

THERMODYNAMIC FUNCTIONS AND MOLECULAR STRUCTURE OF GLASS-FORMING LIQUIDS

Hristo Solunov

*Received on April 3, 2023
Presented by A. Petrov, Member of BAS, on April 25, 2023*

Abstract

In cooperative molecular dynamics, the molecules of the glass-forming liquids are partitioned to sub-molecular units named “beads”. The beads have been empirically defined. Recently, a method for measuring the beads has been suggested. In this method the difference between entropy of the liquid and the crystal, known as excess entropy, has been used. Here, it is found that all other thermodynamic quantities are functions of the number of beads in the molecules, and their number can be measured from each of them. A subject of special interest is to measure the number of beads from the difference in the heat capacity between the liquid and the crystal, and the liquid and the glass as the configuration and the vibrational components in the number of the beads, can be separated. In Adam–Gibbs, post Adam–Gibbs theories as well as the potential energy landscape paradigm the thermodynamic nature of the dynamical phenomena is being studied. From the obtained equations, transition in the opposite direction became possible, namely the thermodynamic functions can be estimated from the dynamic experiments, if the number of the beads in the molecules are known. The theory is examined from the experimental results of 3-bromopentane.

Key words: glass-transition, super cooled liquids, Adam–Gibbs theory, configuration entropy, thermodynamics

Introduction. In the last several decades an increasing interest in glass formation has been observed (for reviews see [1–4] and references therein). ADAM–GIBBS theory [5] is a core giving rise to new theories [6–8] and paradigm [1,9],

helping to go inside of the molecular origin of the glass formation. The success of the Adam–Gibbs theory is the relation of dynamical phenomena with thermodynamics by using configuration entropy, defined as difference between entropy of the liquid and the glass or the crystal. Adam–Gibbs theory is a phenomenological theory, and its original form is an object to criticism [2–4,6–8]. In the post Adam–Gibbs theory [6–8] the majority of the limitations of this theory have been overcome.

The base of Adam–Gibbs (AG) theory is the size of the cooperatively rearranging region (CRR), defined as the number of the molecules rearranging into another configuration by surmounting simultaneously their individual potential barriers. Adam and Gibbs do not provide a relation for the cooperatively rearranging regions only accepting the configuration entropy of the smallest region as a constant.

In an extension of the AG theory, temporarily named Molecular Entropy Theory (MET) [6] an equation for the measuring the size of the (CRR) has been found and interpreted as the number of the beads rearranging during the relaxation time. The beads have been empirically defined [10]. A relation to measuring the partitioning of the molecules to the number of the beads has been suggested [11,12]. In the Random first order transition theory (RFOT) [3,7], the beads have also been accepted as base kinetical units, but due to uncertainty of their estimation in this theory, the last version avoids using them [3]. In General Entropy Theory (GET) [4,8], the beads are named “unaided atom groups” and empirical beads are also used in “four-point” susceptibility approach [2] and Gaussian excitations model [13]. The relation of MET with the later post Adam–Gibbs theories is discussed in [14].

In recent years, Potential Energy Landscape (PEL) [1,9,15,16] has become an active field to study connections between thermodynamic and the dynamical behaviour of glass-forming liquids. The evaluation of the number potential minima (inherent structures) as function of potential depth is a key factor opening the possibility for calculating the configurational entropy defined as the logarithm of the accessible minima. Hence in this way Adam–Gibbs theory is related to the statistics of the PEL. In [17] relation between parameter α determining maximal number of the minima in the empirical distribution functions and the size of the CRR, as well as fragility, has been found. In the equation for the parameter α as well as for the breadth of the distribution, the number of the beads in the molecules is also included. To apply the method of PEL to real molecules, a model of the molecule is needed [16]. With the intention of obtaining a successful model of the molecules of the liquids, knowledge of the number of beads seems to be obligatory.

The number of the structural units or the molecular groups have been assigned as the beads by empirical rules [10]. By measuring partitions of the molecules to the beads [12], it has been found that one and the same structural unit in different

classes of liquids or in the isomers, behaves in a different way. Hence the beads formation depends on the structure of the molecule and this finding allows to clarify the behaviour of the molecule structure in the dynamics of the liquids.

The Adam–Gibbs concept of the dynamic phenomena to be resolved on the thermodynamic base is followed in post Adam–Gibbs theory [6–8] as well as the PEL. In MET, in addition to this concept, transition in the opposed direction has been acquired, namely from the dynamics, the thermodynamic volume of a bead has been measured [18].

Bearing in mind the importance of measuring the partition of the molecules to the beads, the aim of this paper is to suggest new methods for measuring the beads as well as new relations in direction from dynamics to thermodynamics.

