Conditions for Glass Formation

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First International School on Glass Crystallization (ISGlaC) , August 2001, FOZ DO IGUAÇU - PR - BRAZIL

There are three independent possibilities to treat the problem of glass formation:

1. Pure structural
2. Bound strength
3. Kinetic Criteria

STRUCTURAL (GEOMETRIC) APPROACHES

In 1912 **Goldschmidt** formulated a rule according to which for glassformers

$$0.2 < \frac{r_c}{r_a} < 0.4$$

There are many compositions for which this rule is fulfilled and are not glassformers (***BeO, most of the halides)***.

All ionic glassformers satisfy this rule. **This means that this equation is the condition that for glassformers anions are arranged in tetrahedral positions around the cations.**

Zachariasen ***Random Network Theory***

glass-formers are cations that have high valences (>2) and can create three dimensional networks of tetrahedra, which interconnect by corners; not by edges or faces. In the case of silicate, borate and phosphate glasses the networks are formed by the polymerization of polyhedra.

Network Formers : SiO_2, GeO_2, P_2O_5, As_2O_3 ***etc.***

Network Modifiers :

Bridging ***CaO, ZnO, MgO etc.***
Non Bridging Na_2O, Li_2O ***etc.***

Alkali modifiers fit into relatively large holes in the tetrahedral network.
Modifiers are large ions with low charge Na^+, K^+, Cs^+, Zn^{2+}, Pb^{2+} *etc.*

Close packing of spheres of equal size

symmetry	Z	d
Hexagonal	**12**	**0.74**
Tetragonal	**10**	**0.70**
Cubic volume centered	**8**	**0.68**
Simple cubic	**6**	**0.52**
Cubic diamond like	**4**	**0.34**

Existence of spheres of different size increases the close packing

BOUND STRENGTH MODELS

The stronger the bounds in the melts the more sluggish will be the rearrangement process.

Rawson – He takes a quite realistic quantity – the ration of the bound strength to kT_m

Up to here the models do not consider the importance of the cooling rate. Both approaches assume that substances can be divided to glass forming and crystallizing.

NETWORK RIGIDITY APPROACH

According to Thorpe the network switches from floppy to rigid if the number of solid bridges between the network formers exceeds a certain threshold value. The kinetics of phase transition (**and most the nucleation processes)** is very sensitive to the rigidity of the network. Slightly above the threshold concentration of rigid bonds some tiny floppy regions still exist inside the rigid network. They can **serve as active centers** for the nucleation process. Much later, nucleation can appear in the rigid part of the network. Therefore, a certain interval of concentration of rigid bonds in which a bimodal size distribution function of the crystalline particles will be observed. This is confirmed by experimental data.

Two sources of constraints are involved. One is generated by the fixed length of the bridges connecting NF (bridge stretching constraints BC). There is one BC constraint associated with each bridge. Therefore, the average number m_l of BC per node is

$$m_l = \frac{r}{2}$$

The fixed angle between bridges give rise to the second sort of constraints (bridge bending constraints BB). For r coordinated node, the number of

$$m_b = 2r-3$$

bending constraints is m_b The overall constraints number is the sum

$$m = m_l + m_b.$$

The degrees of freedom (per node) is equal to the dimension d of the space. Every constraint disables one degree of freedom. Therefore, the fraction f of enabled degrees of freedom is given [5] as:

$$f = d + 3 - 2.5 < r >$$

It is seen that $<r_{cr}>$ is the average number of constraining bonds per NF at which f = 0. For a three dimensional network: $<r_{cr}> = 2.4$

GLASS FORMING ABILITY

– accounts for the ease by which melts can be cooled to form glasses.

Critical Cooling Rate q_c

GLASS STABILITY

- accounts for the resistance of glasses towards devitrification upon reheating

Hruby Parameter

$$K_H = \frac{T_{cr} - T_g}{T_m - T_{cr}}$$

KINETIC APPROACH

- **Tammann** - Glasses are formed when nucleation vs temperature curve **does not overlap** with the growth rate vs temperature curve
- **Dietzel –** Crystallization stability depends on the crystal growth rate G
- **Turnbull –** Determines the kinetic stability in cooling experiments through the steady state nucleation rate J_o
- **Gutzow –** relates the glass stability to the non-steady-state time lag

Tammann model is still on a **qualitative** level. **Every of other three** approaches assumes that one of the three parameters is dominant and completely neglects the other two.

Uhlmann – formulated a criterion for vitrification based on the synthesis of nucleation and growth via the kinetics of overall crystallization (Equation of Kolmogorof – Avrami).

