



On the temperature dependence of the Adam-Gibbs equation around the crossover region in the glass transition

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H I G H L I G H T S

- In the supercooled regime, a constant or a temperature dependent potential energy hindering the cooperative rearranging regions, appear depending on the region under study.
- The constancy of the energy term in the Adam-Gibbs equation depends on the temperature region it is studied, and on the assumptions made upon the calorimetric properties of the glassformer.

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The Adam-Gibbs equation has been used for more than five decades, and still a question remains unanswered on the temperature dependence of the chemical potential it includes. Nowadays, it is a well-known fact that in fragile glass formers, actually the behavior of the system depends on the temperature region it is being studied. Transport coefficients change due to the appearance of heterogeneity in the liquid as it is supercooled. Using the different forms for the logarithmic shift factor and the form of the configurational entropy, we evaluate this temperature dependence and present a discussion on our results.

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1. Introduction

The explanation of the phenomenology of the glass transition remains still nowadays an open issue in thermal physics, although it has been widely studied for many decades. Nevertheless, at present we do not have a totally accepted theory to explain its relaxational and calorimetric behaviors under different circumstances. One of the main characteristics of a liquid, when it is being supercooled, is that its viscosity grows strikingly fast as the temperature approaches the glass transition temperature T_g . In fact, a well known and generally accepted definition for the glass transition temperature, for the kind of glassformers herein considered, is the value at which the shear viscosity reaches 10^{13} poise.

As a supercooled liquid approaches the glass transition temperature T_g , it becomes largely heterogeneous. Its flow becomes highly sluggish and the diffusion of a given tracer is enhanced. The viscosity of the liquid presents different behaviors as the temperature is lowered. The existence of a crossover temperature T_c , between the glass transition and

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melting temperatures has been proven, both from experimental and theoretical points of view [1–29]. This temperature lies within the interval range $(1.15T_g, 1.28T_g)$. It is important to point out that, even the same notation is used in Mode Coupling Theory [30–33], it does not represent its theoretical critical temperature.

As far as the calorimetry of supercooled liquid, in 1948, Kauzmann [34] presents a first step towards a statistical physics model. Ten years later, Gibbs and di Marzio [35] present their model, where they consider the glass transition as an Ehrenfest second order phase transition. This last model prevails up to our days as a still good approximation even though the glass transition is not a phase transition [36]. They present calorimetric results on the configurational entropy and the key to evaluate heat capacities.

In 1965, Adam and Gibbs (AG) found a relationship between the temperature dependence of the viscosity of a supercooled liquid and its calorimetric properties through the statistical physics point of view of what they define as a cooperatively rearranging region (CRR) [37]. They proposed that the relaxation times or the viscosities of the system, in the glass transition vicinity, were related with the probabilities of cooperative rearrangements of molecules in a CRR, defined as a subsystem of the liquid, which upon a sufficient amount of energy, it may rearrange itself into another configuration. At these low among a great number of molecules and configurational degrees of freedom persist. In this sense, the thermodynamic description of the glassformer may be understood as configurational.

One of the main physical properties used to study the relaxation and transport processes in supercooled liquids is the Logarithmic Shift Factor defined as

$$\log a_T = \log \frac{\eta(T)}{\eta(T_s)} = \log \frac{\tau(T)}{\tau(T_s)} \quad (1)$$

where τ and η represent, respectively, the relaxation time of a given relaxation process and the viscosity of the supercooled liquid, and T_s is a reference temperature.

Glassformers may be considered, according to Angell's definition [38], as strong and fragile. Our study is focussed in the fragile glassformers.

In this kind of supercooled liquids, $\log a_T$, presented in Eq. (1), may be given by two widely used, physically and mathematically equivalent, phenomenological equations [39–41]. On one hand, the Vogel–Tammann–Fulcher (VFT) equation [42–44].

$$\log a_T = A - \frac{B}{T - T_0} \quad (2)$$

where A and B are temperature independent parameters and T_0 is defined as the temperature where the configurational entropy vanishes, the isoentropic temperature.

