Sub-molecular dynamics in liquids and polymers

Hristo A Solunov
University of Plovdiv „P. Hilendarski”, 4000 Plovdiv, Bulgaria.
E-mail: solunov@uni-plovdiv.bg

Abstract. An extension of Adam-Gibbs theory at its molecular level is proposed. New relations, measuring the number of the configurations within the cooperatively rearranging regions, are found. By these relations the transformation of activated-hopping to free-diffusion dynamics can be observed as a measurement of the number of the sub-molecular dynamic units, known in the literature as “beads”. Two new methods for measuring the number of the beads in the molecules have been found. One of the methods used the thermodynamics results, and the second one used both the thermodynamics and relaxation ones. The measured number of beads in the twelve liquids is compared with the measuring by other theories. The evolution of the liquid state by measuring the number of the configurations within the cooperatively-rearranging regions is presented. With the suggested equations, the molecular level of Adam-Gibbs theory becomes a completed theory, permitting all molecular quantities, in the theory, to be measured by experimental results.

1. Introduction

1.1 Adam-Gibbs conception for cooperative molecular dynamics
One of the most successful approaches to dealing with the structural relaxation has been the Adam-Gibbs (AG) theory [1]. According to the theory the temperature dependence of the relaxation times $\tau(T)$ is determined by the probabilities of cooperative rearrangements. AG defined “a cooperatively rearranging region as a subsystem of the sample which, upon a sufficient fluctuation in energy, can rearrange into another configuration independently of its environment. The number of molecules or the (monomeric segments in the case of polymers) in such a cooperative region will be denoted by $z$.” The relation is

$$\tau(T) = A_G \exp \left( \frac{z^* \Delta \mu}{kT} \right), \quad (1)$$

where $A_G$ is a constant, $z^*$ is a critical lower limit size of cooperatively rearranging region (CRR), $\Delta \mu$ is largely the potential energy hindering the cooperative rearrangement per monomer segment, $k$ is Boltzmann constant and $T$ is temperature. AG expresses the critical size $z^*$ using the configuration entropy of this region

$$S^*_{cz} = \frac{\Delta S_{\mu}}{N_A} z^* = k ln 2, \quad (2)$$
where $\Delta S_\mu$ is molar configuration entropy and $N_A$ is Avogadro number. Inserting $z^*$ from equation (2) into equation (1) they obtain

$$
\tau = A_g \exp\left(\frac{c}{\Delta S_\mu}\right),
$$

where the constant

$$
C = N_A \Delta \mu ln 2.
$$

AG assume the number of the configurations in Boltzmann equation for $s_{\mu}^*$ to be $w^*_z=2$ in agreement of their conception for simultaneously surmounting the individual potential barriers by the molecules into the CRR.

It will be mentioned that AG theory has two levels a molecular given by equation (1) and a macroscopic one given by equation (3).

### 1.2. Wunderlich’s introduction of the sub-molecular units in the dynamics of liquids

By investigating a variety of the supercooled liquids Wunderlich [2] found that, if the molecules (or monomeric segments in polymer) are assumed as constructed by sub-units, named beads, the value of heat capacity differences between liquid and the glass $\Delta C_p(T_g)$ =11.3 J/(K mol of beads) appeared as „universal”, where $T_g$ is the glass-transition temperature. Wunderlich introduced empirical rules for estimating the number of beads in the molecules and units as -CH2-, -CH3, -CH4, or -O- are counted as beads. Wunderlich’s beads coincided with Bunn’s “chain units,” connected with “round rotation bonds” as one of the factors determining the melting temperature. Accepting the conception of the beads, Bestul and Chang [3] defined the “universal” rule for the configuration entropy $\Delta S(T_g)$ =2.9 J/(K mol of beads).

In an extended AG theory [4-6] the beads have been accepted as basic dynamics units, and on the basis of “universal” rules, the number of beads in the CRR at the $T_g$ has been estimated as 4 beads [4]. A method for measuring the number of beads in the molecules by investigating the pressure dependence of relaxation times has been obtained [5].

The theory of the random first-order transition [7] also accepts the beads as basic dynamic units in the liquids, and the entropy of fusion of a Lennar-Jones spherical bead at the melting point has been estimated as 13.8 J/K mol beads. In this way the ratio of the mol entropy $\Delta S_\mu(T_m)$ to this value, measured the number of beads in the molecules. Naturally this is an approximation method as the Lennar-Jones potential can be applied to a very close class of liquids.

