Viscosity, entropy and fragility

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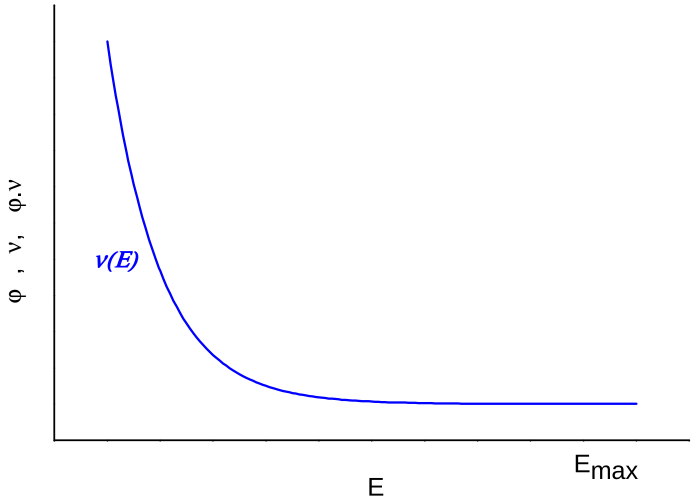
2008

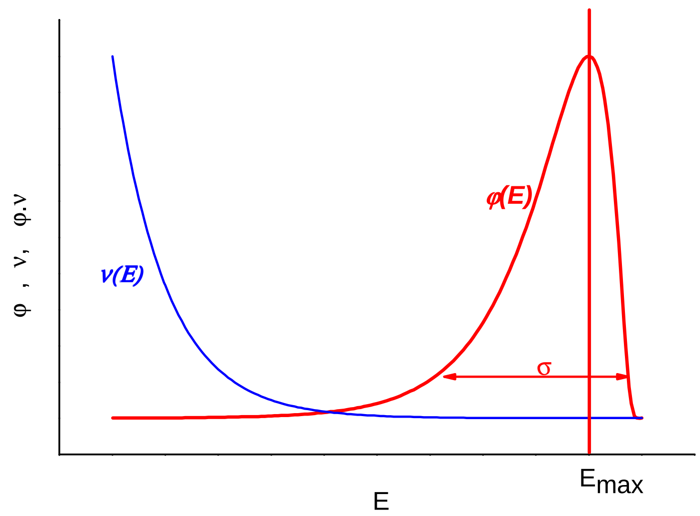
Average frequency

$$\nu = \nu_o e^{-\frac{E}{RT}}$$



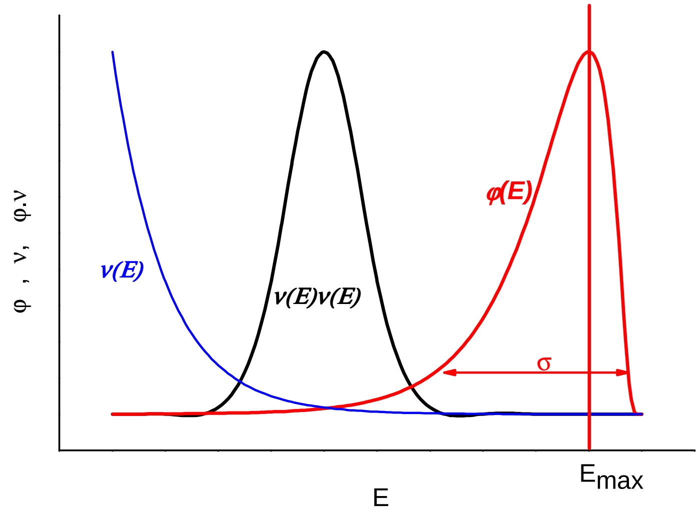
Average frequency

$$\varphi(E)$$



Average frequency

$$< \nu > = \int_0^{E_{max}} \varphi(E) \nu(E) dE$$



Jump frequency model

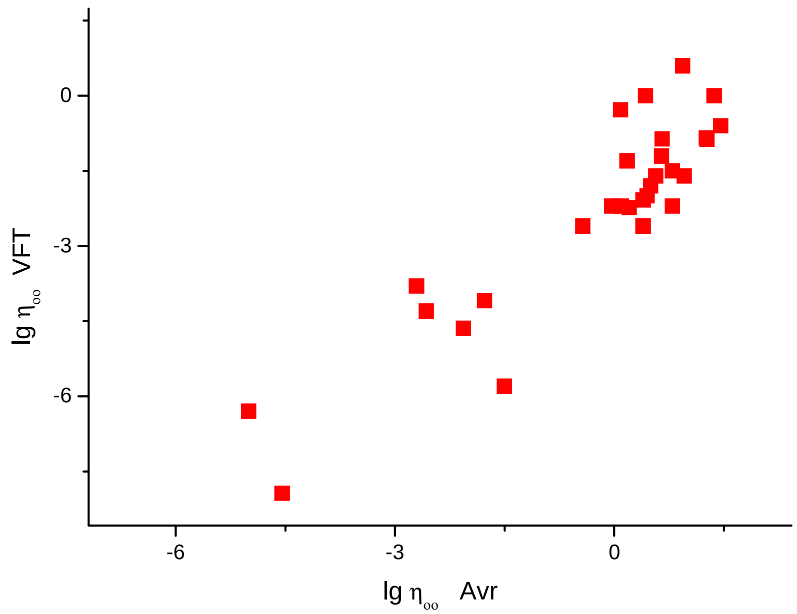
$$<\nu>=\int_0^{E_{max}} \frac{\exp\left(\frac{E-E_{max}}{\sigma}\right)}{\sigma\left(1-\exp(-)\frac{E_{max}}{\sigma}\right)}\nu_o \exp\left(-\frac{\mathrm{E}}{\mathrm{kT}}\right)dE$$