Temperature – Time – Transformation (TTT) curves

$$a(t) = 1 - \exp\left\{ -c_g \int_0^t J(t') \left[\int_{t'}^{t} \mathrm{G}(t'')dt'' \right]^d dt' \right\}$$

at isothermal conditions, for J=const and G=const’

$$\boxed{a(\mathrm{t}) = 1 - \exp\left(\frac{\mathrm{c_g}}{\mathrm{d}+1} \mathrm{JG^d t^{d+1}} \right)}$$

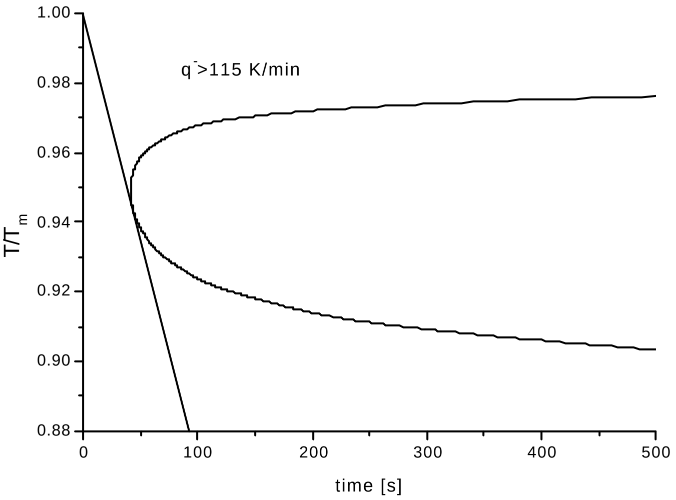
The time necessary to reach a given degree of crystallinity is:

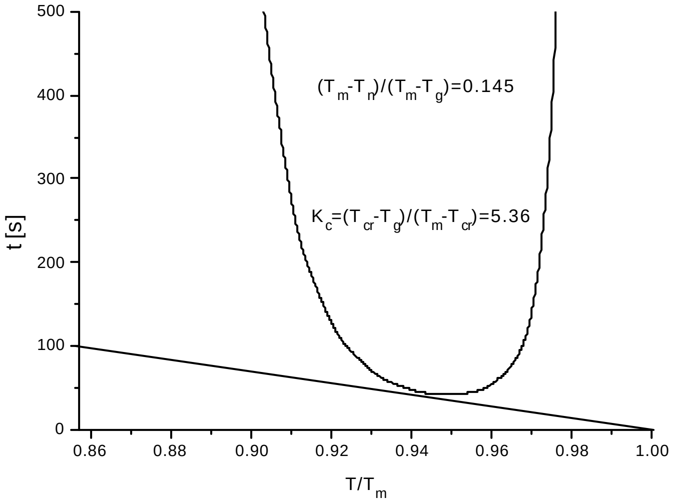
$$\mathrm{t_x} = \left(-\frac{(\mathrm{d}+1)\ln(1-\mathrm{x})}{\mathrm{c_g JG^d}} \right)^{\frac{1}{\mathrm{d}+1}}$$

If there is considerable induction time t_c

$$\mathrm{t_x} = \mathrm{b}t_{\mathrm{c}} + \left(-\frac{(\mathrm{d}+1)\ln(1-\mathrm{x})}{\mathrm{c_g JG^d}} \right)^{\frac{1}{\mathrm{d}+1}}$$

When *T* is changing *G,J* and t_c change too. The relationship between *T* and t_x is known as: **TTT** ***Temperature Time Transformation*** **curves**





Weinberg Model

$$q = \frac{dT}{dt}$$

$$\alpha(q) = 1 - exp\left\{ -\frac{4\pi}{3q}\int_{T_m}^{T} J(T', \Phi = 1)\left[\frac{1}{q}\int_{T'}^{T} G(T'')dT''\right]^3 dT' - \frac{4\pi}{3}N\left[\frac{1}{q}\int_{T_m}^{T} G(T'')dT''\right]^3 \right\}$$

Critical cooling rate could be very different from the Critical Heating rate!

$$\frac{c_g}{q^-}\int_{T_m}^{T_g} J(T')\left[\frac{1}{q^-}\int_{T'}^{T_g} G(T'')dT''\right]^d dT' \neq \frac{c_g}{q^+}\int_{T_g}^{T_m} J(T')\left[\frac{1}{q^+}\int_{T'}^{T_m} G(T'')dT''\right]^d dT'$$

$$I \equiv c_g \int_{T_m}^{T_g} J(T')\left[\int_{T'}^{T_g} G(T'')dT''\right]^d dT'$$