An approach to measure the number of beads in the molecular liquids has been suggested by Moynhian and Angell [8]. In this bond lattice model of liquids, only one part of the $\Delta S_\mu$ curve was fitted by the estimated number of beads.

Until recently in an entropy theory [9], the chemical groups, are being used as the basic dynamic units. By reason of the huge mathematical complexity of the theory the calculation has been done for the polymers constructed by -CH-, -CH3- and -CH2 groups coinciding with the beads, naturally the results obtained confirm the majority of the results of the extended AG theory.

Although the importance of the identification the basic dynamics units in the molecular dynamics of liquids is great, till now only empirical rules, [2, 3] and approximated [7, 8] or time consuming [5] methods exist.

The aim of this study is to find methods for measuring the number of the basic configuration units in the molecule of liquids, directly from the extended AG theory. On the way to finding a solution of this task it was necessary to estimate the number of the configurations in the CRR. The relations for this number have been found.
2. Theory

2.1. Including the sub-molecular dynamic in the Adam-Gibbs theory
The extended AG theory has some common as well as some different issues, with AG one, discussed in [4-6]. As has been mentioned not the molecules but the beads have been accepted as basic dynamic units, and instead of the equation (2) the configuration entropy of the CRR is given by

$$ s_{cz} = \frac{\Delta S_{\mu}}{nN_A} z, $$

(5)

where $n$ is the number of the beads in the molecule, hence $n$ is a new parameter not exist in the original AG theory, measuring the configuration sub-units in the molecule. The number of the occupation states or the configurations in the CRR $w_z$ was not fixed

$$ s_{cz} = klnw_z. $$

(6)

From equations (5) and (6) we obtain

$$ Rlnw_z = \frac{\Delta S_{\mu}}{n} z. $$

(7)

2.2. Measuring the size of the CRR in the extended Adam-Gibbs theory
In the extended AG theory the size of the CRR has been found out by using the VTF equation for the temperature dependence of the relaxation times

$$ \tau(T) = A exp\left(\frac{B}{T-T_0}\right), $$

(8)

where $A$ and $B$ and the $T_0$ are empirical constants. In the extended AG theory an equation similar to the equation (1) is obtained with replacing $z^*$ with the most-probable size of the CRR in the system $z (T)$ and $\Delta\mu$ with the average potential barrier of the beads within this region. Looking in this way at the equation (1) it becomes equivalent to equation (8), both governing the most probable relaxation time and, thus, we obtain

$$ z(T) = \frac{T}{T-T_0}, $$

(9)

$$ \Delta\mu = kB, $$

(10)

and $A_g = A$. It was accepted and proved that equation (9) gives the number of beads in the CRR.

2.3. The number of configurations in the CRR
Coming back to equation (7) we realize that with the experimental values of $\Delta S_{\mu}$, $z(T)$, estimated by equation (9) and the empirical values of $n$, the number of configurations in the CRR $w_z$ can be measured. It has been done for different classes of liquids, and the specific constant for every liquid was obtained. It is interesting that the number of configurations per a bead in the CRR $w_z/z(T_g)$, as the average values, were obtained to be equal; for the alcohols it was 1.97, for the oxygen glass it was 1.9 and for the low molecular liquids $\approx2$ [6]. Having in mind these results, we assume

$$ w_z = 2z(T_g). $$

(11)
The equation (11), obtained, seems to be logical as every rearrangement by means of overcoming a potential barrier separates two equilibrium states, or, two conformations. On the other hand, as the $z(T)$ decreases with the increasing the temperature, while the $w_z$=constant, this means that part of the configurations are transformed into free-diffusion or non-activated $w_{zf}$ and

$$w_z = 2z(T_g) = 2z(T) + w_{zf}(T).$$

(12)

2.4. Measuring the number of the configuration beads in the molecules

From equations (7) and (11) it follows that

$$n = \frac{\Delta S_p(T_g)z(T)}{R\ln z(T_g)}.$$  

(13)

This is a general equation for measuring the number of the configuration beads in the molecules. From the relations in [6] it can also be presented as

$$n = \frac{\Delta C_p(T_g)T_g}{T_K R \ln z(T_g)},$$

(14)

where $T_K$ is Kauzman temperature excepted to be equal of $T_g$. Ties equation can be applied to $\Delta C_p(T_g)$ jump between the glass and the liquid for the non-crystallizing liquids, and to both the crystal and the liquid, as well as for the glass and liquid for one and the same substance. It will be mentioned that the configuration entropy, defined by AG, at present, is assumed as exceed entropy and is larger than the net configuration one, due to the vibration entropy difference between the liquid and the crystal [8-10]. Hence the measurement by equation (13) gives the number of beads or the degree of freedom according to the crystal, as is done in the other theories, while by using $\Delta C_p(T_g)$ between the glass and the liquid will eliminate the difference between the vibration entropies and, practically, the results will be then, corresponding to the net configuration entropy.