$$<\nu>=\frac{\left[1-e^{-E_{max}\left(\frac{1}{RT}-\frac{1}{\sigma}\right)}\right]}{\left(\frac{\sigma}{RT}-1\right)\left(1-e^{-\frac{E_{max}}{\sigma}}\right)}\nu_o e^{-\frac{E_{max}}{\sigma}}$$

$$<\nu>\approx\nu_o\frac{RT}{\sigma}e^{-\frac{E_{max}}{\sigma}}$$

$$\lg\eta=\lg\eta_\infty+\frac{E_{max}}{2.3\sigma}$$

$$\lg\eta_\infty=\lg\eta_o+\lg\frac{\sigma}{RT}\approx\lg\eta_o+1.5$$



$$\lg \eta = \lg \eta_{\infty} + \frac{1}{2.3} \frac{E_{max}}{\sigma}$$

Entropy dependence

$$\sigma = \sigma_g \exp\left[\frac{2(S - S_g)}{ZR}\right]$$

$$\eta = \eta_\infty \exp\left\{\varepsilon \exp\left[\frac{2(S - S_g)}{ZR}\right]\right\}$$

$$\varepsilon = \frac{E_{\max}}{\sigma_g}$$

Let S_g is the entropy at temperature T_g at which lg η =12.5 [Pa.s]

$$\lg \eta = \lg \eta_\infty + (12.5 - \lg \eta_\infty)\exp\left(\frac{2(S - S_g)}{ZR}\right)$$

$$S(T) = S_g + \int_{T_g}^{T} C_p d\ln \tilde{T} \approx S_g + C_p \ln\left(\frac{T}{T_g}\right)$$

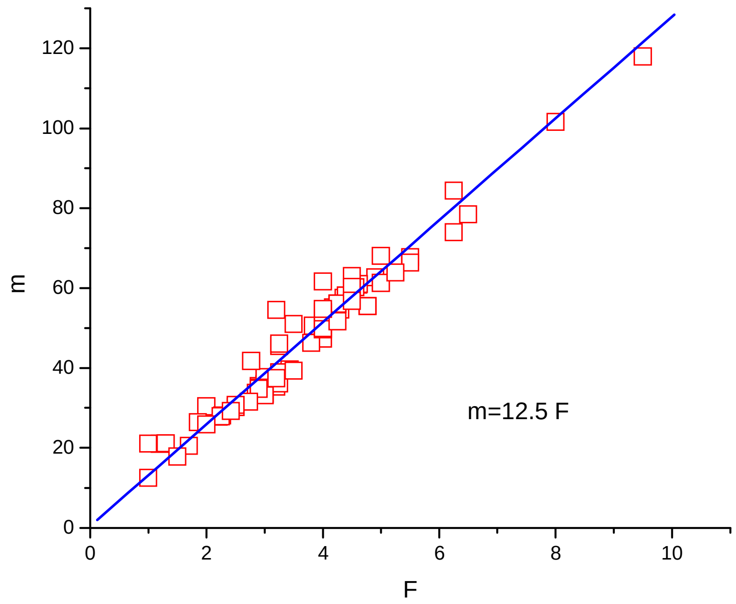
$$\eta = \eta_\infty \exp\left[2.3\left(12.5 - \lg \eta_\infty\right)\left(\frac{T_g}{T}\right)^F \right] \qquad F = \frac{2C_p}{ZR}$$

$$\eta = \eta_\infty \exp\left[2.3(12.5 - \lg\eta_\infty)\left(\frac{T_g}{T}\right)^F\right]$$

$$F = \frac{2C_p}{ZR} = \frac{2*3R}{ZR} = \frac{6}{Z} = 1.2 \pm 0.25$$

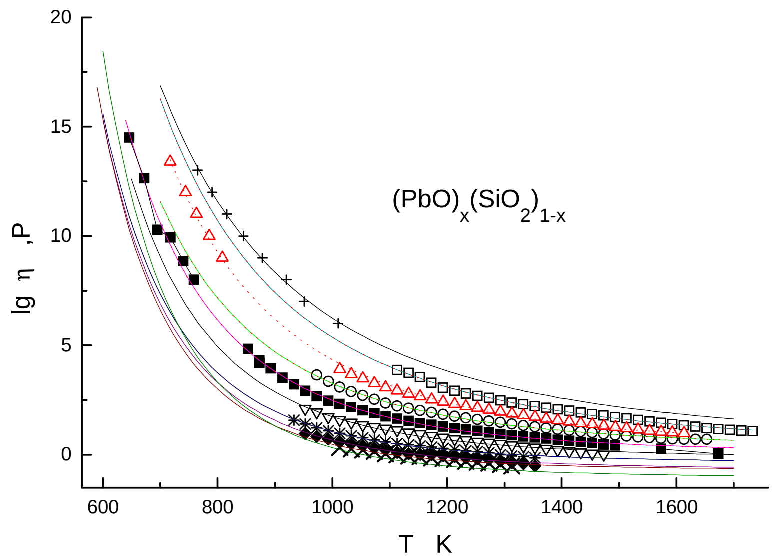
There is a simple relation between F the Angel's fragility parameter *m*

