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FRENKEL´S VISCOSITY FORMULA RECALCULATED THROUGH MACROSCOPIC DISPERSION PARAMETERS.

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ABSTRACT

Using a new mean velocity equation for turbulent flows it is possible to write the classical J.I. Frenkel´s equation for viscosity of liquids as function of some macroscopic parameters related with fluvial dynamics.   This new formula opens several windows to understanding fluid dynamics and put it as function of easy to measure data. The new discussed model starts from an application of mechanical relativity principle (Galileo´s) to different motions in tracer dynamics which leads to a relationship between mean velocity of flow and transport parameters, including a function that is linked whit viscosity. Some practical calculations are done at the end of article.

Keywords: Liquid state physics, mass transport, random motions.

INTRODUCTION

J.I. Frenkel was a brilliant Russian physicist who studied solid and liquid molecular mechanics. His viscosity formula is one of most known in technical literature (Frish *et al*, 1967), where *A* is approximately a constant and *W* is the energy of the well of potential of each molecule in equilibrium, in low temperature range, near to crystallization point, equation (1).

$$\eta = A \, e^{\frac{W}{KT}} \tag{1}$$

Frenkel proposed this formula starting from the idea of *mobility* of individual particles of liquid (Frenkel, 1955). This characteristic measures the average velocity that can acquire them respect to surrounding particles under the action of external forces. The mobility leads to *fluidity* concept which is the reciprocal of viscosity coefficient, *η*.   Then properly the dynamic viscosity coefficient is inversely proportional to diffusion Coefficient which is favored by mobility.   The diffusion Coefficient in liquids is proportional to *Exp (-W/KT)* leading to equation (1). This idea, as several others are coming from the Frenkel´s theory of liquids based on solids structure (Gueguzin, 1983) (Kitaigorovski, 1961). The numerical value of *A*

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was obtained by Frenkel considering a Stokes's force, i.e. Non-turbulent case, which is temperature and pressure dependent. Theoretical values of *A* were very small considering experimental data, forcing the multiplication by a function which recovers the proper scale. Whit these remarks, the Frenkel´s formula has been applied successfully in several cases. The viscosity is important whatever kind of regime because, as was pointed out by several authors (Peralta-Fabi, 2001), in real turbulent process there is a waterfall of disordered energy transmission composed by whirlpools of progressively decreasing size. The smaller ones disappear by the effect of viscosity which is then the last stage. The aim of this paper is to link this concept (including Frenkel´s one) with a definition of mass transport in which appear several macroscopic fluvial parameters.

Regarding the equation (1) for liquids energy *W* is much smaller than in that in crystals (perfect solid) which is near the value of the heat of vaporization while for simple liquids as water is rather near to the value of fusion heat. Roughly speaking *W* is near to 2400-10000 Cal/mol range, if absolute temperature is within the range of 200K-800K (Frenkel, 1955)(Moore,1983). This value will be important in the verification procedure for the new equations.

A NEW FORMULA FOR MEAN VELOCITY OF FLOW USING A MASS TRANSPORT CONCEPT.

When a tracer is poured in flow dispersion and diffusion processes take place. This leads to a relative motion of tracer in flow which may be viewed by several observers in different reference systems. A general condition that should be obeyed by them is that mechanical relativity principle holds in any time. This means that Galileo´s composition must be applied to diffusion-dispersion velocities, *+Vdiff, -Vdiff*, and flow mean velocity, *Ux*. (Constain *et al*, 2007) Figure 1.
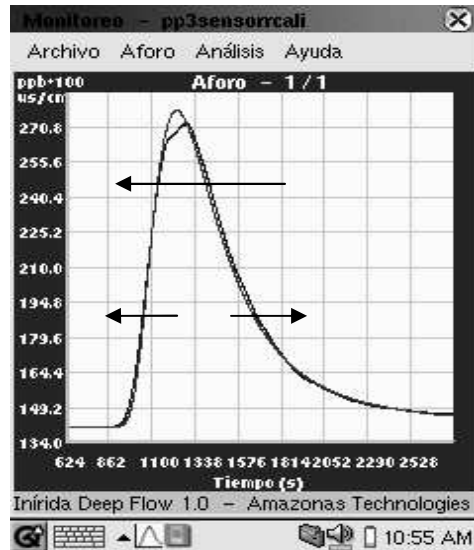