In the extended AG theory the constant $C$ in equation (3) is given by $C = Unlnw_z$ [6] where $U = N_A\Delta \mu = RB$ or $C = RBnlnw_z$. Hence, $n$ can be measured by

$$n = \frac{c}{BR\ln z(T_g)}.$$  

(15)

3. Application of the theory

3.1. Measuring the number of beads in the molecules of liquids by experimental results

In table I the thermodynamic results for the substances investigated in [8] are plotted. The majority of these liquids are also investigated in [7], and in this way, we can compare the measured values for $n$ on one and the same basis. The measured number of the beads is marked as; $n_e$ estimated by the empirical rules [11], $n_t$ by the thermodynamic method, suggested in this paper, $n_A$ by the excitation model [8], and $n_W$ by the first- order transition theory [7].

The first liquid in table 1 is 3-methylpentane, where in the third place in the molecule one -CH$_3$ group is attached to the backbone of it. All -C-C- bonds in the molecule are single, permitting rotation, and this is the reason why $n=6$ beads, as estimated in [11]. It will be mentioned that in the very similar molecule of 2-methy pentane, where in the same manner one -CH$_3$ group is attached in the second place in the molecule, $n=5$ has been assumed in [3]. As can be seen from the table I the beads, nearest to 5-6 numbers in this molecule, are measured by the method, suggested, in this paper. The same concerns for the second liquid 3–brompentane. In alcohols from Ethanol to Glycerol all methods find out an increase in the number of the beads with the increase the number of structural units. And again, the number of beads, measured by method, suggested in this paper, is closest to the
empirical values and the corresponding structure of the molecules.

In table 1 Toluene is the simplest molecule that comprises a phthalate ring. Privalko [11] estimated the phthalate ring as equivalent to three beads, and by adding -CH$_3$ group, the molecule of Toluene is estimated to behave, as such of 4 beads. In the following molecule Ethyl benzene one -CH$_2$ is added and the configurations then increase. The molecule of o-therphenyl is constructed by three phenyl rings and Privalko then assumed every ring to be valid to 3 beads. It should be mentioned that the central ring is attached by one bond to every one side ring, and is not equivalent to them. Generally, the effective beads of the given structural unit would depend on the way it is attached or interacted with the nearest structural units. It is interesting that the number of beads measured for the o-therphenyl by the method, suggested in this study, practically coincides with the number, measured by means of the relaxation volume of a bead $n=6.5$ [5]. For Se and ZnCl$_2$ a very close number is estimated by all methods. As is can be seen from table 1 in the simplest case the beads coincided with the structural units but in general they are different.

For the 3-brompentane in [10] AG constant $C=79.6$ kJ/mol has been measured and in [13] the VTF constant $B=861.2$ K, and using $z(T_g)$ from table 1 by equation (15) we obtain $n=5.1$ beads.

From the $\Delta C_p (T_g)=72$ J/mol K between glass and liquid [14] and the data for 3-brompentane in table 1 by the equation (14) we then measured $n=5.1$ beads.

3.2. Transformation of the activated-hopping to free-diffusion dynamics

In figure1 the evolution of liquid dynamics measured by the number of the configuration in the 3-brompentane is plotted. It is assumed at $T_g$ dynamics to be 100 % activated (for the most probable CRR) and with increasing the temperature this dynamics is continuously transformed in the free-diffusion one. At the crossover temperature $T_c$ of the mode-coupling-theory (MCT) the free-diffusion