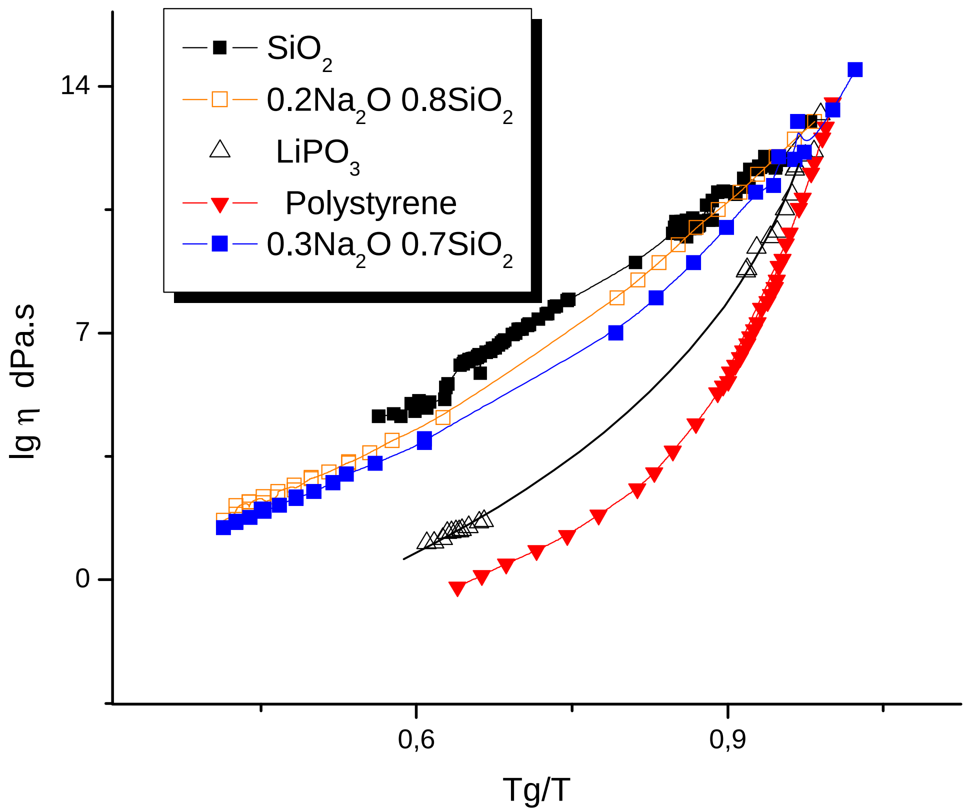
$$m = \left(\lg\frac{\eta_g}{\eta_\infty}\right)F$$



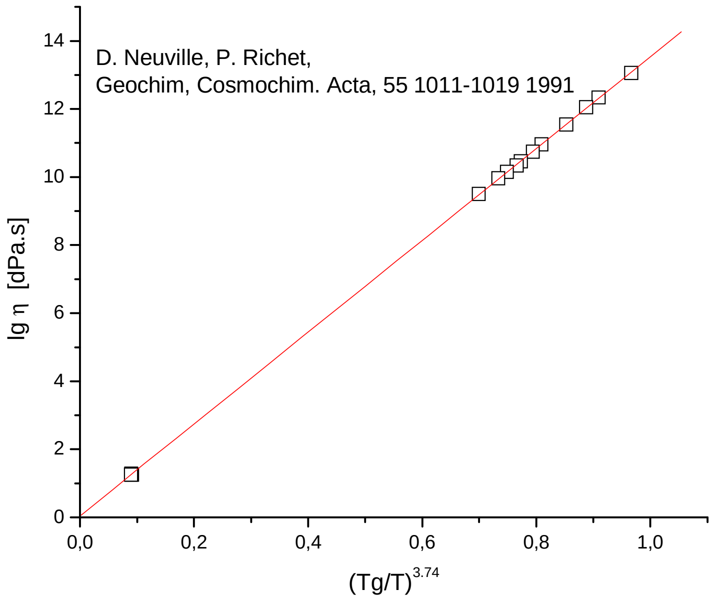
m
120
100
80
60
40
20
0
0
2
4
6
8
10
F
m=12.5 F