Theory. In the MET Hirai–Eiring quasi-lattice model of the liquid with occupied and free lattice place is assumed, but with a revision, the beads occupy the lattice place instead of the molecules. Hirai–Eiring named the free places “holes”. The fluctuation in free volumes with raising the temperature from below at the glass-transition temperature opens a hole large enough for a bead to overcome its barrier, jump into it and start the rearrangement. The same procedure is repeated several times, the beads rearrange bead by bead as each of them overcomes its individual potential barrier, practically statistically independent, and in this way, forming a cluster with the size $j(T)$ and average potential barrier u [6]. The relaxation time is given by

$$(1) \quad \tau(T) = \tau_0 \exp \left(\frac{j(T)u}{k_B T} \right),$$

where τ_0 is the vibration relaxation time, T is the temperature and k_B is the Boltzmann constant. This model provides advantage to form intramolecular clusters especially in organic liquids and polymers, where the chemical groups are fit together with the covalent bonds stronger, than London’s dissipation and dipole-dipole intra- and intermolecular interactions. Viscosity is related to tear up and recover the intermolecular interaction.

The temperature dependence of the relaxation time is given by the VTF empirical relation

$$(2) \quad \tau(T) = A \exp \left(\frac{B}{T - T_0} \right),$$

where A , B and T_0 are material constants. In comparing equations (1) and (2) one obtains

$$(3) \quad j(T) = \frac{T}{T - T_0}$$

and $u = k_B B$ and $\tau_0 = A$.

Adam and Gibbs defined configuration entropy with the equation

$$(4) \quad \Delta S_{\text{conf}} = \int_{T_2}^T \Delta C_p d \ln T',$$

where ΔC_p is the difference between the heat capacity of the supercooled liquid and glass and T_2 is a temperature at which configuration entropy vanishes in Gibbs and DiMarzio's theory. As the heat capacity of the glass can be measured only to the glass-transition temperature T_g , Adam and Gibbs accepted ΔC_p as a constant. This fact is an object of criticism to the theory and when configuration entropy is used, heat capacity of the glass is extrapolated, or model functions are used [20]. Many scientists used the excess entropy, where difference between heat capacity of the supercooled liquid and the crystal is used $\Delta C_{plcr}(T)$ and T_2 is replaced with Kauzmann temperature T_K [19,20]. Kauzmann's temperature is the intersect point of the extrapolated entropy of liquid with the entropy of the crystal [19,20]. In the last case, the difference between vibration entropy in the liquid and the crystal is neglected and $T_2 = T_K$ is assumed [19,20]. RICHERT and ANGELL [19] found that if the excess heat capacity follows hyperbolic low $\Delta C_{plcr}(T) = QT^{-1}$, where Q is a constant, the VTF temperature T_o is equal to the Kauzmann's temperature $T_0 = T_K$.

In the MET, the configuration entropy of the CRR is

$$(5) \quad s_{ccrr} = \frac{\Delta S(T)}{nN_A} j(T),$$

where $\Delta S(T)$ is configuration entropy of a mol molecules ($JK^{-1} \text{ mol}^{-1}$), $j(T)$ is the size of the CRR in units of bead, N_A is Avogadro number and n is the number of the beads in the molecule. In the Adam-Gibbs theory, the number of beads n is not present because they use the hard sphere model to model the liquid, whereas in MET all intramolecular configurations are accounted for by n .

According to the model of the cooperative molecular dynamic in MET at the glass-transition temperature, every bead overcomes its individual potential barrier and, in this way, creates a new configuration in the CRR. As every barrier separated two potential minima follows

$$(6) \quad w_j = 2j(T_g),$$

where w_j is the number of configurations in the cooperative cluster. Using Boltzmann equation for the configuration entropy of the CRR one obtains

$$(7) \quad s_{ccrr} = k_B \ln w_j = k_B \ln 2j(T_g).$$

Plugging this relation in (5) one obtains

$$(8) \quad \Delta S = nRj(T)^{-1} \ln 2j(T_g) = nR \ln 2j(T_g) \left(1 - \frac{T_0}{T}\right),$$

where R is the universal gas constant. The last equation has been used for measuring n [11,12]. From (4) and (8) one obtains

$$(9) \quad \Delta C_p = T \frac{d(\Delta S)}{dT} = \frac{nRT_0 \ln 2j(T_g)}{T},$$

and configuration enthalpy

$$(10) \quad \Delta H = nRT_0 \ln 2j(T_g) \ln \left(\frac{T}{T_g} \right).$$

The thermodynamic functions are summarized in Table 1.

