Journal of Thermal Analysis and Calorimetry, Vol. 67 (2002) 239–248

MUTUAL INTERDEPENDENCE OF PARTITIONS FUNCTIONS IN VICINITY T_g OF TRANSITION*

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Abstract

The solid–liquid transition is described by use of the model incorporating the non-linear interactive oscillators. The individual non-linear oscillators are formed from the mechanical units of about the monomer size and produce the vibrations on the lower amplitude level, for the solid phase, either in amorphous or in crystal-like form. As the temperature starts to overpass the Vogel̍s temperature, the vibrations of individual units are big enough to cause the permanent displacements of the individual vibrating particles; the material starts to flow and the process of diffusion begins as well. As the temperature is passing through T_g vicinity, the large mechanical heterogeneity's start to appear as the small percentage of oscillators enlarge their amplitude of vibrations enormously and act as the local stress perturbations centers. These centers are responsible for the destruction of original matrixes and the sharp onset of fluidity and diffusion takes place. The upper amplitude of vibration motion is the basic property of a liquid state. The whole system of vibrations in matrix is described by use of techniques of deterministic chaos theories. It is shown as well, how the mutual interplay of the partition functions (vibration and cohesive), plays the important role in transition from liquid to solid states.

Keywords: diffusion, entropy, fluidity, glass transition, non-linearity, solid–liquid transition, temperature, theory, unharmonic oscillators, vacancies, vibrations

The vibration structures in condensed state and quantitative description of vacancies creation

The ensemble of on low amplitude vibrating particles can represent the glassy solids as well as the crystal like materials. It is assumed that the individual vibrating particles of about a monomer size [1] are localized in the non-linear potential valleys [2–4], where they perform the oscillations due to the energy of thermal motion:

$$U-U_0=\frac{1}{2}f\xi^2-\frac{1}{3}g\xi^3-\frac{1}{4}c\xi^4 \quad (1)$$

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[*] The major part of this paper was presented as Special Lecture at Solid State Chemistry Congress, September 3–8, Prague 2000, Book of Abstracts, p. 285–290, Eds P. Bezdička and T. Grygar, ISBN 80-238-5520-4

1418–2874/2002/ $ 5.00
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where U_0 is the basic level of internal energy, $\xi=r-r_0$ is the deviation from the equilibrium position and r_0 is defined as half of the distance separating the bottoms of two potential valleys. Only for solid state the bottom of r_0 has a constant position.

For the liquids r_0 has to be subjected to diffusion movements. It is assumed, that many vibrations inside of potential valley take place before the diffusion jump occurs.

Parameters f, g, c can be determined from the experiment based upon the values of specific heat c_v or thermal expansion coefficient α. On micro-level these parameters f, g, c depend mainly on the distances of closest neighbors in vicinity of particles considered.

$$c_V=k_B\left[1+\left(\frac{3c}{2f^2}+\frac{15g^2}{9f^3}\right)k_BT\right] \tag{2}$$

$$\alpha=\frac{1}{r_0}\frac{g}{f^2}k_B \tag{3}$$

It can be seen from Eqs (2) and (3) that the parameters f, g, c act selectively on the levels of the thermal expansion coefficient α or on the level of specific heat c_v [5]. The shape and character of non-linear valley depends on the separation of particles, in close vicinity of vibrating particle [2–4], however the solid state physics keeps the positions of particles, for the majority of cases, constant as the temperature rises and no diffusion changing the mutual particles position is permitted. (See the calculation of specific heat presented by Debye [6], for example).

The interactive non-linear system

To treat the transition of solid into the liquid state, we place the non-linear potential valley into the equation of motion:

$$m\frac{\delta^2\xi}{\delta t^2}+\frac{\delta U}{\delta\xi}=F_{ext} \tag{4}$$

where m is the mass of vibrating particle. F_{ext} represents the interactions of given particle with its vicinity and it will depend on level of vibrations, cohesive forces and mutual interactions of particles. The existence of acoustic waves of different wavelengths, in sense of Debye's theory, will guarantee the real existence of F_{ext}.