The other phenomenological relation is the Williams–Landel–Ferry (WLF) equation [45],

$$\log a_T = -\frac{C_1(T - T_s)}{C_2 + T - T_s} \quad (3)$$

In their original work, WLF chose the adequate reference temperature T_s for several glassformers, such that, the constants C_1 and C_2 had the same value for all the systems under study. Nowadays, the WLF is quite successful, but the values of the constants may be different for each supercooled liquid.

The AG work remains up to our days as a good model to begin with the study of the glass transition and glassy systems. Nonetheless, several questions remain still open on the evaluation of the configurational entropy, the behavior of the energy barrier, and the non-Arrhenius behavior of transport properties.

Several issues have been presented in the last few years on different aspects of the AG model. In their work, based on free volume theories, Adam and Gibbs [37] consider that the energy needed to attain a new configuration may be expressed in terms of the size, or number of molecules, of a rearranging of the size.

On one hand, instead, the Random First Order Transition Theory (RFOT) [46–49] considers its dependence namely depends on the length scale of a given region, that is, on the correlation length among a great number of unrelated stable configurations. In both cases there might be a connection between the size or length of the region with the heterogeneity as it will be discussed in the last section.

As far as the free volume is concerned, in the shoving model [50–52], sudden molecular rearrangements take place, and to attain them, molecules must *shove aside* their surrounding neighbors.

In a very complete work, Dudowicz, Freed and Douglas [53] present the strengths and weaknesses of both the original Gibbs di Marzio theory and the Adam Gibbs model. Although new experimental and simulation techniques give results that agree with the AG model, in the cases when it breaks down, the Generalized Entropy Theory [54–56] presents a new way to evaluate the configurational entropy and studies the variations in fragility for different glass formers.

An interesting application of all these ideas is the one performed by Schweizer and Saltzman in the case of glassy transitions in colloidal suspensions using the Ideal Mode Coupling Theory [57–60]

It is very important to notice that in all the new insights to deal with the study of the glass transition, specially in fragile glassformers, we still find the use of the Stickel's derivative method [6–10] and the fragility index introduced by Böhmer and Angell [61] in recent works of Sokolov, Novikov and co workers [62,63] to prove the feasibility of phenomenological results for super Arrhenius forms for the viscosity or relaxation times.

More than fifteen years ago, C. A. Angell [64] summarized what he considered ten key questions, that remain open, in the study of the behavior of glassformers in the neighborhood of the glass transition. In this work, we try to present an answer to the second one concerning the feasibility of the constancy of $2.303 \frac{\Delta\mu_c^*}{k_B}$ in the Adam-Gibbs equation, namely

“Why do structural glasses exhibit such a range of fragilities?”

where he mentions that “the constancy of this term is hardly to be expected”. This quote makes reference to the fact that a constancy of the chemical potential is hardly to be accepted. A non temperature dependent chemical potential in the AG equation is still an open issue [65–67].

The purpose of this work is to find the temperature dependence of the chemical potential introduced by Adam and Gibbs, in the complete range of temperatures of the glassformers between T_g and T_m . First of all, in Section 2, we present a brief summary of the AG theory. Then, in Section 3, we present our results to express the LSF in the two different temperature regions that will be used to express the AG equation. In Section 4 we present analytical expressions for ΔC_p which enable us to evaluate the configurational entropy. Finally, in Section 5, we present our results on the dependence of the chemical potential with temperature, depending on the region we are working on. Finally, we present some brief conclusions.

2. The Adam-Gibbs theory

Adam and Gibbs proposed a statistical physics model in order to relate $\log a_T$ with the calorimetric properties of different glassformers [37]. Since the supercooled liquid preserves only its configurational degree of freedom, all the thermodynamic properties they derive are only configurational.