Fig. 1. Galilean composition of velocities in tracer motion

Providing that such composition takes place, a function *Φ,* as ratio of involved velocities is defined:

$$\phi = \frac{V_{diff}}{U_x} \qquad (2)$$

If a Brownian diffusion is considered, then it can be written the following equation, with Δ and τ length and time diffusion-dispersion characteristic parameters:

$$V_{diff} = \frac{\Delta}{\tau} = \frac{\sqrt{2E\tau}}{\tau} = \sqrt{\frac{2E}{\tau}} \qquad (3)$$

This leads to a definition for longitudinal dispersion Coefficient, E.

$$E = \frac{\phi^2 U_x^2 \tau}{2} \qquad (4)$$

Considering the classical Fick´s equation for concentration of tracer with a poured mass M, and Ah, cross section of tracer flow:

$$C(t) = \frac{M}{A_h \sqrt{4\,E\,t}} e^{-\frac{(X-U_x t)^2}{4\,E\,t}} \qquad (5)$$

There is a relationship between time as independent variable, t, and characteristic period, τ, defined by means of Poisson´s distribution applied to plume dynamics:

$$\beta = \frac{\tau}{t} \approx 0.215 \qquad (6)$$

Replacing equation (4) in equation (5) it stands a relationship containing discharge Q as the product $Ah*Ux$:

$$C(t) = \frac{M}{Q\,\phi\,t\sqrt{2\pi\beta}} e^{-\frac{(X-U_x t)^2}{2\,\beta\,\phi^2\,U_x^2\,t^2}} \qquad (7)$$

This is a new definition for plume transport in flows which takes into account for Galileo´s composition principle, and then describing properly real tracer plumes in flow. This model (smooth line) is shown in Figure 1 beside experimental curve (broken line).

RELATIONSHIP BETWEEN MASS TRANSPORT AND HYDRAULIC PARAMETERS

Either diffusion or dispersion may separate randomly two particles which are put together in an initial time. Figure 2 Then an incremental length δX is caused by a dispersive obstacle δY in a velocity field characterized by transversal gradient, in a characteristic time τ:

$$\delta X = \left(\frac{\partial u_x}{\partial Y} \right) \delta Y \, \tau \qquad (8)$$

Using classical definition for viscosity with a friction force *fr* and an application area *Aa* (in X-Z plane).

$$\left(\frac{\partial u_x}{\partial Y} \right) = \frac{f_r}{\eta \, A_a} \qquad (9)$$
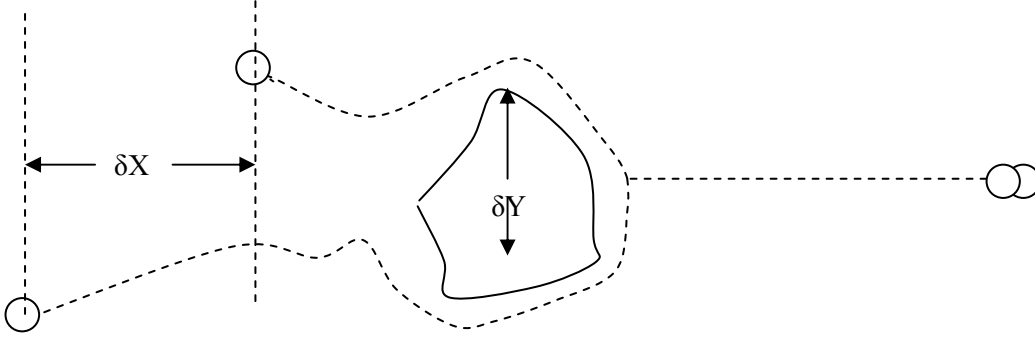

Fig. 2. Random separation of a pair of diffusive particles

It is necessary now to define Reynolds number in a general way as follows:

$$R_e = \frac{\frac{1}{2} m \, u_x^2}{f_r \, \delta X} \qquad (10)$$

Here *m* is the mass of fluid involved in the volume $Aa * \delta Y$. Then combining these relationships equation (8) remains as follow:

$$\delta X = \frac{m \, u_x^2 \, \delta Y \, \tau}{2 R_e \, \delta X \, \eta \, A_a} \qquad (11)$$