| Substances | $T_m$ K | $T_g$ K | $T_k$ K | $\Delta S_g (T_m)$ | $\hat{z}(T_g)$ | $n_e$ | $n_r$ | $n_A$ | $n_W$ |
|------------|---------|---------|---------|-----------------|----------------|------|------|------|------|
| 3-methylnpentane CH$_3$-CH$_2$-CHCH$_2$-CH$_2$-CH$_3$ | 110.3 | 77 | 35.6 | 48.10 | 3.6 | 6 | 5.9 | 3 | 3.5$^a$ |
| 3-brompentane CH$_3$-CH$_2$-CHBr-CH$_2$-CH$_3$ | 167.3 | 108 | 84.0 | 50.19 | 4.5 | - | 5.5 | 3 | 3.6 |
| Ethanol CH$_3$-CH$_2$-OH | 159 | 97 | 71.5 | 31.01 | 3.8 | 3 | 3.1 | 2 | 2.3 |
| n-propanol CH$_2$-CH$_2$-CH$_2$-OH | 148.8 | 96.2 | 71.8 | 36.25 | 3.9 | 4 | 4.1 | 2 | 2.6 |
| Ethylene glycol HO-CH$_2$-CH$_2$-OH | 260.5 | 152.7 | 119.7 | 45.42 | 4.6 | - | 4.5 | 3 | 3.3 |
| 1,3 Propanediol HO-CH$_2$-CH$_2$-CH$_2$-OH | 248.2 | 145 | 108.6 | 52.16 | 4.0 | - | 5.4 | 6 | 3.7 |
| Glycerol HO-CH$_2$-CH$_2$OH | 291 | 190 | 136.7 | 62.8 | 2.6 | 6 | 8.7 | 7 | 4.5 |
| Toluene C$_6$H$_5$-CH$_3$ | 172.2 | 117 | 99.9 | 37.25 | 6.8 | 4 | 3.9 | 1 | 2.7 |
| Ethyl benzene C$_6$H$_5$-CH$_2$-CH$_3$ | 188.1 | 115 | 89.4 | 51.47 | 4.5 | 5 | 5.7 | 3 | 3.7$^a$ |
| o-therphenyl C$_{18}$H$_{14}$ | 329.4 | 246 | 204.1 | 52.2 | 5.9 | 9 | 6.7 | 2 | 3.8$^a$ |
| Se | 494.3 | 304 | 210.7 | 12.46 | 3.3 | - | 1.4 | 1 | 0.9 |
| ZnCl$_2$ | 591$^b$ | 380 | 250 | 17.32 | 2.9 | 1 | 2 | - | 1.2 |

$^a$ The liquids not investigated in [9], measured by the method in the same reference.

$^b$ The data from [12] and [14].
dynamics became 48% and at $T_m$ it is equal to 55% from the total dynamics. For the 3-brompentane the $T_c=140$ K. According the MCT at $T_c$ a crossing from the activation-hopping to the free-diffusion dynamics occurs. Hence the result in figure 1 may be accepted to demonstrate such a behavior. It will be mention that above transformation depends on the fragility of the liquids [15].

4. Conclusions
On the basis of extended AG theory a detailed dynamics in liquids emerges. The repeated units, the molecules in liquids or the monomeric segments in polymers, in dynamics break dawn to configuration beads. In the simplest case the beads coincided with the structural units (the chemical groups, the ions and the atoms) but, in general, they are different. During the relaxation time several beads are rearranging forming the cooperatively rearranging regions. The cooperatively rearranging regions can be smaller or larger than the molecules. At the glass transition temperature all rearrangements in the cooperative rearranging regions are activated-hooping. With increasing the temperature, above the glass-transition, the activated-hooping configurations are transformed in free-diffusing ones. At the melting temperature approximately half of the configurations are activated-hooping while the other half are free-diffusion ones.

References
[1] Adam G and Gibbs J 1965 J. Chem. Phys. 43 139
[2] Wunderlich B 1960 J. Phys. Chem. 64 1052
[3] Bestul B A and Chang S S 1964 J. Chem. Phys. 40 373
[4] Solunov Ch 1999 Eur. Polymer J. 35 1543
[5] Solunov H (Ch) 2002 J. Phys. Condense Matter 14 7297
[6] Solunov H (Ch) 2005 J. Optoelectronics and Advanced Materials 7 365
[7] Stevenson J D and Wolynes P G 2005 J. Phys. Chem. B 109 15093
[8] Moynihan T and Angell C A 2000 J. Non-Cryst. Solids 274 131
[9] Dudowich J, Douglas F and Freed F 2014 J. Chem. Phys. 141 234903
[10] Takahara S, Yamamuro O and Matsuto T 1995 J. Phys. Chem. 99 9589
[11] Privalko V P 1980 J. Phys. Chem. 84 3307
[12] Angell C A 1997 J. Res. Natl. Inst. Stand. Technol. 102 171
[13] Richert R and Angell C A 1998 J. Chem. Phys. 108 901
[14] Wang L M Angell A C and Richert R 2006 J. Chem. Phys. 125 074505
[15] Solunov H (Ch) 2006 J. Non-Cryst. Solids 352 4871