The core of their theory lies in the fact that the viscosity or the relaxation times in kinetic experiments in supercooled liquids are determined in terms of the probability of rearrangements in what they define as “a cooperatively rearranging region”, i.e., a subsystem of the supercooled liquid, that, given a large enough fluctuation in energy, may rearrange itself into another configuration. The probability of a given rearrangement depends on the number of molecules z considered therein. They propose the partition function of the isothermal–isobaric ensemble to describe the probability of the relevant fluctuations as,

$$\Delta_c(z, P, T) = \sum_{E, V} w(z, E, V) \exp(-E/k_B T) \exp(-PV/k_B T) \quad (4)$$

where w is the degeneracy of the energy level E and volume V of the subsystem, and P and T represent the pressure and temperature, respectively, that allow a transition. We may evaluate the configurational Gibbs free energy as,

$$G_c = z\mu_c = -k_B T \ln \Delta_c \quad (5)$$

in terms of the configurational chemical potential $\Delta\mu$ that may be interpreted as the potential free energy that inhibits a rearrangement from taking place.

Thus, the probability of a rearrangement, $W(T)$, is given by

$$W(T) = A \exp(-z^* \Delta\mu/k_B T) \quad (6)$$

In Eq. (6), k_B is the Boltzmann’s constant and A represents the frequency factor which is independent on T and z . There is a critical lower value of the size of the CRR, z^* , for which the transition probability exists, and it is characterized by a critical configurational entropy s_c^*

$$z^* = \frac{N_A s_c^*}{S_c} \quad (7)$$

N_A is Avogadro number and represents the molar configurational entropy of the system. Thus, the average transition probability may be finally written as,

$$\bar{W}(T) = \bar{A} \exp\left(-\frac{\Delta\mu_s^*}{k_B T S_c}\right) \quad (8)$$

where, again, \bar{A} is temperature independent factor.

Since the relaxation time or the viscosity are related reciprocally with the transition probability, Eq. (8), one may write $\log a_T$, as,

$$\log a_T = \log \frac{\tau(T)}{\tau(T_s)} = \log \frac{\eta(T)}{\eta(T_s)} \propto \frac{1}{\bar{W}(T)} \quad (9)$$

with, T_s is a reference temperature. Therefore, using Eqs. (6)–(8), Eq. (9) may be written as,

$$-\log a_T = 2.303 \left(\frac{\Delta\mu_s^*}{k_B}\right) \left[\frac{1}{T_s S_c(T_s)} - \frac{1}{T S_c(T)}\right] \quad (10)$$

In Eq. (10), the configurational chemical potential $\Delta\mu$ is considered by AG as the potential free energy needed to attain the cooperative rearrangement per molecule, and it is considered as temperature independent. In their paper [37] they suggest that a detailed study would be published, but up to our knowledge, this publication was never accomplished. Depending on the interest of using Eq. (10), one may evaluate either the calorimetric or the relaxation properties.

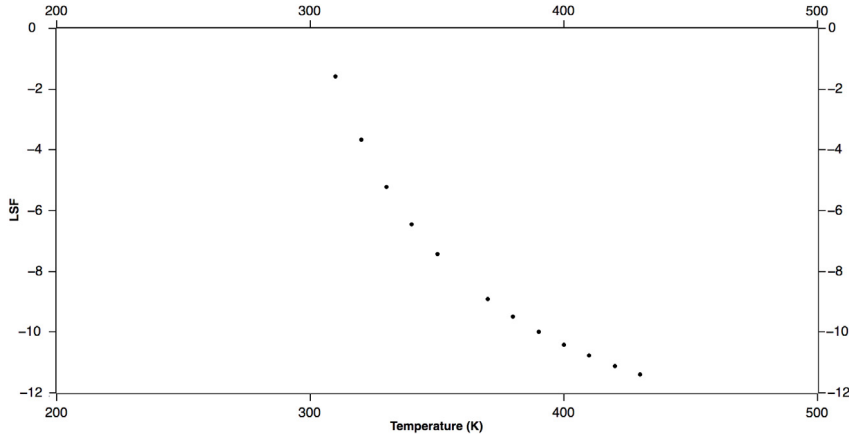


Fig. 1. Plot of the LSF vs. T for PVAc for temperatures from T_g to T_m .

Table 1

Values of m and b , given in Eq. (11), for the studied liquids for temperatures above T_c .