The density of water may be written as:

$$\rho = \frac{m}{A_a \, \delta Y} \qquad (12)$$

Involving *m* of equation (12) in equation (11), doing a rearrangement for δX and replacing dynamic viscosity for kinematic one it has:

$$\delta X^2 = \frac{\delta Y^2 u_x^2 \, \rho \, \tau}{2 R_e \, \eta} = \frac{\delta Y^2 u_x^2 \, \tau}{2 R_e \, \nu} \qquad (13)$$

Regarding the fractal nature of dispersion, microscopic level may be reflected easily with the same

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mathematical structure in macroscopic (human) scale. Then, a microscopic relationship which was stated initially for only two particles may be expanded for an entire ensemble of them (macroscopic view) in such a way that a proportion factor, θ, converts δX in a characteristic diffusion distance, Δ, and δY and τ in macroscopic averaged parameters. Then calculations until here were done in a mean time. New values are space averaged once tracer has filled uniformly the cross section of flow, i.e. in "complete mixing" condition. In this case, after this integration process, Ux, is the mean space value of velocity along cross section.

$$\Delta^2 = 2\left(\frac{\theta \, \delta Y^2 U_x^2}{4 R_e \nu}\right)\tau \tag{14}$$

This is an equation in the Smoluchwsky´s form for a one dimension diffusion (dispersion) process. Then consequently:

$$E = \frac{\theta \, \delta Y^2 U_x^2}{4 R_e \, \nu} \tag{15}$$

Now, using equation (4) it holds:

$$\frac{\theta \, \delta Y^2 U_x^2}{4 R_e \, \nu} = \frac{\phi^2 U_x^2 \, \tau}{2} \tag{16}$$

And then:

$$\theta = \frac{2 R_e \nu \, \phi^2 \, \tau}{\delta Y^2} \tag{17}$$

Using a well known specific definition for Reynolds number in streams, Nebrasov (1968):

$$R_e = \frac{4 \, R_h^{\frac{3}{2}} \, C_h \sqrt{S}}{\nu} \tag{18}$$

Replacing this in equation (17) it holds:

$$\theta = \frac{8 \, R_h^{\frac{3}{2}} \, \phi^2 \tau \, C_h \, \sqrt{S}}{\delta Y^2} \tag{19}$$

And this in equation (15), regarding also the Chezy´s equation (uniform flow) remains as follow:

$$E = \frac{2 \, R_h^{\frac{5}{2}} C_h^{\,3} S^{\frac{3}{2}} \phi^2 \, \tau}{R_e \nu} \tag{20}$$

This is an interesting value for longitudinal dispersion coefficient whereas put it as function of mass transport, hydraulic and geomorphodynamic parameters, not in statistical or semi empirical mode. Finally, clearing dynamic viscosity coefficient as function of hydraulic and mass transport parameters:

$$\eta = \left(\frac{2 R_h^{\frac{5}{2}} C_h^{3} S^{\frac{3}{2}} \tau \, \rho \, \phi^2}{R_e E} \right) \tag{21}$$

This equation will be used to define a Frenkel`s equivalent formula.

THE THERMODYNAMIC NATURE OF Φ FUNCTION AND ITS APPLICATION TO VISCOSITY EQUATION.

From classical thermodynamics it has the Gibbs –Helmholtz equation which relates *available* energy (enthalpy) *ΔH*, *useful* energy (free enthalpy) *ΔG* and entropy of an isobaric and isothermal system *ΔS*, which may be the feasible environment of development of tracer plume in streams.

$$\Delta G = \Delta H - T \Delta S \tag{22}$$

Considering a tracer as an ideal gas with low concentration condition, the following definition holds for an isothermal increment of entropy, and considering the relationship between volume and discharge:

$$\Delta S = R \, n \, Ln\left(\frac{V_f}{V_i} \right) = R \, n \, Ln\left(\frac{Q \, t}{V_i} \right) \tag{23}$$

Using equation (7) for peak condition and developing $\sqrt{2\pi\beta} \approx 1.16$:

$$\Delta S = R \, n \, Ln\left(\frac{M}{V_i \, C_p \, \phi \, 1.16} \right) \tag{24}$$