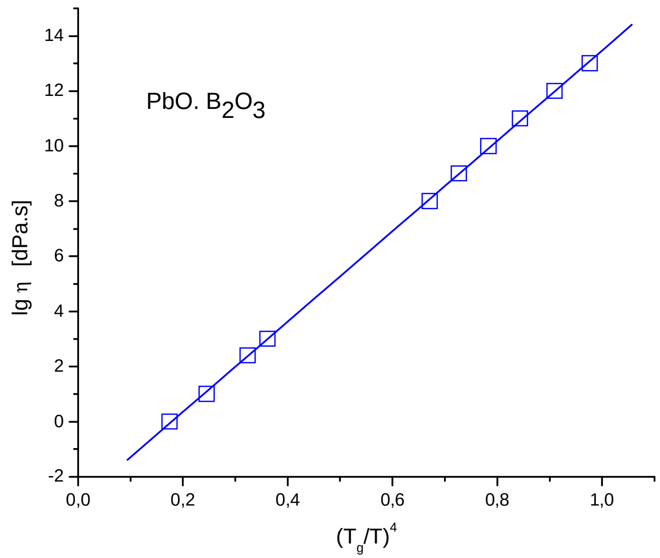
Experimental data

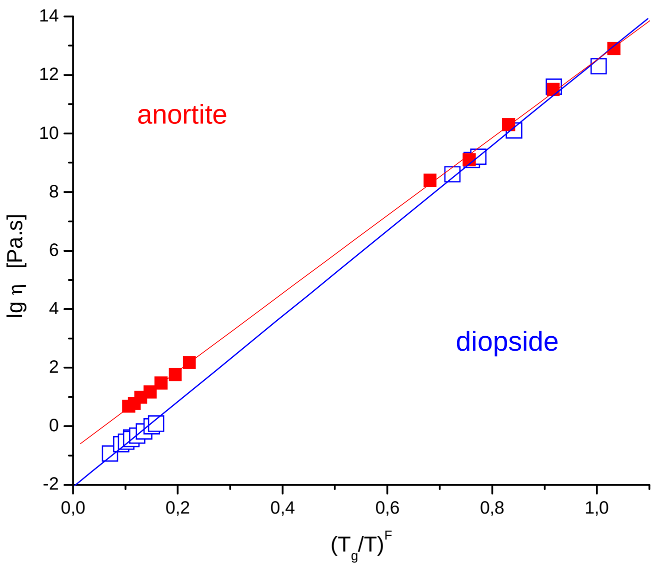




SiO2
0.2Na2O 0.8SiO2
LiPO3
Polystyrene
0.3Na2O 0.7SiO2
14
7
0
lg η dPa.s
0,6
0,9
Tg/T

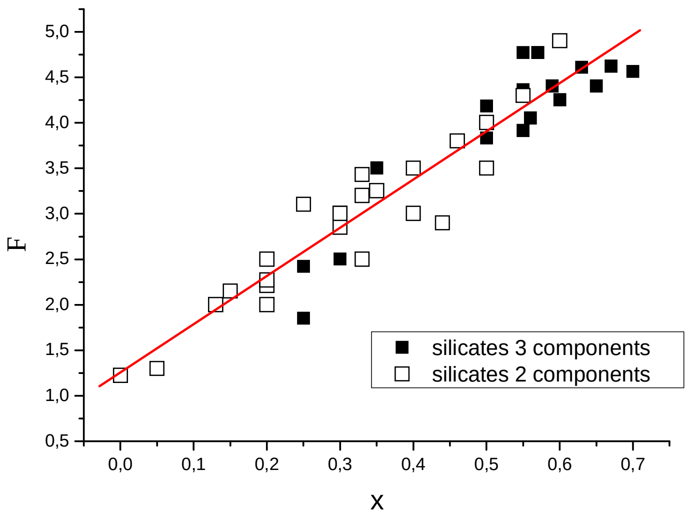

D. Neuville, P. Richet,
Geochim, Cosmochim. Acta, 55 1011-1019 1991
lg η [dPa.s]
(Tg/T)^3.74
0,0
0,2
0,4
0,6
0,8
1,0
0
2
4
6
8
10
12
14


PbO. B2O3
lg η [dPa.s]
(Tg/T)^4
0,0
0,2
0,4
0,6
0,8
1,0
-2
0
2
4
6
8
10
12
14


anortite
diopside
lg η [Pa.s]
(Tg/T)^F
0,0
0,2
0,4
0,6
0,8
1,0
-2
0
2
4
6
8
10
12
14

Dependence of F on composition x

$(Me_2O)_x\ (SiO2)_{1-x}$



$$F = \frac{2C_p}{ZR}$$

$$C_p(x) = C_p(0) + 3RxZ$$

$$F(x) = F(0) + \frac{2 \cdot 3RZx}{RZ} = F(0) + 6x$$

$$\eta = \eta_\infty \exp\left[2.3(13.5 - \lg \eta_\infty)\left(\frac{T_g}{T}\right)^F\right]$$

$$\eta = \eta_o \exp\left(\frac{B}{T - T_o}\right)$$

$$\eta = \eta_o \exp\left(\frac{\mathrm{B}}{\mathrm{T}\Delta \mathrm{S}}\right)$$

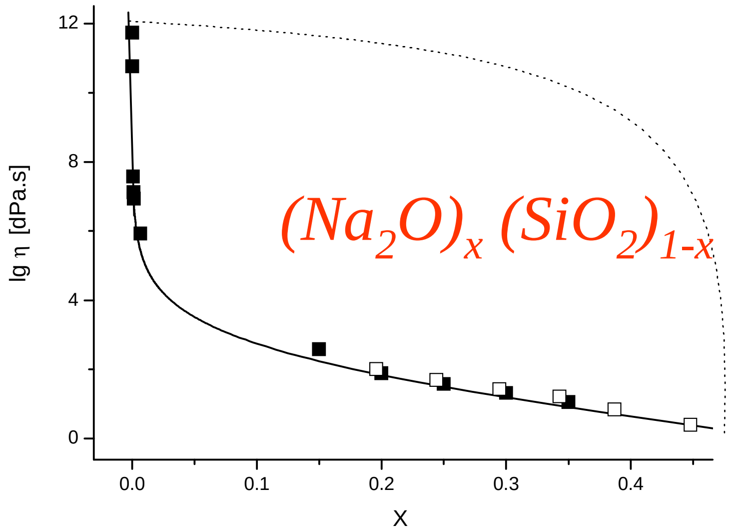
$$\eta_g = \eta_o \exp\left(\frac{B}{T_g - T_o}\right)$$

$$\eta_g = \eta_o \exp\left(\frac{B}{\mathrm{T}_g \Delta \mathrm{S}_g}\right)$$

$$\eta = \eta_o \exp\left(2.3(13.5 - \lg \eta_o)\frac{T_g - T_o}{T - T_o}\right)$$

$$\eta = \eta_o \exp\left(2.3(13.5 - \lg \eta_o)\frac{\mathrm{T}_g \Delta \mathrm{S}_g}{\mathrm{T}\Delta \mathrm{S}}\right)$$

$$\nu_i = \nu_o \exp\left(-\frac{E_i}{RT}\right) \qquad Q_i(x) = \frac{4!}{i!(4-i)!}(1-x)^{4-i}x^i \qquad \langle\nu\rangle = \sum_{i=0}^{4} Q_i(x)\,\nu_i$$