$$\boxed{q^-_{cr} = \sqrt[d+1]{\frac{I}{ln(1-a_c)}}}$$

$$r_k = \frac{2sV_c}{\Delta m} = \frac{2ad_o}{1-\frac{T}{T_m}} \approx \frac{d_o}{1-\frac{T}{T_m}} \quad ; \quad \frac{dr_c}{dT} = \frac{d_o}{T_m\left(1-\frac{T}{T_m}\right)^2} \quad ; \quad \frac{dr}{dT} = \frac{G}{q}$$

$$q_m = \frac{GT_m\left(1-\frac{T}{T_m}\right)^2}{d_o} = \frac{zT_m}{4pat_ç}\left(1-\frac{T}{T_m}\right)^3\left[1-\exp\left(-\frac{\Delta S_m}{R}\left(\frac{T_m}{T}-1\right)\right)\right]$$

When $\frac{\Delta S_m}{R}$ **increases G(T) and J(T) curves are separating**

Crystallization rate:

$$G = zW\ \frac{d_o}{t}\left[1 - exp\left(-\frac{Dm}{RT}\right)\right]$$

$$t = \frac{h}{E_{\infty}}$$

here $E_{¥}$ is the shear modulus at high frequencies. $E_{¥}$~10^{10} Pa.

Skapski-Turnbull : $$s = a\ \frac{DH_m}{V_c^{2/3} N_a^{1/3}} \approx a\ \frac{DS_m T_m}{N_a d_o^2}$$

$$G = z\frac{d_o}{4pat_{\text{ç}}}\left(1 - \frac{T}{T_m}\right)\left[1 - \exp\left(-\frac{\Delta S_m}{R}\left(\frac{T_m}{T} - 1\right)\right)\right]$$

Nucleation rate:

$$J_{st} = z_k\frac{kT}{d_o^4\text{ç}\left(1 - \frac{T}{T_m}\right)}\sqrt{\frac{DS_m}{R}F\ \frac{T_m}{T}}exp\left(-\frac{2\frac{DS_m}{R}}{\frac{T}{T_m}\left(1 - \frac{T}{T_m}\right)^2}F\right) = z_k\frac{RT_m}{V_c d_o\text{ç}\left(\frac{T_m}{T} - 1\right)}\sqrt{\frac{DS_m}{R}F\ \frac{T_m}{T}}exp\left(-\frac{2\frac{DS_m}{R}}{\frac{T}{T_m}\left(1 - \frac{T}{T_m}\right)^2}F\right)$$

VISCOSITY

Vogel-Fulcher-Tammann equation

$$h = h_0 \exp\left(\frac{\mathrm{B}}{\mathrm{T - T_o}} \right)$$

Adam and Gibbs equation

$$h = h_0 \exp\left(\frac{\mathrm{B}}{\mathrm{T\Delta S)}} \right)$$

Avramov’s equation

$$h = h_o\, exp\left[e \left(\frac{T_g}{T} \right)^{a} \right]$$

fragility parameter $a = \frac{2C_p}{RZ}$; $e = 2.3l\ (12.5 - lgh_o)$

Adam and Gibbs assumed that the barrier to rearrangement is proportional to *n*, and determined the temperature dependence of *n* in terms of the configurational entropy, *DS* . Their result for the viscosity is

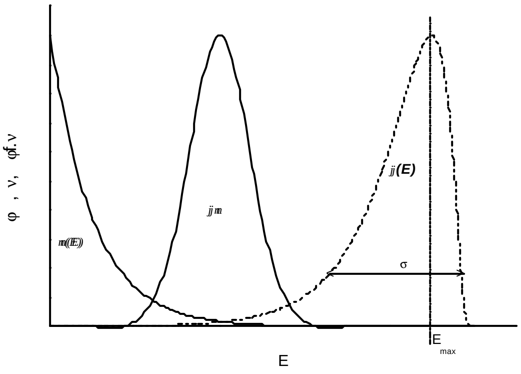
$$h = h_o \exp\left(\frac{\Delta m \ln w^*}{T\Delta S} \right)$$

where w* is the number of configurations available to the smallest group of atoms that can undergo a cooperative rearrangement (w*~2).