T a b l e 1

Thermodynamic and statistical quantities as
function of number of the beads in the molecules.
Units J, K, mol

Quantity	Equation
ΔC_p	$nRT_0 \ln 2j(T_g)T^{-1}$
ΔH	$nRT_0 \ln 2j(T_g) \ln \left(\frac{T}{T_g} \right)$
ΔS	$nR \ln 2j(T_g) \left(1 - \frac{T_0}{T} \right)$
α^1	$n \ln 2j(T_g)$
$N_A \bar{\epsilon}^2$	$n2RT_0 \ln 2j(T_g)$

^{1,2}Parameters determining the number of the minima
and breadth of the hyperbolic distribution function [17]

As it can be seen from Table 1, all thermodynamic and statistical quantities are functions of the number of the beads in the molecules. Hence, from each one of these quantities n can be measured. Note that since $T_0 = T_K$ it becomes possible to obtain thermodynamic quantities from dynamic experiments (relaxation times, viscosity and diffusion), where the VTF equation is applied. Generally, this is possible if n is known.

Discussion of the experimental results. Prediction of the thermodynamic functions from the dynamic experiment per mol of the beads.

For the temperature dependence of dielectric relaxation times for 3-bromopentane Richert and Angell [19] obtain, $\log \tau(T) = -12.9 + 374.1(T - 82.9)^{-1}$. From the hyperbolic approximation for the excess entropy, they obtained $T_K = 82.5K$. Hence for 3-bromopentane practically $T_0 = T_K$. Defining T_g as temperature where $\tau(T_g) = 100 \text{ sec}$ from the above equation they estimated $T_g = 108 \text{ K}$. From equation (3) one obtains $j(T_g) = 4.3$ bead. Obtaining T_0 and $j(T_g)$ from the dynamic experiment one can predict (calculate) the thermodynamic and statistic function in Table 1 per bead where $n = 1$. For example, for the $\Delta C_{\text{bead}} = 1483.1 \text{ T}^{-1} \text{ JK}^{-1} \text{ mol bead}^{-1}$ is obtained.

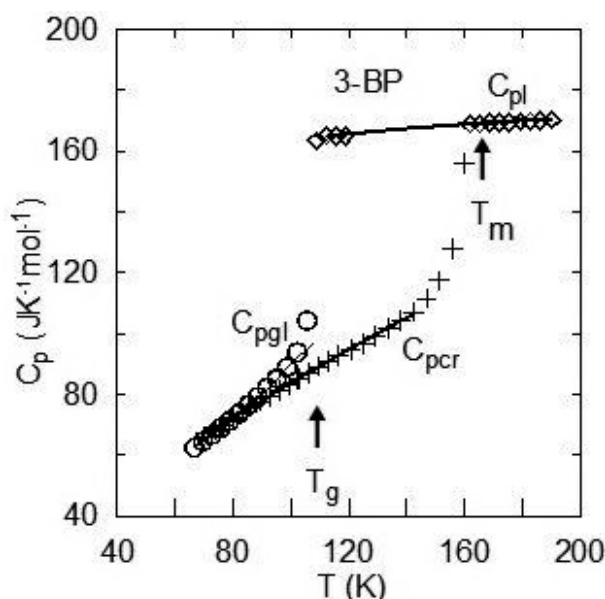


Fig. 1. Heat capacity of the liquid (rhombs), glass (circles) and crystal (crosses) of 3-bromopentane. The results are from [20]. The thickish lines are polynomials fits listed in Table 2 and the tin line is extrapolation the heat capacity of the glass to the glass transition temperature

Prediction of the thermodynamic functions from the dynamic experiment per mol of the molecules. To calculate thermodynamic function per mol of the molecules from that of the mol of the bead it is necessary to know the n . The simple way to estimate the number of beads in molecules is to use data for temperature and entropy of melting from a reference book and to divide entropy of melting by the entropy of a bead from (8) with $n = 1$. For 3-bromopentane enthalpy of melting is 8400 Jmol^{-1} at temperature of melting 167.3 K and entropy of melting $50.2 \text{ JK}^{-1}\text{mol}^{-1}$ [20]. From (8) for $n = 1$ $\Delta s_{\text{bead}}(167.3) = 9.03 \text{ JK}^{-1} \text{mol bead}^{-1}$ and in this way $n = 5.5$ beads and $\Delta C_{\text{pexc}} = 8.157T^{-1} \text{ kJK}^{-1}\text{mol}^{-1}$.