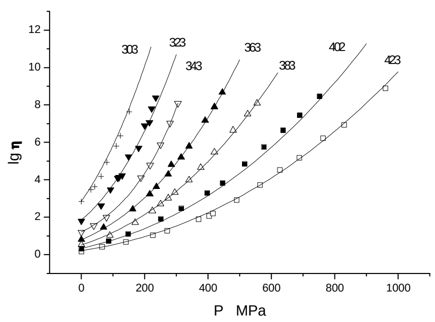


Pressure dependence of viscosity

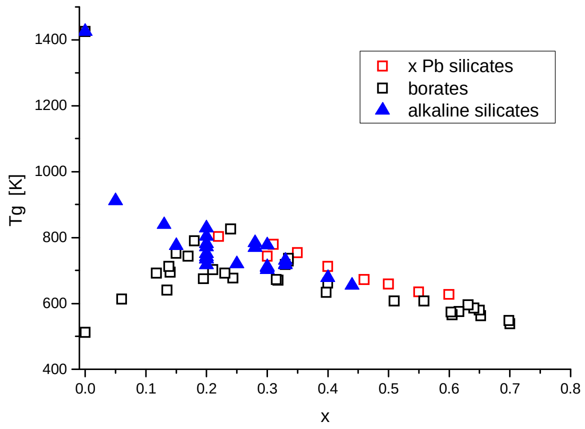
$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P = \kappa V \qquad S - S_o = V_m \int_{P_0}^{P} \kappa dp \qquad \kappa = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \approx k_o \frac{\Pi}{\Pi + P}$$

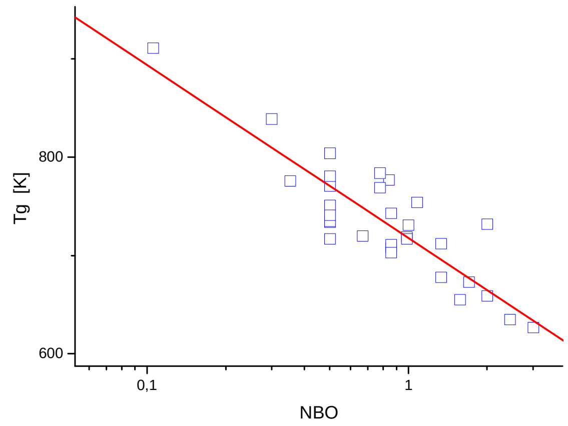
$$S = S_g + C_p \ln\frac{T}{T_g} - \kappa_o V_m \Pi \ln\left(\frac{\Pi + P}{\Pi + P_o}\right)$$

$$\eta = \eta_\infty \exp\left\{2.3(13.5 - \lg\eta_\infty)\left(\frac{T_g(P)}{T}\right)^F\right\} \qquad T_g(P) = T_{go}\left(1 + \frac{P}{\Pi}\right)^{\beta/F} \qquad \beta = \frac{2}{ZR}\kappa_o V\Pi$$



Dependence **Tg** on composition **x**





Melting point

The Clausius- Clapeiron equation states

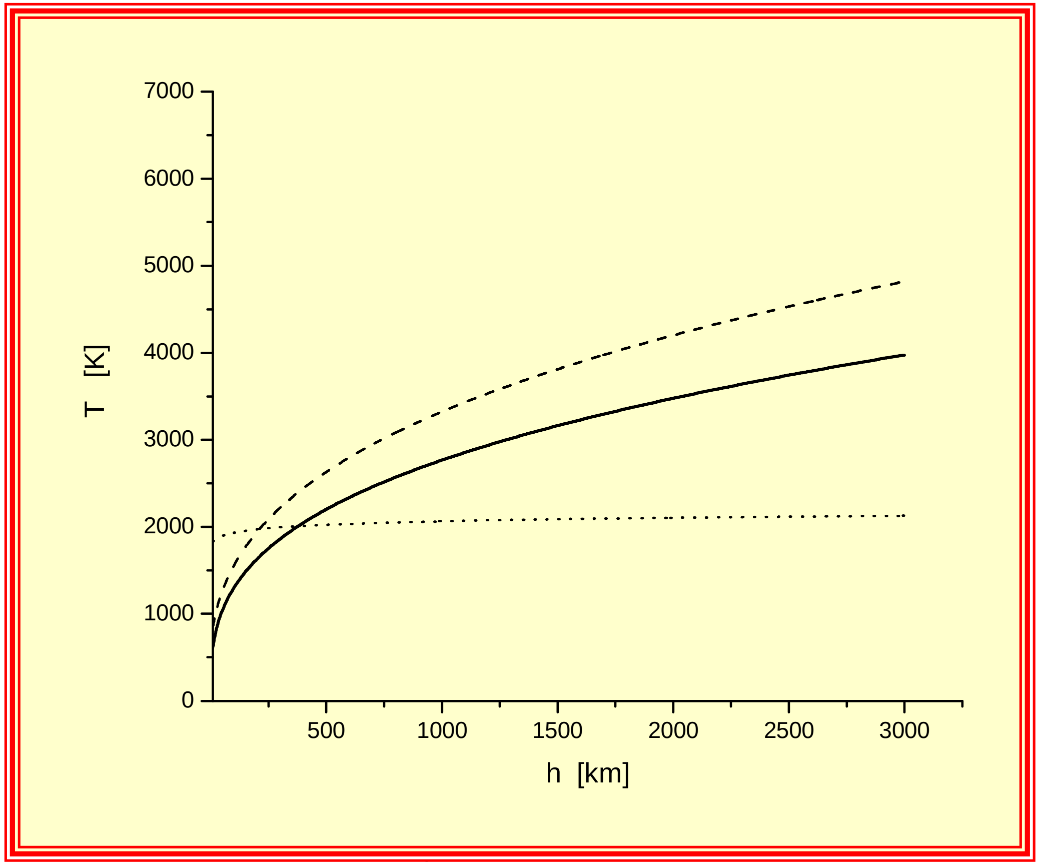
$$\frac{dT_m}{dP} = \frac{V_f - V_c}{S_f - S_c} \equiv \frac{\Delta V}{\Delta S}$$