Knowing that mass of tracer *M* divided by initial volume *Vi* is initial concentration, *Ci,* it holds:

$$\Delta G = \Delta H - T\left\{ R \, n \, Ln\left(\frac{C_i}{C_p \, \phi \, 1.16} \right) \right\} \tag{25}$$

Clearing *Φ* is easy to see its thermodynamic nature:

$$\phi = \left(\frac{C_i}{C_p \, 1.16} \right) e^{-\frac{\Delta H - \Delta G}{n \, R \, T}} \tag{26}$$

Reordering the signs in exponent:

$$\phi = \left(\frac{C_i}{C_p 1.16} \right) e^{\frac{\Delta G - \Delta H}{nRT}} = \phi_0 \, e^{\frac{\Delta E}{nRT}} \tag{27}$$

Including this definition of *Φ* outside of parenthesis in equation (21) remains:

$$\eta = \left(\frac{2R_h^{\frac{5}{2}} C_h^{3} S^{\frac{3}{2}} \tau \, \rho}{R_e E} \right) \left(\phi_0^2 \, e^{\frac{2\Delta E}{nRT}} \right) \qquad (28)$$

Putting this definition in the Frenkel`s form:

$$\eta = \left(\frac{2R_h^{\frac{5}{2}} C_h^{3} S^{\frac{3}{2}} \tau \, \rho \, \phi_0^2}{R_e E} \right) \left(e^{\frac{2\Delta E}{nRT}} \right) \qquad (29)$$

The expression within first factor of right member may be named as A':

$$A' = \left(\frac{2R_h^{\frac{5}{2}} C_h^{3} S^{\frac{3}{2}} \tau \, \rho \, \phi_0^2}{R_e E} \right) \qquad (30)$$

The equation (29) is similar but not the same Frenkel´s classical definition (1) whereas the equivalent A' factor is calculated here by means of macroscopic (averaged) parameters. Some remarks should be state now about this equation. First: Frenkel did his definition in the laminar case where appears viscosity alone while equation (29) concerning both viscosity and turbulence actions. As was state before, viscosity is the last stage in the chain of energy transference in turbulence, and then finally heat dominates the whole picture. So there is no conceptual problem with this aspect. Second: Frenkel´s formula was stated using Boltzmann constant, k, rather than Universal gas constant, R. this means only that Frenkel´s view is about microscopic world while equation (28) is regarding human (macroscopic) level. This difference does not lead to a mistake whereas W and ΔE are energies defined also for these different worlds. In Frenkel´s picture a vibrating molecule of liquid which remains in a fixed position in a point of minimum energy may leave this place if thermal motions of neighbor molecules are sufficient to transfer kinetic energy greater than W. In the other level, tracer evolves spending the original formation energy progressively due to turbulence represented by $T\Delta S$ (Prigogine $et\ al$, 1998). It is important to note that exponential in equation (26) is time decaying function while in equation (29) is increasing due to the change in sign to allow writing it in the Frenkel´s form. This asymmetric view is coming from the fact that while Frenkel´s equation for viscosity is considering as an $inverse$ process for diffusion (or better $self\text{-}diffusion$) the equations of author follows the opposite direction starting from diffusion and ending in viscosity. This fact has to be taken into account in numerical calculations using equation (27) remembering that sign is actually opposite. A finally remark on factor two affecting ΔE in equation (29): which is not the exactly Frenkel´s form. It is easy to see that one may split Φ squared in two equal factors with exponent one, and putting one factor inside and left other outside, then is solved the subject.

APPLICATION OF DEVELOPED MODEL TO SOME NATURAL STREAMS

Following is presented two different experiments in which there is applied the equations devised in this paper. The verification procedure uses the fact that W and ΔE energies in both equations (1) and (29) should be convergent if these relationships are speaking of the same thing. Frenkel had established that W is in the range of 2400 - 10000 Cal/mol based on theoretical consideration of his model. So, if the author´s equation is congruent with current theory ΔE should be in the same range.

First experiment: measurements in a small channel.

It was done a tracer experiment in a small channel showed in Figure 3 with related data in Table 1.