While in crystal the building units (hereafter referred as molecules) meet always the same barrier, there is a more or less broad distribution in amorphous state. The average jump frequency is determined by

$$< n >= \int n(E) j(E) dE$$

$$n_i = n_o \exp\left(-\frac{E_i}{RT} \right)$$



Let T_g is the temperature at which viscosity is:
lgh (T_g)º lgh$_g$=12.5 Pa.s

Vogel-Fulcher-Tammann equation

$$lg h_g = 12.5 = lg h_0 + \frac{1}{2.31}\frac{B}{T_g - T_o}$$

$$B = 2.31(12.5 - lg h_0)(T_g - T_o) = e(T_g - T_o)$$

Vogel-Fulcher-Tammann equation

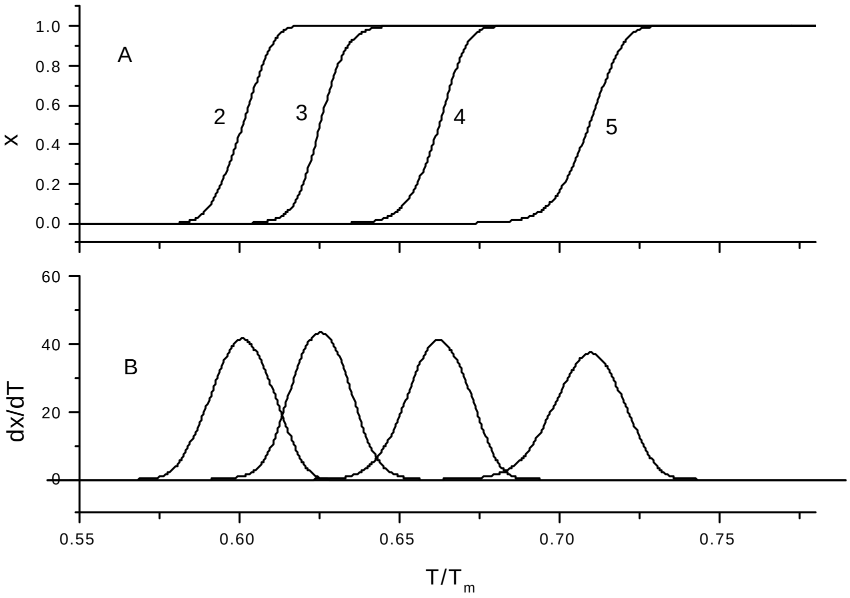
$$h = h_0 exp\left(e\,\frac{T_g - T_o}{T - T_o} \right)$$