Prediction of the configurational thermodynamic functions. The measuring of the number of the beads from ΔC_{plgl} opens possibility with a good approximation the configuration thermodynamic function to be calculated. In Figure 1, the heat capacity of the liquid, glass, and crystal in the glass-transition range of the 3-bromopentane are shown.

The results obtained from the polynomials fit, in the temperature range used ΔT with the corresponding coefficient of the determination R_d are listed in Table 2.

From Table 2, one obtains $\Delta C_{\text{plg}}(T_g) = 66.97$, and $\Delta C_{\text{plcr}}(T_g) = 76.15 \text{ JK}^{-1}\text{mol}^{-1}$. The difference between excess and configuration heat capacity at

T a b l e 2

Temperature dependence of the heat capacities

Heat capacity	Equation $\text{JK}^{-1} \text{mol}^{-1}$	ΔT K	R_d
Liquid	$C_{pl} = 149.19 + 0.176T - 0.000344T^2$	112–190	0.9917
Glass	$C_{pg} = 35.76 + 0.1305T + 0.00406T^2$	66–88	0.99996
Crystal	$C_{pcr} = 19.47 + 0.7155T - 0.0007475T^2$	71–142	0.99997

T_g $9.18 \text{ JK}^{-1}\text{mol}^{-1}$ will be prescribed to vibration component in the first one. From (9) $\Delta C_{\text{bead}}(T_g = 108) = 13.73 \text{ JK}^{-1}\text{mol bead}^{-1}$. These results give the n from configuration heat capacity $n_{\text{conf}} = 4.9$ beads and from excess heat capacity $n_{\text{exc}} = 5.5$ beads. The obtained value for n from configuration heat capacity, practically coincided with the empirical assigned value for the number of the beads in the 3-bromopentane $n_e = 5$ beads.

In Figure 2 the configuration heat capacity per bead estimated from dynamic experiments (9) is shown.

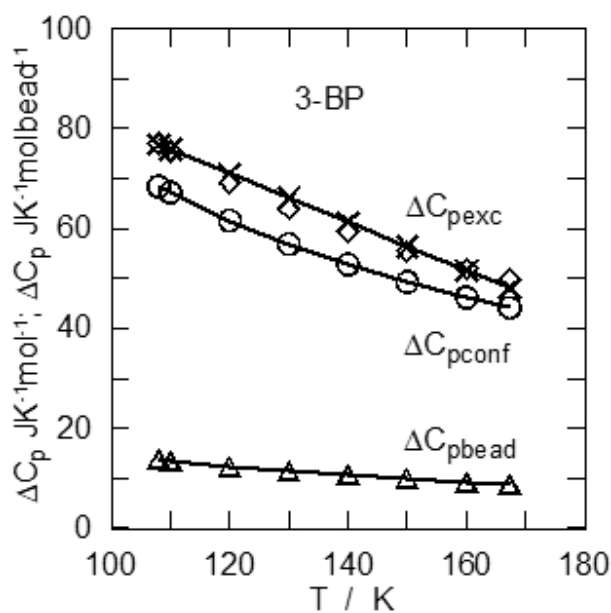


Fig. 2. The configuration heat capacity per bead obtained from dynamic experiment (triangles). The thermodynamic excess heat capacity from polynomials in Table 2 (x 's). The configuration (circles) and excess (rhombs) heat capacities per molecule predicted from that of the bead from dynamical experiment

Predicted the excess and configuration heat capacities per mol from this of the mol of bead, obtained from dynamics, in Fig. 2 are calculated by multiplying that of the bead correspondingly with 5.6 and 4.9 the number of the excess and the configuration bead in the molecule of 3-bromopentane. The excess capacity estimated from the polynomial fit in Table 2 is also given. Small difference in the predicted and measured excess capacities is observed since one can estimate excess heat capacity per mol from that per bead in the hyperbolic approximation, whereas the heat capacities in Table 2 were obtained by polynomial fit. The polynomial fit of the heat capacities is practiced in adiabatic and DSCs. The difference in both approximations is material dependent, and hyperbolic is accurate for many substances [19]. The estimated configuration heat capacity in Fig. 2 per molecule is “exact” configuration heat capacity corresponding to VTF equation and Adam–Gibbs theory.

Generally, a supercooled liquid is observed in the temperature domains close to glass transition and melting temperatures, as crystallization cannot be avoided in other temperature ranges as in Fig. 1. Similar behaviour is observed for the water. In this case, the heat capacity of the super cooled liquid can be estimated from the heat capacity of the crystal from the suggested procedure.

Conclusions. The number of beads in the molecules explicitly present in the thermodynamic and the parameters of the statistical functions of the glass-forming liquids and can be estimated from each of them.