In general F_{ext} can be taken as a functional [7], of integrals over the moments I_{ph} and coordinates I_{cf}, which form the partition function Z:

$$F_{ext}=\Psi(I_{ph},I_{cf}) \tag{5}$$

Both integrals I_{ph}, I_{cf} are defined in relation to partition function Z:

$$Z=\frac{1}{(2\pi h)^{3N}}\frac{1}{N!}I_{ph}I_{cf} \tag{6}$$

and can be considered as mutually interdependent.

I_{ph} stands for the integral over the moments of particles ($mv=p$) in phase space:

$$I_{\mathrm{ph}}=\int...\int\int \exp-\left(\frac{\widetilde{K}(p)}{k_{\mathrm{B}}T}\right)...\mathrm{d}p_{1\mathrm{x}}\mathrm{d}p_{1\mathrm{y}}......\mathrm{d}p_{\mathrm{Nz}} \tag{7}$$

where

$$\widetilde{K}(p)=\frac{1}{2m}(p_{1\mathrm{x}}^2+p_{1\mathrm{y}}^2+......+p_{\mathrm{Nz}}^2) \tag{8}$$

and I_{cf} stands for:

$$I_{\mathrm{cf}}=\int...\int\int \exp-\left(\frac{U(q)}{k_{\mathrm{B}}T}\right)...\mathrm{d}x_1\mathrm{d}y_1\mathrm{d}z_1......\mathrm{d}x_{\mathrm{N}}\mathrm{d}y_{\mathrm{N}}\mathrm{d}z_{\mathrm{N}} \tag{9}$$

where

$$U(q)=\frac{1}{2}\sum_{\mathrm{i,j}}u(r_{\mathrm{ij}}) \tag{10}$$

$u(r_{\mathrm{ij}})$ represents the cohesive energy of mutual interactions of particle (i) and particle (j) and r_{ij} stands for the particles distance. For the solids the changes of I_{cf} are usually not considered because the individual vibrating units have constant positions in sample under investigation. In other words, for solids the thermal motion of individual particles is not strong enough to dislodge the individual vibrating units from their average position.

[In the following text we take as the solids the glasses under the Vogel's temperature T_{V} and the crystals under the melting point T_{m}. (The Vogel's temperature for polymers is about 52 K under T_{g} but for inorganic glasses this difference can be even larger)].

The bottom of potential valley keeps in solids the constant position relatively to placements of the particles in closest vicinity and all particles are forced to vibrate only on the lower amplitudes, characteristic of non-linear oscillators. The thermal expansion is considered to be connected usually only to homogeneous volumetric expansion and differentially small shifts in frequencies, according to law of Gruneissen [8].

For solids, the constants of *f, g, c* of Eq. (1), will depend on the average positions of particles forming the system. This is not the case for the liquid state, where the migration of particles or the switch to higher amplitudes (according to Figs 1 and 2, for minority of particles), are permitted.

The positions for the vibrating particles for liquids will eventually change in time, as the migration of particles occur, due to the process of diffusion. The parameters *f, g, c* appearing in Eqs (1)–(3) take the form:

$$\begin{aligned} f&=f_1[x_1(t),y_1(t),z_1(t),x_2(t),y_2(t)..........x_{\mathrm{n}}(t),y_{\mathrm{n}}(t),z_{\mathrm{n}}(t).........,F_{\mathrm{ext}}(T,t)]\\ g&=f_2[x_1(t),y_1(t),z_1(t),x_2(t),y_2(t)..........x_{\mathrm{n}}(t),y_{\mathrm{n}}(t),z_{\mathrm{n}}(t).........,F_{\mathrm{ext}}(T,t)]\\ c&=f_3[x_1(t),y_1(t),z_1(t),x_2(t),y_2(t)..........x_{\mathrm{n}}(t),y_{\mathrm{n}}(t),z_{\mathrm{n}}(t).........,F_{\mathrm{ext}}(T,t)] \end{aligned} \tag{11}$$

where f_1, f_2, f_3 are symbols of functional dependence and T is temperature.