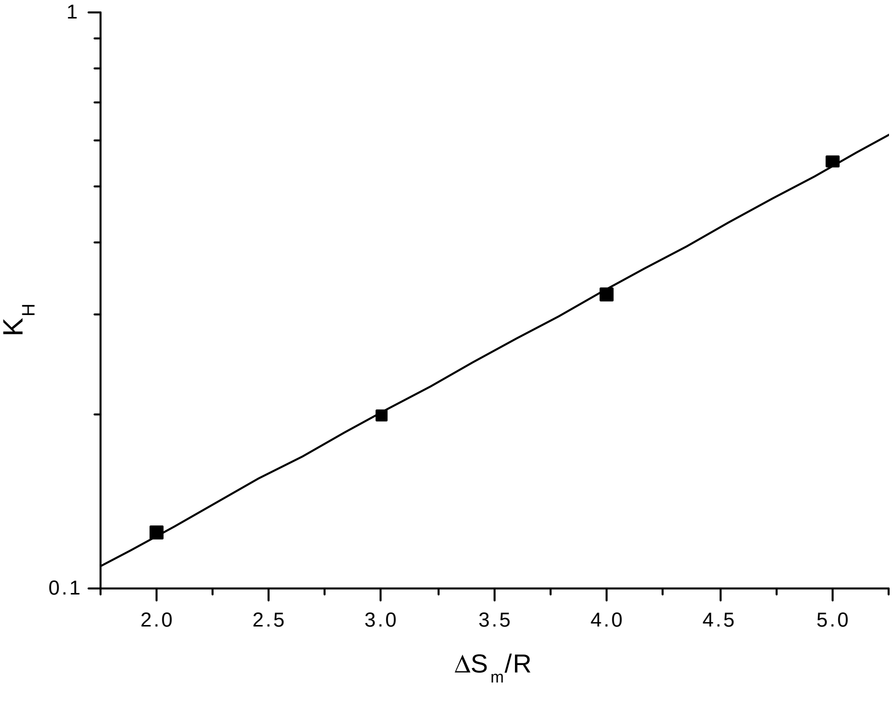
Adam and Gibbs equation

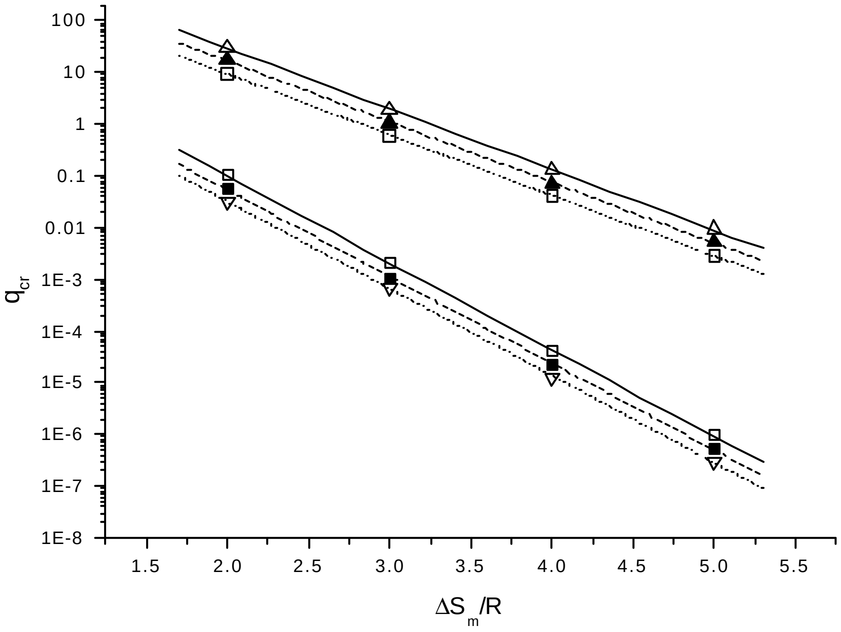
$$h = h_0 exp\left(e\,\frac{T_g DS_g}{TDS)} \right)$$

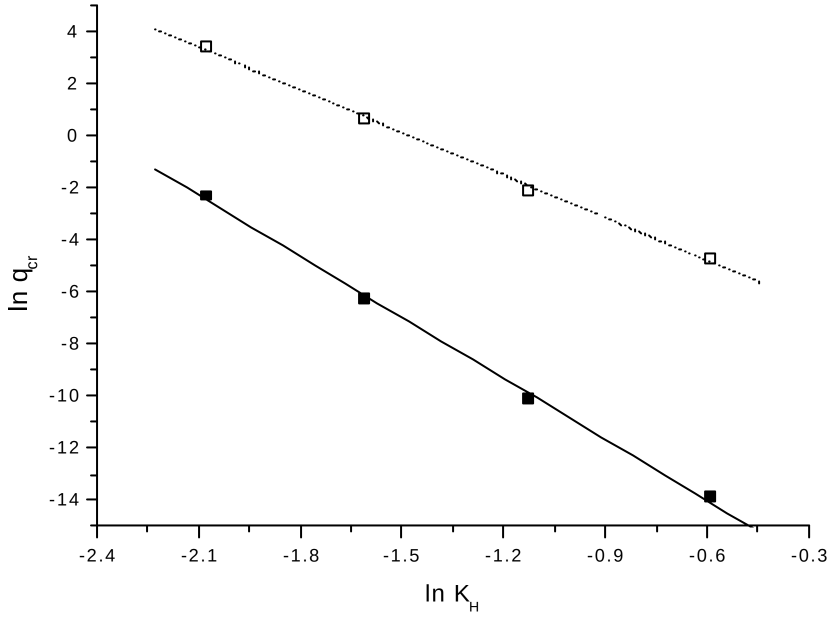
Avramov's equation

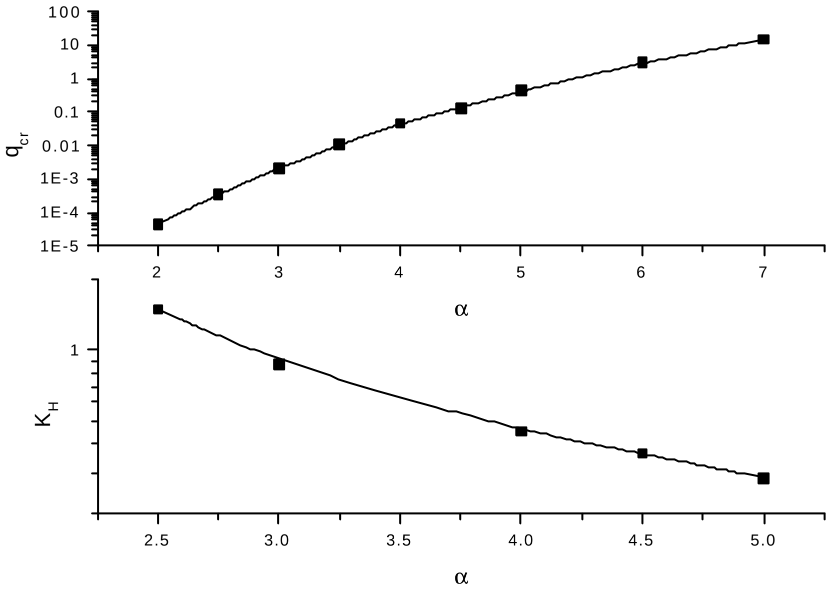
$$h = h_o\, exp\left[e\left(\frac{T_g}{T} \right)^a \right]$$