An informative way to measure the partition of the molecules to the beads is from the difference of the heat capacity between the liquid and the crystal, and the liquid and the glass at the glass-transition temperature, as separation of the configuration and the vibration components is estimated.

The number of beads estimated from the difference between heat capacity of the super cooled liquid and the glass, corresponds to the Adam–Gibbs theory and VTF equation.

The thermodynamic and the statistical functions can be estimated from dynamic experiments if the number of beads in the molecule are known.

REFERENCES

- [1] SCIORTINO F. (2005) Potential energy landscape description of supercooled liquids and glasses, *J. Stat. Mech. Theory Exp.*, P05015.
- [2] BERTHIER L. et al. (2005) Direct experimental evidence of a growing length scale accompanying the glass transition, *Science*, **310**, 1797–1800.
- [3] LUBCHENKO V. (2015) Theory of the structural glass transition: a pedagogical review, *Adv. Phys.*, **64**, 283–443.
- [4] XU W.-S., J. F. DOUGLAS, Z.-Y. SUN (2021) Polymer glass formation: Role of activation free energy, configurational entropy, and collective motion, *Macromolecules*, **54**, 3001–3031.

- [5] ADAM G., J. H. GIBBS (1965) On the temperature dependence of cooperative relaxation properties in glass-forming liquids, *J. Chem. Phys.*, **43**, 139–146.
- [6] SOLUNOV C. (H). A. (1999) Cooperative molecular dynamics and strong/fragile behavior of polymers, *Eur. Polym. J.*, **35**, 1543–1556.
- [7] XIA X., P. G. WOLYNES (2000) Fragilities of liquids predicted from the random first order transition theory of glasses, *Proc. Natl. Acad. Sci. USA*, **97**, 2990–2994.
- [8] DUDOWIES J., K. F. FREED, J. E. DOUGLAS (2008) Generalized entropy theory of glass-formation, *Adv. Chem. Phys.*, **137**, 125–222.
- [9] DEBENEDETTI P. G., F. H. STILLINGER (2001) Supercooled liquids and the glass transition, *Nature London*, **410**, 259–267.
- [10] WUNDERLICH B. (1960) Study of the change in specific heat of monomeric and polymeric glasses during the glass transition, *J. Phys. Chem.*, **64**, 1052–1056.
- [11] SOLUNOV H. A. (2017) Partitioning of molecules of supercooled liquids to coarse grained configuration bead, *C. R. Acad. Bulg. Sci.*, **70**(7), 935–940.
- [12] SOLUNOV H. A. (2019) Relations between the sub-molecular and the cooperative scales in the molecular dynamics of the glass-forming liquids, *J. Non-Cryst. Solids*, **503–504**, 340–351.
- [13] MATYUSOV D. V., C. ANGELL (2007) Gaussian excitations model for glass-former dynamics and thermodynamics, *J. Chem. Phys.*, **126**, 094501–094519.
- [14] SOLUNOV H. (2019) On measuring the characteristic length of the cooperative molecular dynamics in the glass-forming liquids, *J. Phys.: Conf. Series*, **1186**, DOI 10.1088/1742-6596/1186/1/012008.
- [15] RUOCCO G., F. SCIORTINO et al. (2004) Landscapes and fragilities, *J. Chem. Phys.*, **120**, 1066–1080.
- [16] MOSSA S., E. LA NAVE, H. E. STANLEY, C. DONATI, F. SCIORTINO et al. (2002) Dynamics and configurational entropy in the Lewis–Wahnström model for supercooled orthoterphenyl, *Phys. Rev. E*, **65**, 041205-13.
- [17] SOLUNOV H. (2023) On the relation of the potential energy landscape and the cooperatively rearranging region, *J. Phys.: Conf. Ser.*, **2436**, 012030–012036.
- [18] SOLUNOV C. (H). A. (2002) The apparent activation energy and relaxation volume from the point of view of Adam–Gibbs theory, *J. Phys.: Condens. Matter.*, **14**, 7297–7310.
- [19] RICHERT R., C. A. ANGELL (1998) On the link between molecular dynamics and configuration entropy, *J. Chem. Phys.*, **108**, 9016–9026.
- [20] TAKAHARA S., O. YAMAMURO, T. MATSUO (1995) Calorimetric Study of 3-Bromopentane: Correlation between Structural Relaxation Time and Configurational Entropy, *J. Phys. Chem.*, **99**, 9589–9593.

Department of Physics and Technology
“Paisii Hilendarski” University of Plovdiv
24 Tsar Assen St
4000 Plovdiv, Bulgaria
e-mail: solunov@uni-plovdiv.bg