LIQUID	m	b
PIB	13.54	−13.54
PVAc	14.15	−18.54
PS	13.88	−14.54
PP	13.75	−17.52
OTP	13.14	−8.83
Salol	13.27	−15.48

3. The logarithmic shift factor

For almost three decades, highly precise experimental works have proven that neither $\log a_T$ may not be expressed as a VFT in the range of temperatures between T_g and T_m , nor, for temperatures below T_c , either the VFT or the WLF equations describe the temperature dependence of the viscosity on temperature [1–10,24–28]. Some authors have proposed that two VFT equations might be used to describe the behavior in the two intervals around T_c , but a very important issue to be considered is that the physical meaning of T_0 in the VFT equation, Eq. (2), corresponds to the isoentropic Kauzmann temperature T_K , thus it may not be considered as a fitting parameter [68–72].

We have worked with experimental values for fragile glassformers reported for salol and OTP (o-terphenyl) [6,7], and for the polymers PIB (polyisobutylene) [73–75], PVAc (polyvinyl acetate) [76], PS (polystyrene) [75,77–79], and PP (polypropylene) [80]. In Fig. 1, we show $\log a_T$ for supercooled PVAc in the temperature range from T_g to T_m . It is straightforward to notice that the logarithm changes its magnitude order in four, in the region between T_c and T_m that comprises 65 K, and how the order doubles to eight, from T_g and T_c , where 61 K lie.

This fact implies that the dependence of $\log a_T$ with temperature must be given by two different empirical forms, one for each temperature region. In previous works [81–84] we have found two expressions to represent the experimental values of $\log a_T$ for both intervals. In the case of temperatures above T_c , the WLF equation is still valid and it may be rewritten as,

$$\log a_T = m \left(\frac{T_g}{T} \right)^2 + b \quad (11)$$

For temperatures below T_c , we have seen that Eq. (11) is not valid, and the experimental values may be expressed in terms of the form,

$$\log a_T = D(T_A - T)^2 + E \quad (12)$$

As it may be appreciated, both Eqs. (11) and (12) are valid for many fragile glassformers [82]. In Tables 1 and 2, we show the parameters m , b , D , T_A and E of both equations for several fragile glassformers. We may see that the values of the parameters of both tables are given within the framework of the universality of $\log a_T$ in both regions [84]. As an example, in Figs. 2 and 3 we present both relations for PVAc.

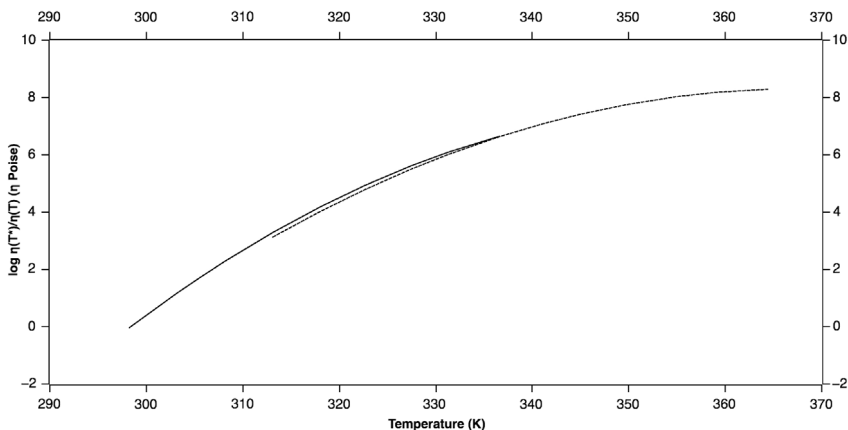


Fig. 2. Plot of the viscosity η vs. T for PDE. The dotted line corresponds to the VFT fit above T_c Eq. (2). The solid line represents the viscosity below this temperature, according to Eq. (12) [74].