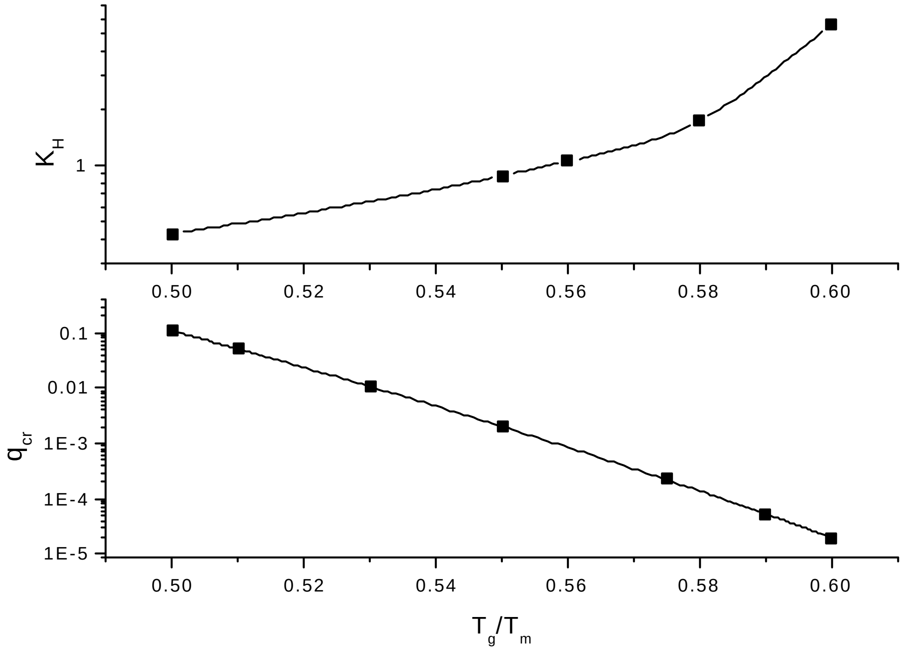

A
2
3
4
5
x
1.0
0.8
0.6
0.4
0.2
0.0
B
dx/dT
60
40
20
0
0.55
0.60
0.65
0.70
0.75
T/T$_m$