Fig. 3. Small channel under study

Table 1. Experiment on channel data

Channel characteristics	Tracer characteristic
Name: "Chorro de plata" channel, Cali, Colombia	Type of tracer: NaCl
Reynolds number: 154000	Mass of tracer (M): 30 gr.
Density of water (ρ) at 27°C: Approx. 996Kg/m3	Peak concentration (Cp): 45.8 mgr/l
	Time of transport (t): 98.7 s.
Dynamic viscosity of water (η) at 27°C: Approx. $0.8 \times 10^{-3} N * s / m2$	Diffusion characteristic time (τ): 21.3 s.
Kinematic viscosity of water (v) at 27°C: Approx. 0.850×10^{-6} m2/s	Longitudinal Dispersion Coefficient (E): 0.12 m2/s
Length (X): 44 m.	Initial Volume of mix (Vi): 8 litters
Width (W): 0.206 m.	Initial concentration of mix (Ci): 3.75 g/l
Wet cross section (Ah): 0.0543 m2.	Asymmetry function (Φ): 0.237
Hydraulic Radius (Rh): 0.0748 m.	Asymmetry function module (Φo): 70.6
Slope (S): Approx. 0.4% (0.004)	Equivalent weight (1 mol of NaCl): 35.45g + 22.99=58.44 g
Mean velocity in stretch (Ux): 0.45 m/s	Number of moles of tracer (n): 0.513
Chezy Coefficient (Ch): Approx. $26\,m^{\frac{1}{2}} / s$	

Temperature(T): 27°C (300K)

Discharge (Q): 0.0245 m3/s.

The verification procedure is starting with basic equation (29) and then replacing values with experimental data.

$$\eta = \left(\frac{2 R_h^{\frac{5}{2}} C_h^{\ 3} S^{\frac{3}{2}} \tau \ \rho \ \phi_0^{\ 2}}{R_e E} \right) \left(e^{\frac{2\Delta E}{nRT}} \right)$$

Next step is to calculate A' factor:

$$A' = \left(\frac{2 R_h^{\frac{5}{2}} C_h^{\ 3} S^{\frac{3}{2}} \tau \ \rho \ \phi_0^2}{R_e E} \right) \approx \left(\frac{2 \times (0.0743)^{\frac{5}{2}} \times 26^3 \times (0.004)^{\frac{3}{2}} \times 21.3 \times 996 \times 70.6^2}{154000 \times 0.12} \right) = 77.5 \ N*s/m^2$$

Then the exponential factor is calculated:

$$e^{\frac{2\Delta E}{nRT}} = \frac{\eta}{A'} = \frac{0.8 \times 10^{-3}}{77.5} = 10.3 \times 10^{-6}$$

Clearing the ΔE energy, knowing that 1 Cal= 4.18 J.:

$$\Delta E = \frac{nRT}{2} Ln\left(\frac{\eta}{A'} \right) = \frac{0.513 \times 8.31 \times 300}{2} \times Ln\left(10.3 \times 10^{-6} \right) \approx -7343 \ J. = -1757 \ Cal$$

The minus sign is due to change of sign in equation (27). Omitting this math convention one may put the energy as a positive entity:

$$\Delta E(Cal \ per \ mol) \approx \frac{1757}{0.513} = 3425 \ Cal/mol$$

This value lies well within the expected range of 2400-10000 Cal/mol.

Second experiment: measurements in a large mountain river.

It was done also a tracer experiment in a large mountain river showed in Figure 4 with major rocks and meanders in its stretch.   Data in Table 2.

Fig. 4. Large mountain river under study

Table 2. Experiment on river data

River characteristic	Tracer characteristics
Name: "Palace" river, Popayan, Colombia	Type of tracer: NaCl
Reynolds Number: 2´951832	Mass of tracer (M): 6000 gr.
Density of water (ρ) at 27°C: Approx. 996Kg/m3	Peak concentration (Cp): 1.98 mgr/l
Dynamic viscosity of water (η) at 27°C: Approx. $0.8 \times 10^{-3} N * s / m2$	Time of transport (t): 722.5 s.
	Diffusion characteristic time (τ): 156 s.
Kinematic viscosity of water (v) at 27°C: Approx. 0.850×10^{-6} m2/s	Longitudinal Dispersion Coefficient (E): 6.4 m2/s
Length (X): 500 m.	Initial Volume of mix (Vi): 22 litters
Width (W): 12 m.	Initial concentration of mix (Ci): 273 g/l
Wet cross section (Ah): 12.8 m2.	Asymmetry function (Φ): 0.41
Hydraulic Radius (R): 0.905 m.	Asymmetry function module (Φo): 118742
Slope (S): Approx. 0.00032	Equivalent weight (1 mol of NaCl): 35.45g + 22.99=58.44 g
Mean velocity in stretch (Ux): 0.692 m/s	Number of moles of tracer (n): 102.6
Chezy Coefficient (Ch): Approx. $40.7 m^{\frac{1}{2}} / s$	
Temperature(T): 27°C (300K)	