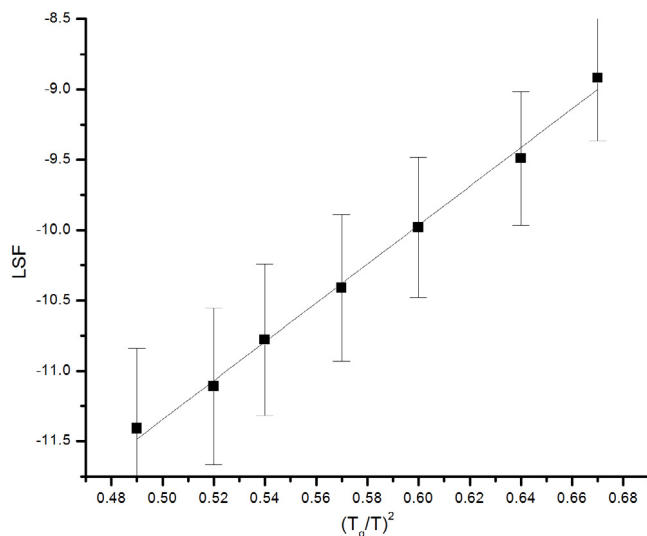


Fig. 3. Plot of the LSF vs. $\left(\frac{T_g}{T}\right)^2$ given by Eq. (11) with error bars of 5% for PVAc (■) for temperatures above T_c .

Table 2

Values of D , T_A and E , given in Eq. (12), for the studied liquids for temperatures below T_c .

LIQUID	D	T_A (K)	E
PIB	.0023	245.21	3.79
PVAc	.0023	365.69	7.86
PS	.0023	432.04	8.06
PP	.0023	317	8.17
OTP	.0023	319.46	10.30
Salol	.0023	291.64	8.48

4. The heat capacity and the configurational entropy

One of the main problems in thermodynamics is the evaluation of the entropy. Since in the case of fragile glassformers many experiments in calorimetry are continuously being performed, it is not difficult to find the data in literature.

We shall now calculate the configurational entropy that appears in the AG equation (10). In the first place, we need to have an analytical expression for the difference of the specific heats, ΔC_p . This difference is defined [85] by,

$$\Delta C_p = C_p^{liq} - C_p^{crys} \tag{13}$$

Table 3

Values of α and β , given in Eq. (14), for the studied liquids for temperatures above T_c .

LIQUID	α	β
PIB	44.06	-.10
PVAc	103.61	-.21
PS	76.05	-.12
PP	69.76	-.16
OTP	27.60	-.06
Salol	183.73	-.29

Table 4

Values of α' and β' , given in Eq. (14), for the studied liquids for temperatures below T_c .

LIQUID	α'	β'
PIB	34.65	-.06
PVAc	107.39	-.22
PS	96.62	-.17
PP	48.78	-.09
OTP	26.07	-.05
Salol	186.75	-.31

where C_p^{liq} and C_p^{crys} are respectively the specific heats of the supercooled liquid and the crystal phase. It is important to point out that the behavior of this difference is given, mainly, by the change of C_p^{liq} as temperature diminishes.

Using available data for both the specific heat of polymers, through from one of the most important databases, the ATHAS (Advanced Thermal Analysis System) [86], and corresponding data for fragile supercooled liquids [87–89], we may easily find that ΔC_p , may be expressed in terms of a linear equation, with different coefficients, in both $T < T_c$ and $T > T_c$ temperature regions, that is,

$$\Delta C_p = \alpha - \beta(T - T_g) \quad (14)$$

where the values of the coefficients α and β are given in Tables 3 and 4, respectively, for both regions.

Finally, we may evaluate the mathematical form for the configurational entropy, $S_c(T)$, through its definition.

$$S_c(T) = \Delta S_m + \int_{T_m}^T \frac{\Delta C_p}{T'} dT' \quad (15)$$

with ΔS_m the entropy in the melting point.

Using Eq. (14) for the forms for ΔC_p for both temperature regions, and solving the integral given in Eq. (15),

$$\begin{aligned} S_c(T) &= \Delta S_m - \int_T^{T^*} \frac{\alpha - \beta(T' - T_g)}{T'} dT' = \\ &= \Delta S_m - (\alpha + \beta T_g) \ln \left(\frac{T^*}{T} \right) + \beta(T^* - T) \end{aligned} \quad (16)$$

where T^* is the reference temperature to carry on the integration and has different values depending on the integration region, i.e., for $T > T_c$, $T^* = T_m$, and if $T < T_c$, $T^* = T_c$.