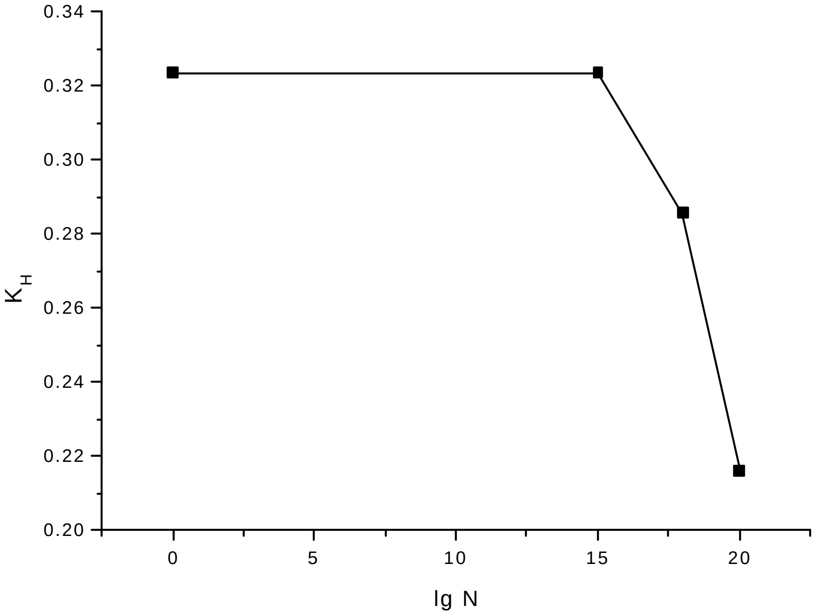

K$_H$
1
0.1
2.0
2.5
3.0
3.5
4.0
4.5
5.0
ΔS$_m$/R

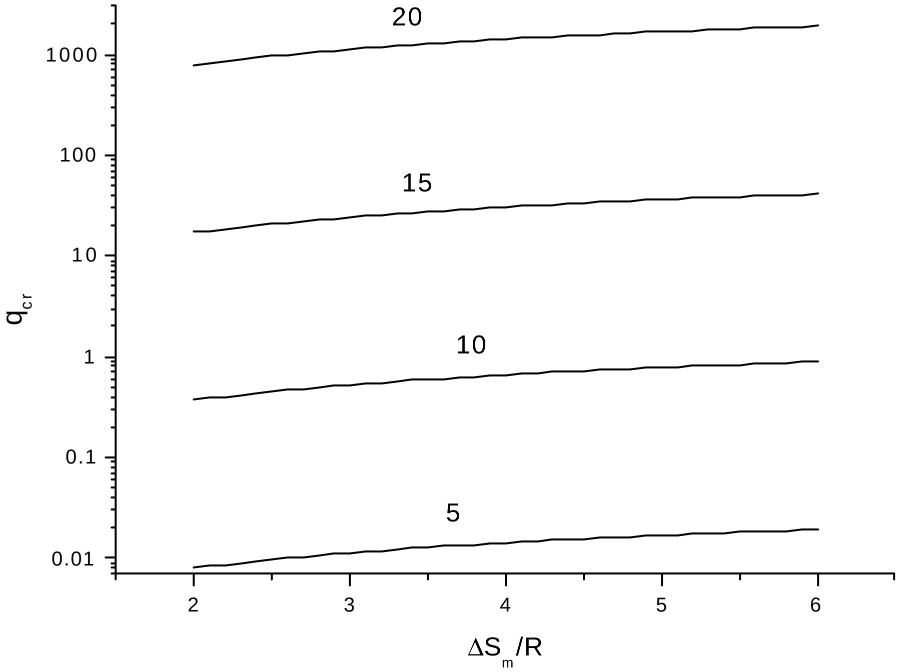

100
10
1
0.1
0.01
1E-3
1E-4
1E-5
1E-6
1E-7
1E-8
q_{cr}
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
$\Delta S_m/R$

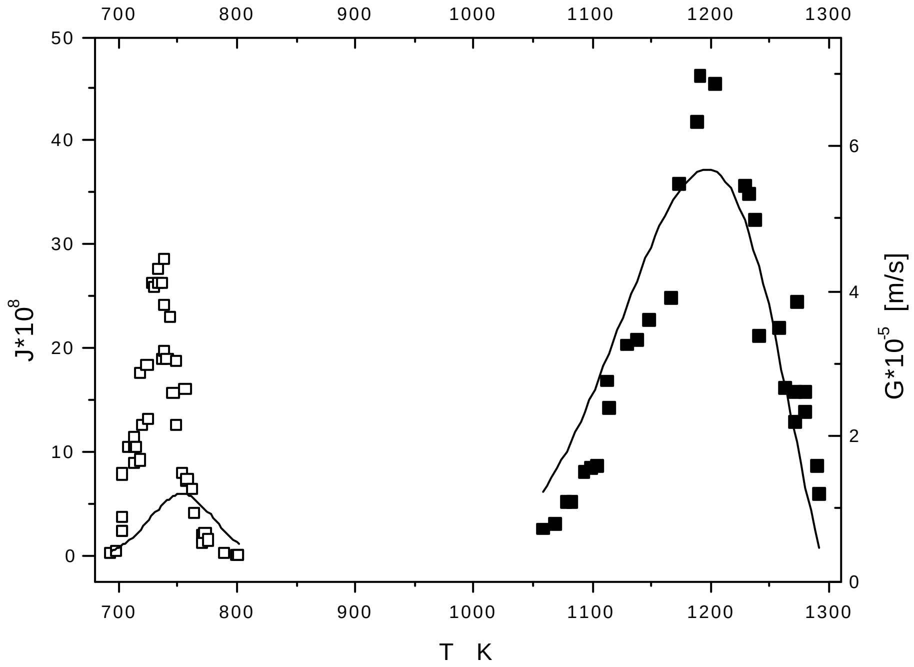

4
2
0
-2
-4
-6
-8
-10
-12
-14
ln q_{cr}
-2.4
-2.1
-1.8
-1.5
-1.2
-0.9
-0.6
-0.3
ln K_H


100
10
1
0.1
0.01
1E-3
1E-4
1E-5
q_{cr}
2
3
4
5
6
7
α
1
K_H
2.5
3.0
3.5
4.0
4.5
5.0
α