$$\frac{\Delta V}{\Delta S} \approx \frac{\Delta V_o}{\Delta S_{mo}} \frac{\Pi}{\Pi + P}$$

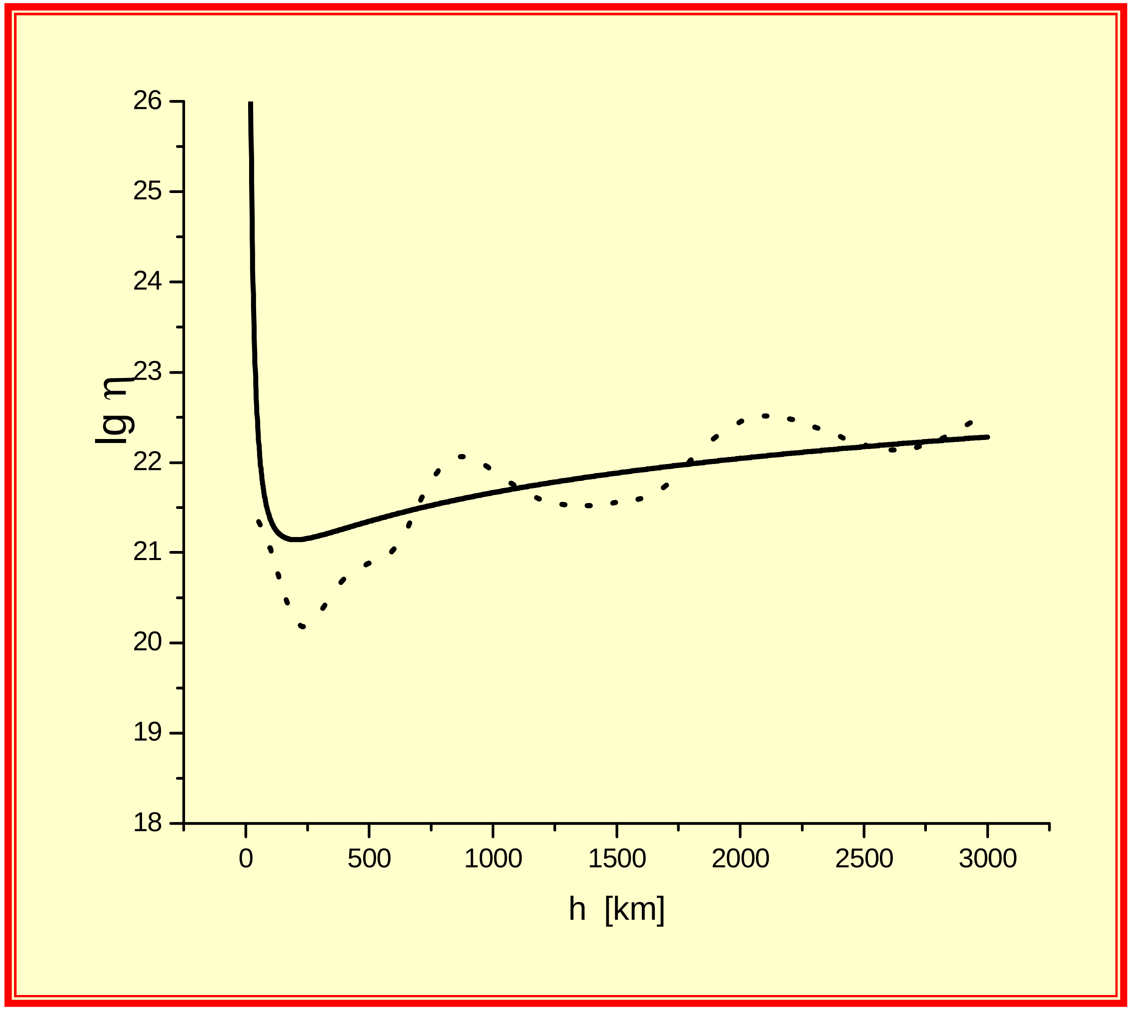
$$T_m(h) \approx T_{mo} + \frac{\Delta V_o}{\Delta S_{mo}} \int_0^{P(h)} \frac{\Pi}{\Pi + P} dP = \frac{\Pi \Delta V_o}{\Delta S_{mo}} \ln \frac{\Pi + P(h)}{\Pi}$$