In Fig. 4, we may see the configurational entropy, Eq. (16), for PIB in the whole temperature region. The behavior of S_c , as temperature drops, is as we expected. The number of the CRR accessible configurations reduces as temperature decreases from T_m to T_c with a rate that is almost half of the corresponding one between T_c and T_g . This means that, as temperature diminishes towards the glass transition temperature, the possibilities of reaching a rearrangement fall with a larger rate towards the isoentropic temperature where the configurational entropy vanishes.

5. Results

In 1965, Adam and Gibbs made two important assumptions in order to obtain the value of the term $2.303 \frac{\Delta \mu_s^*}{k_B}$ in their equation, namely, Eq. (10).

On one hand, they calculate the configurational entropy, $S_c(T)$, considering that the difference of the specific heats, ΔC_p , Eq. (14), is constant. On the other hand, they propose that $\log a_T$ for their glassformers obeys the WLF equation, namely, Eq. (3).

Using these two last facts they obtain $2.303 \frac{\Delta \mu_s^*}{k_B}$ in terms of one of the WLF constants. Thus, they assess that the free energy barrier that needs to be surmounted in order to attain an arrangement within a CRR is temperature independent.

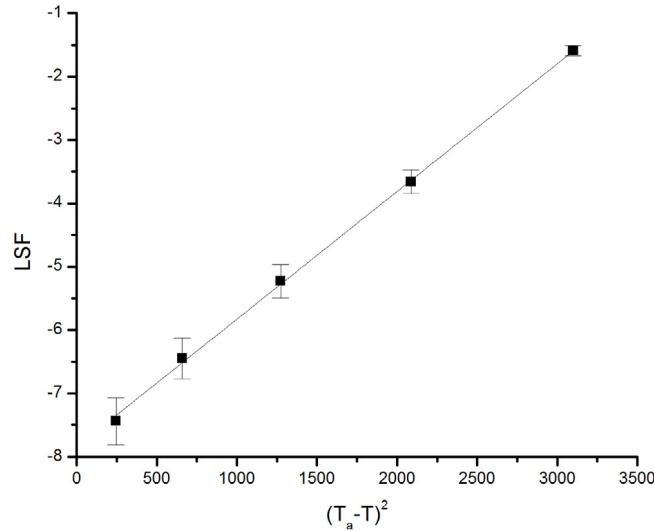


Fig. 4. Plot of the LSF vs. $(T_a - T)^2$ given by Eq. (12) with error bars of 5% for PVAc (■) for temperatures below T_c .

Table 5

The constant values of $\frac{2.303 \cdot \Delta\mu \cdot S_c^*}{k_B}$, given in Eq. (18), for the studied super-cooled liquids for temperatures above T_c .

LIQUID	$\frac{2.303 \cdot \Delta\mu \cdot S_c^*}{k_B}$ (J/mol)
PIB	107,223.12
PVAC	58,462.81
PS	78,810.05
PP	76,320.34
OTP	9,607.80
Salol	10,238.78

However, they left open the possibility that there might actually exist a dependence on temperature of the configurational chemical potential $\Delta\mu$ on Eq. (3) [37]

In this work, as we have presented above, neither the form for the logarithmic shift factor is the same in the temperature regions we are working with, nor ΔC_p is constant.

Thus, we analyze the temperature dependence of the Adam-Gibbs parameter in our two temperature ranges. Using Eq. (10), we may find that,

$$2.303 \frac{\Delta\mu S_c^*}{k_B} = \frac{\log a_T}{\left[\frac{1}{T_s S_c(T_g)} - \frac{1}{T S_c(T)} \right]} \quad (17)$$

In the case of temperatures that lie above T_c , using the expression for $\log a_T$ given by Eq. (11), we get,

$$2.303 \frac{\Delta\mu S_c^*}{k_B} = \frac{m \left(\frac{T_g}{T} \right)^2 + b}{\frac{1}{T_c S_c(T_c)} - \frac{1}{T S_c(T)}} \quad (18)$$

where S_c is given by Eq. (16), for temperatures in the same interval. If we plot $2.303 \frac{\Delta\mu S_c^*}{k_B}$ as a function of temperature, surprisingly, its value remains constant. The values of this constant energy are given in Table 5.