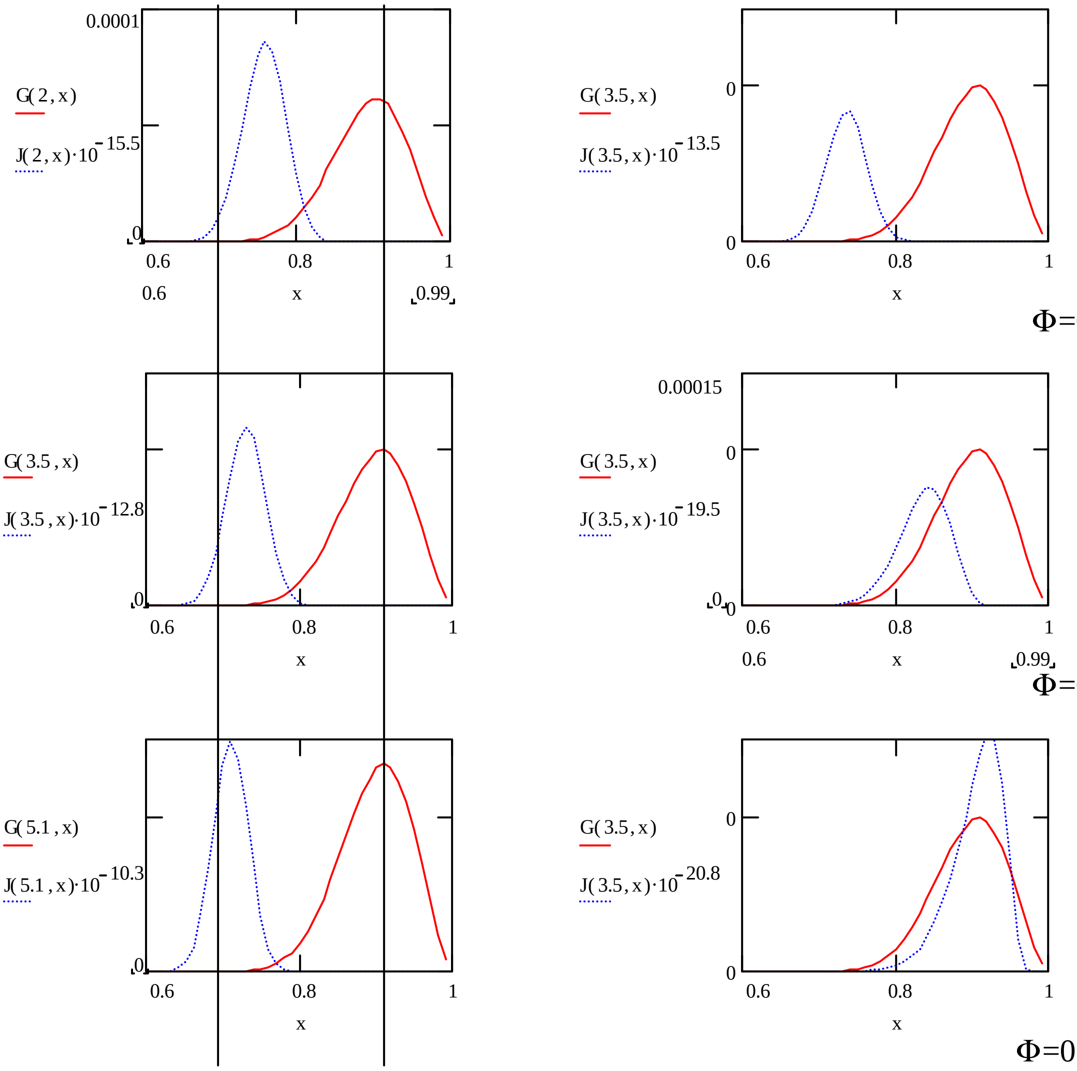

K_H
1
0.50
0.52
0.54
0.56
0.58
0.60
0.1
0.01
1E-3
1E-4
1E-5
q_{cr}
0.50
0.52
0.54
0.56
0.58
0.60
T_g/T_m


0.34
0.32
0.30
0.28
0.26
0.24
0.22
0.20
K_H
0
5
10
15
20
lg N


20
15
10
5
1000
100
10
1
0.1
0.01
q_cr
2
3
4
5
6
ΔS_m/R



700
800
900
1000
1100
1200
1300
50
40
30
20
10
0
J*10^8
6
4
2
0
G*10^{-5} [m/s]
T K


0.0001
G(2 , x)
J(2 , x)·10^−15.5
0
0.6
0.8
1
0.6
x
0.99
G(3.5 , x)
J(3.5 , x)·10^−13.5
0
0
0.6
0.8
1
x
G(3.5 , x)
J(3.5 , x)·10^−12.8
0
0.6
0.8
1
x
0.00015
G(3.5 , x)
J(3.5 , x)·10^−19.5
0
0
0
0.6
0.8
1
0.6
x
0.99
G(5.1 , x)
J(5.1 , x)·10^−10.3
0
0.6
0.8
1
x
G(3.5 , x)
J(3.5 , x)·10^−20.8
0
0
0.6
0.8
1
x

Φ=0.9

Φ=0.1

Φ=0.01

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VISCOSITY

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EXPERIMENTAL DATA

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