Table 1

Parameter	Value
ΔS_{mo}	$3R$ (R is the ideal gas constant) $[J/mol]$
V_{fo}	5.10^{-5} $[m^3/mol]$
V_{co}	$0.9\ V_{fo}$
Π_f	$0.2\ [GPa]$
Π_c	$1.1\ \Pi_f$
k_{fo}	8.10^{-5} $[K^{-1}]$
k_{co}	$0.9\ k_{fo}$
T_{go}	$720\ [K]$

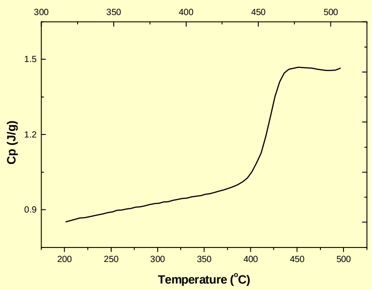


The dependencies on depth *h* of the computed temperatures:
The mantle temperature *T(h)* (solid line),
the glass transition temperature *Tg(h)* (dashed curve)
the melting point *Tm(h)* (dotted line).



The predicted dependence of viscosity on depth *h*. Dotted line is experimental dependence according to Ref.[2].

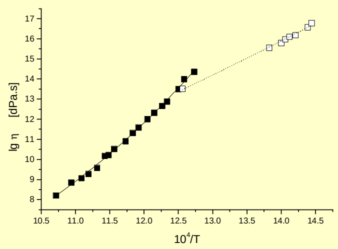
Viscosity of non-equilibrium systems



$$S(T) = S_g + C_p \ln\left(\frac{T_f}{T_g}\right) + C_{gl} \ln\left(\frac{T}{T_f}\right)$$

$$\eta = \eta_\infty \exp\left[2.3\left(13 - \lg \eta_\infty\right)\left(\frac{T_g}{T_f}\right)^F \left(\frac{T_f}{T}\right)^\gamma\right]$$

$$\gamma = F\,\frac{C_{gl}}{C_p}$$



$$\frac{C_{gl}}{C_p} = \frac{C_p - \Delta C_p}{C_p}$$

Literature

I Avramov J. Phys.: Condens. Matter 20 (2008) 244106 (4pp) Pressure dependence of viscosity, or is the earth's mantle a glass?

I.Avramov Journal of Volcanology and Geothermal Research Volume 160, Issues 1-2 , 1 February 2007, Pages 165-174

I.Avramov J. Non-Cryst. Sol. 351 (2005) 3163 - 3173 "Viscosity in disordered media"

I.Avramov, *Physics and Chemistry of Glasses: European Journal of Glass Science and Technology Part B June 2007* **48** (3) pp. 178-181. "Activation energy for structural relaxation of glassforming melts"

I.Avramov, *Physics and Chemistry of Glasses: European Journal of Glass Science and Technology Part B*, **48** (1) (2007) pp. 61-63 "Viscosity activation energy".

I.Avramov, Journal of Non-Crystalline Solids, 354/14 (2008) pp. 1537-1540 "DIFFUSION COEFFICIENT OF FOREIGN PARTICLES IN GLASSFORMING MELTS"

Table 1 Viscosity parameters at about 0.1 MPa; The abbreviation ***FMCAS#*** is for composition of the system Fe_2O_3-MgO-CaO-Al_2O_3-SiO_2 with numbering according to (Solvang , Yue , Jensen , (2004)).

Substance		$\eta = \eta_\infty \exp\left(2.3(13.5 - \lg \eta_\infty)\left(\frac{T_g}{T}\right)^F\right)$	
	$lg\eta_{\infty\ [dPas]}$	T_{go} (K)	*F*
SiO_2	-3.65	1425	1.22
$Li_2O.2SiO_2$	0.96	719	3.43
2 Li_2O.8 SiO_2	0	734	2.25
3Li_2O.7 SiO_2	0 .53	708	3
0.05Na_2O.0.95SiO_2	-3.8	911	1.3
0.14Na_2O.0.875SiO_2	-2.7	839	2
Na_2O. 3SiO_2	0.5	706	2.5
Na_2O.2SiO_2	0.6	731	2.5
15Na_2O. 85SiO_2	0	776	2.15
2 Na_2O.8 SiO_2	0 .1	735	2.27
3Na2O.7SiO2	0.65	711	2.85
3.3Na2O.6.7SiO2	0.4	705	2.8
4 Na_2O.6 SiO_2	0.57	678	3
44Na2O.56SiO2	0.28	655	2.9
Na_2O. SiO_2	0.25	825	4
2 K_2O.8SiO_2	0 .84	751	2.5
3 K_2O.8SiO_2	1.37	703	3
BaO.2SiO_2	-1.5	962	3.25
3 PbO.7SiO_2	0 .66	743	3