The symbols x_1, x_2,..........z_n are the average coordinates of vibrating units of particles forming the system in vicinity of considered particle . For the solid state, and in lines of our model perception, we will assume that, for the low temperatures, the temperature dependent mutual interactive force F_{ext} is not big enough to cause the change in average positions of coordinates, x_1, x_2..........z_n and thus also the parameters *f, g, c* stay as constant. This can be assumed for the systems where all the forms of the diffusion are excluded. The non-existence of diffusion, forms the fundamental idea for c_v perception according to Debye [6] valid for crystals, or for amorphous phase according to Tarasov [9–12] and Wunderlich [13].

As temperature rises, the integral I_{ph} will increase and the average positions of particles in space x_1, y_1,..........x_j, y_j, z_j,..........x_p, y_p, z_p,..........z_n start to be function of

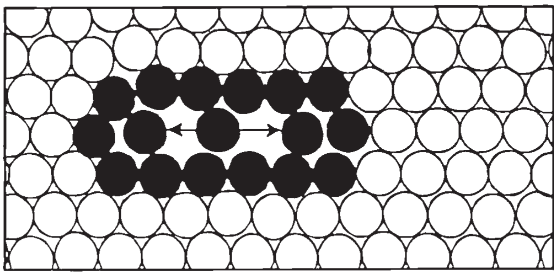


Fig. 1 A schematic picture of vacancy creation in liquid structure. The central particle is able to spatially displace the particles in its own vicinity and substantially enlarge vibration amplitude. The agitated spot will give a rise to entropy change $S=k_B \ln W_{semievap}$ according to Eq. (14)

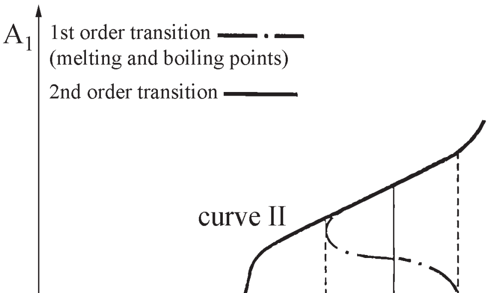


Fig. 2 A schematic view of amplitude rise, for strongly damped non-linear oscillator (curve II) as a function of temperature. The T_g area is characterized by very high viscosity and the amplitude enlargements will proceed according to Eqs (4) and (11) very slowly. Curve I shows the first order transition, such as T_m or T_b boiling points. The analogical, sudden amplitude enlargement and creation or annihilation of semi-evaporated spots in sense of Fig. 1 will proceed in liquid state

time $x_1(t)$,$y_2(t)$... etc. and the diffusion process starts to develop. The diffusion process can act selectively with temperature increase, affecting at low temperature some groups $x_j(t)$, $y_j(t)$, $z_j(t)$ only, then at higher temperature, other groups of particles can be involved as time dependent variable as well. The integral I_{ph} will cause, as the temperature is risen, the changes in structural arrangements of the system and can bring time related changes also into the integral I_{cf}. Through the rise of I_{ph} the system can be brought out of local 'frozen' non-equilibrium configuration eventually and can be heading to another coordinates characteristic of the situation closer toward the equilibrium [14]. This form of interaction is the physical base for the process of glass or crystal annealing, tempering or other forms of materials heat treatment restructuring.

For glasses the 'liberation' of individual groups can be made inside of 'isolated islands' of mobility (Johari–Goldstein β maximum [13, 14]) and does not have to involve the external coordinates, which define the sample external shape. For example, such movements, which can involve the rotational motion of individual groups will be, only mildly, or not at all, connected to the external coordinates defining the laboratory dimensions of sample under studies and thus they will not have strong impact on the thermal expansivity coefficient. Concerning glasses as the temperature rises and passes the Vogel's temperature all particles start to move and the diffusion process starts to take place. Within hours, days or years the external shape of sample will change above T_V as well. The upswing in the c_p value takes place at T_V and at T_g the coefficient α undergoes a step-wise change, too.