In the case of temperatures below T_c , $T_g > T > T_c$, we must take the fit proposed in Eq. (12) for the LSF and the configurational entropy, Eq. (16), for this case. Using these results, we may write,

$$2.303 \frac{\Delta\mu S_c^*}{k_B} = \frac{D(T_A - T)^2 + E}{\frac{1}{T_c S_c(T_c)} - \frac{1}{T S_c(T)}} \quad (19)$$

In Fig. 5 we present the plot of both the energies displayed in Eqs. (18) and (19) in the complete temperature region above T_g as a function of the variable $T - T_g$. This figure enables us to understand the core of our result in the whole temperature region.

Table 6

The linear form of $\frac{2.303 \cdot \Delta\mu_c^*}{k_B}$, given in Eq. (19), for the studied supercooled liquids for temperatures below T_c .

LIQUID	$\frac{2.303 \cdot \Delta\mu_c^*}{k_B}$ (J/mol)
PIB	$-411.19 \cdot T + 153,135$
PVAC	$-236.09 \cdot T + 125,935$
PS	$-534.87 \cdot T + 109,537$
PP	$-294.77 \cdot T + 98,018$
OTP	$-2,085.5 \cdot T + 100,333$
Salol	$-701.22 \cdot T + 42,896$

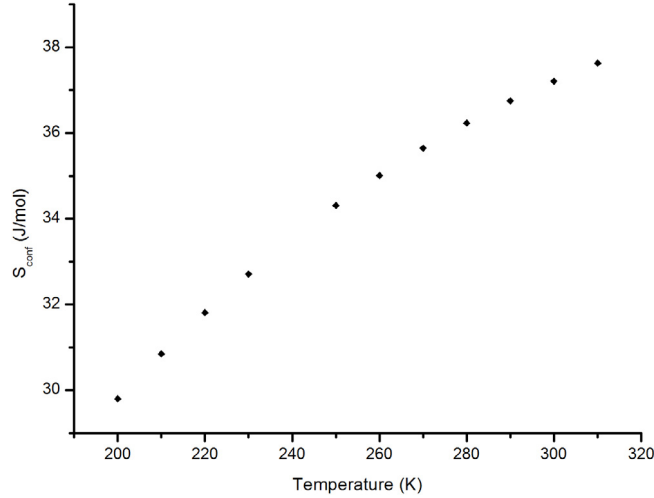


Fig. 5. Plot of the S_{conf} vs. T for PIB (♦) for temperatures from T_g to T_m .

In the case of temperatures above T_c , we may see how the part of the corresponding term $2.303 \frac{\Delta\mu_c^*}{k_B}$ as a function of temperature, remains constant for all our glassformers. This, of course, reproduces the original result [37], in the sense that the necessary energy needed to induce a rearrangement within a CRR is temperature independent. The values of this constant energy are given in Table 5.

Nonetheless, below T_c , this energy is clearly non constant and strongly temperature dependent and may be expressed in function of the linear form, namely,

$$2.303 \frac{\Delta\mu_c^*}{k_B} = LT + G \quad (20)$$

The values of the coefficients of Eq. (20) are given in Table 6.

It is important to point out that the dependence of $2.303 \frac{\Delta\mu_c^*}{k_B}$ with temperature, for $T < T_c$, does not depend on the mathematical representation of the graph that contains the experimental data of $\log a_T$, Fig. 1, in particular, whether it is, either or not, a VFT fit, namely, Eq. (11). In Fig. 6, the steepness of the curve representing $\log a_T$ in the interval comprised between T_g and T_c is visibly larger than the one for temperatures above T_c .

This last result takes us to a long time debate whether this term may be considered constant or not. This question has been open since Adam and Gibbs. Themselves, offered a future demonstration that $2.303 \frac{\Delta\mu_c^*}{k_B}$ was temperature independent [37], which was never published. This constancy has been debated for almost fifty years [90–114]. Several authors have insisted in the fact of the necessary dependence on temperature of this energy [69,115].

