. 6, p. 064504, 2016.
- Avramov, I., Pressure Dependence of Viscosity of Glass-Forming Melts, *J. Non-Cryst. Solids*, vol. **262**, no. 1, pp. 258–263, 2000.
- Avramov, I., Grzybowski, A., and Paluch, M., A New Approach to Description of the Pressure Dependence of Viscosity, *J. Non-Cryst. Solids*, vol. **355**, nos. 10–12, pp. 733–736, 2009.
- Brazhkin, V.V. and Lyapin, A.G., Universal Viscosity Growth in Metallic Melts at Megabar Pressures: The Vitreous State of the Earth's Inner Core, *Phys.-Usp.*, vol. **43**, no. 5, pp. 493–508, 2000.
- Bridgman, P.W., Recent Work in the Field of High Pressures, *Rev. Mod. Phys.*, vol. **18**, no. 1, pp. 1–95, 1946.
- Cohen, M.H. and Grest, G.S., Liquid-Glass Transition, a Free-Volume Approach, *Phys. Rev.*, vol. **B 20**, no. 3, pp. 1077–1098, 1979.
- Doolittle, A.K., Studies in Newtonian Flow. II. the Dependence of the Viscosity of Liquids on Free Space, *J. Appl. Phys.*, vol. **22**, no. 12, pp. 1471–1475, 1951.
- Fokin, V.M., Zanotto, E.D., Yuritsyn, N.S., and Schmelzer, J.W.P., Homogeneous Crystal Nucleation in Silicate Glasses: A Forty Years Perspective, *J. Non-Cryst. Solids*, vol. **352**, nos. 26–27, pp. 2681–2714, 2006.
- Frenkel, Y.I., *The Kinetic Theory of Liquids*, Oxford, UK: Oxford University Press, 1946.
- Gutzow, I.S. and Schmelzer, J.W.P., *The Vitreous State: Thermodynamics, Structure, Rheology, and Crystallization*, Heidelberg, Germany: Springer, 2013.
- Herlach, D., Galenko, P., and Holland-Moritz, D., Metastable Solids from Undercooled Melts, in *Pergamon Materials Series*, Amsterdam, Netherlands: Elsevier, vol. **10**, 2007.
- Kubo, R., *Thermodynamics*, Amsterdam, Netherlands: North-Holland Publishing Company, 1986.
- Macedo, P.B. and Litovitz, T.A., On the Relative Roles of Free Volume and Activation Energy in the Viscosity of Liquids, *J. Chem. Phys.*, vol. **42**, no. 1, pp. 245–256, 1965.
- Mazurin, O.V., *Vitrification*, Leningrad, Russia: Nauka, 1986.
- Ngai, K.L., *Relaxation and Diffusion in Complex Systems*, New York, NY: Springer, 2011.
- Paluch, M., Rzoska, S.J., Habdas, P., and Ziolo, J., On the Isothermal Pressure Behaviour of the Relaxation Times for Supercooled Glass-Forming Liquids, *J. Phys.: Condens. Matter*, vol. **10**, no. 19, pp. 4131–4138, 1998.
- Priven, A.I., Methods of Prediction of Glass Properties from Chemical Compositions, *Glasses and the Glass Transition*, Berlin, Germany: Wiley-VCH, 2011.
- Scarge, C.M., Mysen, B.O., and Virgo, D.E., Pressure Dependence of the Viscosity of Silicate Melts, in *Magmatic Processes: Physicochemical Principles*, B.O. Mysen, Ed., Washington, DC: Geochemical Society Press, vol. **1**, 1987.
- Schmelzer, J.W.P., Kinetic Criteria of Glass-Formation and the Pressure Dependence of the Glass Transition Temperature, *J. Chem. Phys.*, vol. **136**, no. 7, pp. 074512/1–11, 2012.
- Schmelzer, J.W.P. and Gutzow, I.S., *Glasses and the Glass Transition*, Berlin, Germany: Wiley-VCH, 2011.
- Schmelzer, J.W.P., Zanotto, E.D., and Fokin, V.M., Pressure Dependence of Viscosity, *J. Chem. Phys.*, vol. **122**, no. 7, pp. 074511/1–11, 2005.
- Skripov, V.P., *Metastable Liquids*, New York, NY: Wiley, 1974.
- Skripov, V.P. and Faizullin, M.Z., *Crystal-Liquid-Gas Phase Transitions and Thermodynamic Similarity*, Berlin, Germany: Wiley-VCH, 2006.
- Skripov, V.P. and Koverda, V.P., *Spontaneous Crystallization of Undercooled Liquids*, Moscow, Russia: Nauka, 1984.
- Syono, Y. and Manghnani, M.H., *High-Pressure Research: Application to Earth and Planetary Sciences*, Tokyo, Japan: Terra Scientific Publishing Company, 1992.
- Utracki, L.A., Temperature and Pressure Dependence of Liquid Viscosity, *Can. J. Chem. Eng.*, vol. **61**, no. 5, pp. 753–758, 1983.