Under T_V in our model perception the rise in entropy is caused mainly by the vibration modes of entropy only, because as the particles are kept in constant positions and we consider solid state model only. The overall arrangement of particles in vibration levels will define the vibration part of entropy W_{th} [15] (Fig. 3). As it has been shown by Wunderlich [13], the number of particles associated with the boson peaks, tunneling states etc. is for many substances very small and thus, to the Vogel's temperature T_V, the specific heat c_v is almost the same for the crystals as is for the amorphous bodies. The entropy rise in amorphous bodies under T_V is thus connected mainly with the thermal (vibration) entropy rise. For the crystals, because the extra energy, connected to melting phase change is involved, the thermal entropy part plays the crucial role until the melting temperature T_m is reached. For temperatures $T \leq T_m$ (or $T \leq T_g$) we can write:

$$S \cong k_B \ln W_{th} \tag{12}$$

where, W_{th} is the probability connected with the arrangements of particles on different vibration levels of energy.

At the moment when special rearrangements start to play the important role (Fig. 4), the particles positions are changed during time, the another part of the entropy has to be added:

$$S = k_B \ln W_{th} + k_B \ln W_{conf} \tag{13}$$

where W_{conf} is connected with the overall amount of spatial particles displacements.

In many cases this term will be active at temperatures where the crystals are annealed and changes of the structural lattice take place, or for amorphous bodies above

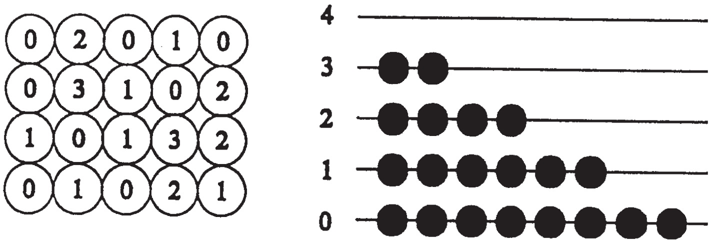


Fig. 3 A schematic picture of thermal (vibration) contribution of entropy. The individual particles (left) are localized at constant average positions in space and vibrate on different energy levels (right). The entropy $S=k_B\ln W_{th}$ is determined through the overall amount of particles arrangements on the different energies levels

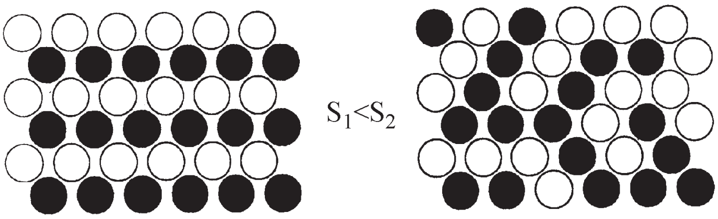


Fig. 4 A schematic view of configurational entropy enlargement $S=k_B\ln W_{cf}$, materialized through the spatial displacements

T_V and below T_g. In certain cases some exceptions can occur, too. For some systems the term W_{conf} can be very active even for temperatures smaller than 1 K. This is valid for crystals [16], as well as for amorphous bodies [17–19].

The mathematical treatment of strong non-linearity's above T_g transition

As the result of rising local expansions the system of Eqs (3) and (4) is strongly non-linear in mathematical sense and the solutions for such systems can be taken from determining chaos theories. According to theories of determining chaos [20–22] Eq. (4) will be prone to show up irregular amplitudes of vibrations with time. The substantial changes in vibration amplitudes can only develop, if the 'cracks' in solid matrix starts to appear. This is actually confirmed from experiments of positron annihilation spectroscopy-PASCA measurements [23–27] which shows that the huge voids start to develop in isolated places in amorphous state above T_V. This voids reach the level larger than 100 Å^3 above T_g. The changes in parameters f, g, c do not have to have even continuous character in local spots. The local highly expansive spots characterized by hundred times larger coefficient of local expansion coefficient α will develop with the onset of liquid state above T_g. The same is valid for the amplitude of vibrations.