Discharge (Q): 8.9 m3/s.	

The verification procedure is starting with basic equation (29) and then replacing values with experimental data.

$$\eta = \left(\frac{2R_h^{\frac{5}{2}} C_h^{\;3} S^{\frac{3}{2}} \tau \; \rho \; \phi_0^{\;2}}{R_e E} \right) \left(e^{\frac{2\Delta E}{nRT}} \right)$$

Next step is to calculate A' factor:

$$A' = \left(\frac{2R_h^{\frac{5}{2}} C_h^{\;3} S^{\frac{3}{2}} \tau \; \rho \; \phi_0^{\;2}}{R_e E} \right) \approx \left(\frac{2 \times (0.905)^{\frac{5}{2}} \times 40.7^3 \times (0.00032)^{\frac{3}{2}} \times 156 \times 996 \times 118742^2}{2'951832 \times 6.4} \right) = 6.97 \times 10^7 \; N*s/m^2$$

Then the exponential factor is calculated:

$$e^{\frac{2\Delta E}{nRT}} = \frac{\eta}{A'} = \frac{0.8 \times 10^{-3}}{6.97 \times 10^7} = 1.15 \times 10^{-11}$$

Clearing the ΔE energy, knowing that 1 Cal= 4.18 J:

$$\Delta E = \frac{nRT}{2} Ln\left(\frac{\eta}{A'} \right) = \frac{102.6 \times 8.31 \times 300}{2} \times Ln\left(1.15 \times 10^{-11} \right) \approx -3222853 \; J. = -771018 \; Cal$$

The minus sign is due to change of sign in equation (27). Omitting this math convention one may put the energy as a positive entity:

$$\Delta E(Cal \; per \; mol) \approx \frac{771018}{102.6} = 7515 \; Cal/mol$$

This value lies well within the expected range of 2400-10000 Cal/mol.

CONCLUSIONS

1. – It is presented a new definition for dynamic viscosity starting from a mean flow velocity of stream which may be compared with formulation presented by J.I.Frenkel many years ago based on molecular considerations.

 2. - The proposed equation to calculate dynamic viscosity of water using macroscopic parameters of mass transport, hydraulics and geomorphology is applied to two experiments. It gives acceptable values for ΔE, equivalent to W in Frenkel´s formula, lying in the expected range of 2400-10000 Cal/mol.

3. - This new formulation may be applied to establish a complete set of information related with water knowledge, especially studies of dynamic contaminations in Mixing length and uniform flow condition.

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APPENDIX I. NOTATION

The following symbols were used:

Aa= Appl. area   A = Frenkel´s Coefficient for viscosity   Ah = Cross sectional area of flow

A´= Viscosity coeff. of new equation β= Ratio between τ and t   C(t) = Concentration

Cp = Peak concentration   Ci = Initial concentration   Cf = Final concentration   Ch= Chezy´s Coef.

ΔG=Free enthalpy   E= Longitudinal Dispersion Coef. ΔE= Energy gap of new viscosity equation

Q = Discharge   fr = resistance force Φ= Asymmetry function ΔH= Enthalpy

M= Tracer mass   m = Mass of a particle   n= number of moles η= dynamic viscosity Coef.

R= Gas Constant   Rh = Hydraulic radius   Re= Reynold´s number

ν= kinematic viscosity Coef.   S= Slope ρ = Water density τ= Diffusion char. time

Ux= Mean flow velocity   Vdiff = Diffusion velocity. Δ= Diffusion char. Length

W= Frenkel´s energy gap   K = Boltzmann Constant.   T = Absolute temperature   ux=inst. Vel.