6. Discussion

As a supercooled glassforming liquid is cooled towards the glass transition temperature T_g , its dynamics becomes increasingly heterogeneous presenting magnified diffusion mechanisms. As it has been extensively revised in the literature [81–83,115–140], the Stokes–Einstein (SE) relationship between the diffusion coefficient D of a spherical tracer of radius a in a fluid whose viscosity is η , namely,

$$D = \frac{k_B T}{6\pi a \eta} \quad (21)$$

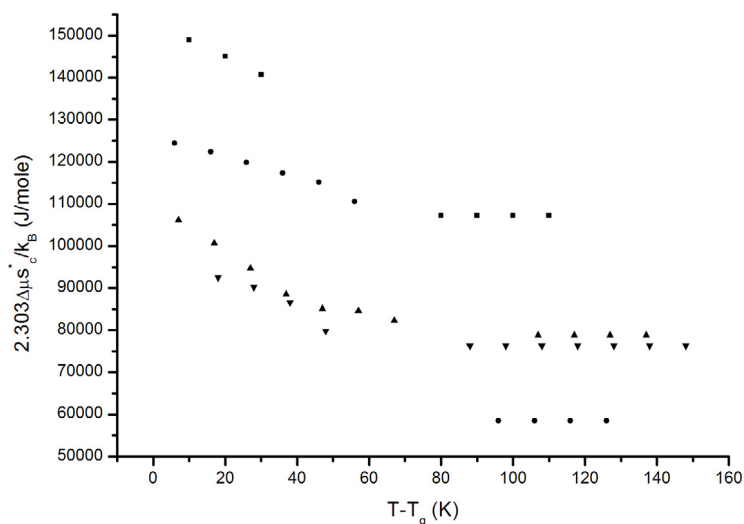


Fig. 6. Plot of $2.303 \frac{\Delta\mu_c^*}{k_B}$ vs. $(T - T_g)$ for temperatures from T_g to T_m . The four glassformers that are presented are PIB (■), PVAc (●), PS (▲) and PP (▼).

breaks down for temperatures below T_c and the diffusion process is enhanced. In this region the diffusion coefficient may be expressed in terms of the relation

$$D \sim \eta^{-\xi} \quad 0 < \xi < 1 \quad (22)$$

The temperature dependence of $2.303 \frac{\Delta\mu_c^*}{k_B}$ gives us a clue to understand the decoupling between the viscosity and the diffusion coefficient below T_c . As the supercooled liquid enhances its sluggishness, on one hand, the CRR need more energy to be able to change towards a given configuration. On the other hand, the viscous regime becomes more heterogeneous. This idea may be modeled as a “bottlenecking” [119] due to thermally activated excitations that permit rearrangements of groups of CRR. These thermal fluctuations appear due to the difference of the potential energy, mainly, the temperature dependent configurational chemical potential, which increases as temperature is lowered. Thus, the tracer takes advantage of this sluggishness and enhances its diffusion within the glassformer [81,82].

7. Conclusions

As it has been discussed, for more than five decades, the AG equation has been used for different types of materials including fragile glass forming liquids and polymers.

The Adam Gibbs equation relates three terms as we have discussed throughout this work, the logarithmic shift factor, the configurational entropy and the energy needed to surmount a given configuration of a cooperatively rearranging region. Nowadays, several issues remain open in the region below the temperature T_c .

We have developed this work in a trendline towards obtaining a result that may share some light on the prediction about the temperature dependence of the configurational chemical potential in this region, since this parameter in the AG equation cannot be determined by a theory or an experiment. As a first step, we have used earlier results on the form of $\log a_T$. Then, we have calculated the configurational entropy using experimental calorimetric measurements. Finally, we have obtained the temperature dependence of $2.303 \frac{\Delta\mu_c^*}{k_B}$, as it has been proposed by several authors.

The importance of this work relies on the possibility of interconnecting previous results on the Stokes–Einstein breakdown [81–84] and the thermodynamic cause of the thermal fluctuations that provoke this decoupling between both transport coefficients for supercooled glassformers in the region below T_c .

Acknowledgments

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