The strong non-linearity of Eqs (4) and (11) will mathematically justify the amplitude switch in localized spots (Figs 1 and 2), where the central particle is able to push aside the particles in its vicinity and create the highly expansive spot. Such highly expansive spots are responsible for the high expansion coefficients of liquids. The entropy contribution connected with the semi-evaporated state (Fig. 1), which is created inside the liquid system in vacant areas, can be eventually contemplated as well:

$$S = k_B[\ln W_{th} + \ln W_{conf} + \ln W_{semievap}] \tag{14}$$

Because the vacancies areas, thanks to the reports of PASCA experiments have a well defined size, (which is larger than the Van der Waales volume, but smaller than the critical volume of particles involved), we can estimate the change of enthalpy connected with the semi-evaporated state. It can be taken as the fraction of evaporation enthalpy ΔH_{evap}.

To take the $\Delta H_{semievap}=\Delta H_{evap}/n$, where '$n$' is about 2–4, will be in agreement with the PASCA experiments as well as with the Eyring's [28, 29] estimate on viscosity.

To find a fast solution of Eq. (4) and provide illustrative examples, which can be easily visualized, the second order differential Eq. (4) is usually turned into two separate first order differential equations. This procedure is usually performed in the determining chaos theories [30, 31] as well as in the studies of 'organized structures' [32], or in studies of non-equilibrium thermodynamics [33].

By choosing the variables $A_1 \equiv \xi$ and $A_2 \equiv \mathrm{d}\xi/\mathrm{d}t$ we can rewrite Eq. (4) into the forms [34, 35]:

$$\frac{\mathrm{d}A_1}{\mathrm{d}t} = \alpha_{11} A_1 + \alpha_{12} A_2 \tag{15}$$

$$\frac{\mathrm{d}A_2}{\mathrm{d}t} = \alpha_{21} A_1 + \alpha_{22} A_2 \tag{16}$$

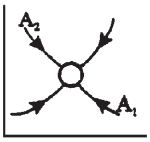
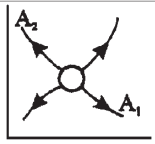
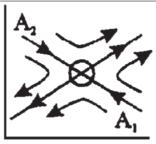
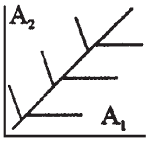
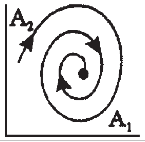
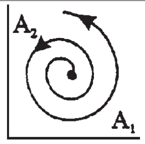
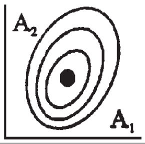
Equations (15) and (16) can be analyzed further in the vicinity of vibration stationary point. The system of Eqs (15) and (16), will have non-zero solution only if

$$\det\begin{vmatrix} \alpha_{11}-\lambda & \alpha_{12} \\ \alpha_{21} & \alpha_{22}-\lambda \end{vmatrix} = 0 = \lambda^2 + a_1\lambda + a_2$$

where $-a_1 = \alpha_{11} + \alpha_{22}$, $a_2 = \alpha_{11}\alpha_{22} + \alpha_{12}\alpha_{21}$.

The changes from a solid to a liquid state, as well as the other higher temperature transitions, can be investigated through the change of parameters a_1 and a_2 within certain range. The overall view of the interactions taken as dominating in given type of transition provides Table 1 [35].