3.5 PbO.6.5SiO_2	0.53	754	3.25
4 PbO.6SiO_2	0 .24	712	3.5
4.6 PbO.5.4SiO_2	0.32	673	3.8
PbO. SiO_2	-0.03	659	4
5.5 PbO.4.5SiO_2	-0.2	635	4.3
6PbO.4SiO_2	-0.3	627	4.9
97 8B_2O_3 2 17SiO_2	1.38	520	3.25
94B_2O_3 5 95SiO_2	1.29	525	3
89 3B_2O_3 10 7SiO_2	1.45	527	3
51 6B_2O_3 48 4SiO_2	0.6	582	1.5
44 6B_2O_3 55 4SiO_2	-0.02	682	1
B_2O_3	0.95	511.5	2.75
14 5Na_2O.86 5B_2O_3	-0.7	695	4.25
33 3Na_2O 66 7B_2O_3	-1.5	744	4.5
6Li_2O.94B_2O_3	0.1	612	4
14.9Li_2O.86.1B_2O_3	-0.2	695	4.7
33.5Li_2O.66.5B_2O_3	-1.6	754	4.7
19.5K_2O.80.5B_2O_3	-0.16	675	4
24.4K_2O.75.6B_2O_3	0	677	4

$18BaO.82B_2O_3$	-0.97	790	4
$23.9BaO.76B_2O_3$	-0.9	826	4.5
$33PbO. 67 B_2O_3$	-2.9	718	4
$PB_2:PbO.2 B_2O_3$	0.09	780	9.5
P_2O_5	-4.87	522	1
$Li_2O. P_2O_5$	0.14	580	5.4
$Na_2O. P_2O_5$	0.43	544	5.5
GeO_2	1.34	923	1.4
$5Na_2O.95GeO_2$	0.11	695	2.25
$10Na_2O.90GeO_2$	-0.14	743	4.5
$29.6Na_2O.70.4GeO_2$	0.43	710	6.5
$20PbO.80GeO_2$	0.33	716	4.25
$30PbO.70GeO_2$	0.66	679	6.25
$40PbO.60GeO_2$	0.25	715	5
$50PbO.50GeO_2$	0.33	626	5.25
Polystyrene	2.3	370	7
Glycerine	-2.2	177	3.2

Multicomponent and	geoscientificall y	relevan t	systems
$20.96Na_2O.9CaO.70SiO_2$	0.22	775	2.83
$21Na_2O.9CaO.70SiO_2$	0.8	777	3.2
$19Na_2O.9CaO.72SiO_2$	0.4	784	2.9
$21Na_2O.7CaO.72SiO_2$	0.5	769	2.9
$Na_2O.2CaO.3SiO_2$	-2.57	821	2.77
$2Na_2O.1CaO.3SiO_2$	-4.54	742	3.2
$CaO.\ Al_2O_3.\ 2SiO_2$	-2.06	1105	3.5
$(CaO)_{0.423}(Al_2O_3.)_{0.083}(SiO_2)_{0.494}$	-0.7	1043	4.18
$(CaO)_{0.439}(Al_2O_3.)_{0.083}(SiO_2)_{0.456}$	-0.7	1057	4.36
$(CaO)_{0.461}(Al_2O_3.)_{0.105}(SiO_2)_{0.414}$	-0.7	1065	4.4
$(CaO)_{0.479}(Al_2O_3.)_{0.127}(SiO_2)_{0.373}$	-0.7	1075	4.61
$(CaO)_{0.505}(Al_2O_3.)_{0.147}(SiO_2)_{0.330}$	-0.7	1084	4.62
$(CaO)_{0.351}(Al_2O_3.)_{0.164}(SiO_2)_{0.498}$	-0.7	1066	3.83
$(CaO)_{0.385}(Al_2O_3.)_{0.151}(SiO_2)_{0.441}$	-0.7	1075	4.05
$(CaO)_{0.405}(Al_2O_3.)_{0.174}(SiO_2)_{0.395}$	-0.7	1089	4.25
$(CaO)_{0.427}(Al_2O_3.)_{0.225}(SiO_2)_{0.348}$	-0.7	1093	4.4
$(CaO)_{0.459}(Al_2O_3.)_{0.247}(SiO_2)_{0.294}$	-0.7	1104	4.56
$(CaO)_{0.428}(Al_2O_3.)_{0.143}(SiO_2)_{0.428}$	0.88	1056	4.77
$Na_2O.\ Al_2O_3.\ 6SiO_2$	-8.58	1012	1
$2Na_2O.1CaO.3SiO_2$	-5.54	742.3	3.2
5Na2O.10MgO.10Al2O3.75 SiO_2	-1.77	1016	1.85
$10Na_2O.10MgO.10Al_2O_3.70\ SiO_2$	0.21	979	2.5

$15Na_2O.10MgO.10Al_2O_3.65\ SiO_2$	1.26	961	3.5
$20Na_2O.10MgO.10Al_2O_3.60\ SiO_2$	1.27	899	3.5
$10Na_2O.10MgO.5Al_2O_3.75SiO_2$	0.4	933	2.42
$10Na_2O.10MgO.80SiO_2$	-0.43	828.5	2
Albite	-0.7	1051	1.9
Haplogranite	-3.6	1081	1.36
Diopside $CaMgSi_2O_6$	-1.07	974	3.5
Diopside 80 Anortite 20	-0.66	997	3.82
Diopside 64 Anortite 36	-0.03	1011	4.25
Diopside 40 Anortite 60	0.27	1034	4.31
Diopside 20 Anortite 80	0.23	1079	4.32
Anortite $CaAl_2Si_2O_8$	0.26	1126	4.53
FMCAS23	-0.81	993	3.69
FMCAS19	-0.72	979	3.58
FMCAS20	-0.59	968	3.61
FMCAS21	-0.67	955	3.58
FMCAS22	-0.65	949	3.59