Table 1 The dominant types of particles interactions for different phenomena in condensed and gas phases rising from Eqs (4) and (11) [35]. Different types of singular points

Shapes of trajectories	Name of singular point	Roots properties	Values of coefficients, a_1, a_2	Phenomenon
	stable node	real $\lambda_1<0$ $\lambda_2<0$	$a_1^2-4a_2>0$ $a_2>0$ $a_1>0$	fast condensation
	unstable node	real $\lambda_1>0$ $\lambda_2>0$	$a_1^2-4a_2>0$ $a_2>0$ $a_1<0$	situation above Boyle temp.
	saddle point	real $\lambda_1<0$ $\lambda_2>0$	$a_1^2-4a_2>0$ $a_2<0$ $a_1\neq0$	the area of critical point
	infinite amount of saddle points	real $\lambda_1=0$ $\lambda_2>0$ a) $\lambda_1<0$ b)	$a_1^2-4a_2>0$ $a_2=0$ $a_1\neq0$	the area of critical point
	stable focal point	complex $\mathrm{Re}(\lambda_1)<0$	$a_1^2-4a_2>0$ $a_2>0$ $a_1>0$	condensation
	unsteady focal point	complex $\mathrm{Re}(\lambda_1)>0$	$a_1^2-4a_2>0$ $a_2>0$ $a_1<0$	sublimation
	stable oscillations	complex $\mathrm{Re}(\lambda_1)=0$	$a_1^2-4a_2>0$ $a_2>0$ $a_1=0$	stable vibrations in condensed phase

The liquids show us the very interesting phenomena of local high level expansion in discrete points associated with internal surface enlargement due to the existence of vacancies. The existence of vacancies stems from the considerations of high non-linearity of Eqs (4) and (11). On the surfaces of vacancies the internal energy is always higher than in the bulk. So the liquid system represents the foamy like structure which enlarge its surface from inside. The vacancies are not empty voids, but are filled up with actively moving particles. In this way the higher transitions such as the boiling or critical point can be contemplated as well (Table 1). While only few vacancies exist (according to Bueche [36] the ratio of vacancies to vibrating particles is equal at T_g, 1:40) at lower temperatures, at the critical temperature the amount of vacancies reaches the level at which the condensed phase disintegrates completely [34] and all oscillating particles are able to reach the upper vibration amplitude with the addition of a very tiny amount of energy.

Conclusions

We have presented the coherent model, where the integral characteristic of cohesive forces I_{cf} is varied by increasing vibrations of mass units as temperature rises. The level of vibrations is characterized by the integral I_{ph} performed over the moments of individual particles. The increase in I_{ph} can act selectively at low temperatures, affecting few coordinates or few particles inside the sample only. As the temperature is further increased, the influence of I_{ph} on the I_{cf} will rise as well and more particles will be able to enter into the process of diffusion. Finally, the vibration units, forming the basic frame of the sample, will be involved in diffusion and material starts to flow. Not only T_g and T_m transitions, but all the higher transitions, such as the boiling and critical points, can be treated. Besides Eq. (11), which can serve for the best justification of rising non-linearity, there can be another explanation given for the cracks and voids developments stemming from perturbations of regular basic cohesive or repulsive forces. As the electrons are in general responsible for cohesive forces these electrons are perturbed by vibration moments of nucleuses and they can lose their bonding character at certain atoms. This is how melting and T_g transitions have been presented in the Lindemann [37] and Kanno's [38] theories. The theory just presented thus fits well into the general lines of melting theory of Lindemann, (where the vibration amplitudes of nucleuses takes about 25% of radiuses of electrons shells [39]), or [38], (where the amplitudes for T_g transition are smaller than at T_m, by factor of about 0.80). Looking back into Table 1, we can state, that at Boyle temperature the bonding electrons are 'panted out' to the level, that they completely loose their cohesive interaction ability and system behaves as ideal gas. The ability to cover all transitions within one conceptual theory seems to be the major contribution of the theory presented.

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The authors express thanks and gratitude to Academy of Sciences of Czech Republic for project financing. The grant A 401 0101 is specially acknowledged.

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