New scaling of Adam-Gibbs relation in glass-forming systems

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ABSTRACT

In this letter we introduced a new scaling method based on Adam-Gibbs model. Moreover, generalised critical-like expression of configurational entropy $S_C(T) = S_0 \left(1 - \frac{T_K}{T}\right)^n$ is used. Obtained values of pseudocritical exponent $n$ seem to be universal for studied systems and corresponds well with thermodynamic data. Relation between dynamic portrayal represented by primary relaxation time and thermodynamic (specific heat capacity) is in a good agreement.

In our last paper [1] we introduced a critical-like relation for configurational entropy. It based on calculations of specific heat capacities between supercooled liquid and glassy state. Parametrised relation may be expressed as follows:

$$S_C(T) = S_0 \left(1 - \frac{T_K}{T}\right)^n$$

(1)
where $S_0$ is an entropy of a liquid at high temperature, $T_K$ is a Kazumann temperature and $n$ is a pseudocritical exponent.

A characteristic feature of the configuration entropy $S_C(T)$ is its sharp decrease near the glass transition. This fact is associated with a certain "paradox" [2]. Assuming the outflow of kinetic effects, there is a limit to the possibility of reducing $T_g$, because at some point the extrapolated entropy of the liquid would be lower than the entropy of the crystal ($S_{\text{liq}} < S_{\text{cr}}$), which would lead to a negative configurational entropy of $S_C(T) < 0$. The above situation is physically incorrect, therefore the limiting value of the configuration entropy is the temperature $T(S_C = 0)$, called the temperature $T_0$ or the Kauzmann temperature $T_K$ [2-4]. The entropy crisis, or Kauzmann paradox, concerns precisely the negative value of the configuration entropy below $T_g$. It seems that the creation of glass is the solution to the above problem by supplying entropy to the system at the point of the glass transition and trapping it in the form of an amorphous state [5-9]. The entropy crisis provides us with one more very important information about the value of $T_g$. Well, for an arbitrarily slow cooling process, $T_K$ is the limit value $T_g, T_g \rightarrow T_K$ when $\dot{T} = 0$.

Assuming the cooperative nature of molecular reorientation in 1965, Adam and Gibbs (AG) noticed that the smallest size of cooperatively rearranging regions (CRR) should be defined by two different configuration states [5-9]. They defined CRR as the smallest volume that can change its configuration independently of adjacent areas. Moreover, based on the theory of critical phenomena [10-12], they determined that with a decrease in temperature, the size of the CRR correlation radius increases. Due to the activation energy is proportional to the CRR volume, i.e. $E_a \propto \xi_{\text{CRR}}^3$, Adam and Gibbs determined the relationship between the relaxation time and the number of molecules inside the cooperatively rearranged regions.
\[ \tau = \tau_{AG} \exp \left( \frac{A_{AG}}{TS_c(T)} \right) \]

(2)

where \( A \) is the energy barrier between the states, \( \tau_{AG} \) is the coefficient related to the high temperature dynamic region, and \( S_c(T) \) is the configuration entropy assuming that \( N(T) \sim S_c(T) \).

From a thermodynamic point of view, the configuration entropy can be related to the change in specific heat at the transition to the glass state \( \Delta C_p^g \). Assuming that \( \Delta C_p^g \approx A/T \) model leads directly to the VFT relation for the temperature dependence of the relaxation time. This allows the size of the cooperatively ordered regions to be estimated by the relation \( N(T) \sim [A(T - T_0)]^{-1} \), where \( T_0 \) is the temperature describing the ideal transition to the glass state.

Although the Adam-Gibbs model does not answer the overall size of the CRR at glass transition temperature \( T_g \), it has been extremely successful in many experimental fields because it easily combines dynamic and thermodynamic properties. Moreover, it partly explains the sharp increase in relaxation time during lowering the temperature and contributes to the description of the glass transition as being perfectly continuous. Therefore, the Adam-Gibbs model provides a good starting point for a critical-like description.

Fig. 1 shows the dependence of the relaxation time distribution on the temperature for all tested systems. Due to the primary relaxation process in the ultraviscous (supercooled) region, the typical Arrhenius behaviour does not occur.
According to the dynamic-thermodynamic description of the supercooled region, it is possible to substitute the generalized configuration entropy equation (1) to the Adam-Gibbs relation (2), which allows for the scaling procedure. However, one assumption should be made, namely that the Kauzmann temperature value was determined from the fit of the configuration entropy. The above procedure will allow to check whether during the analysis of dynamic data (primary relaxation time) it is possible to obtain the value of the exponent $n$ identical for the measurements of the specific heat capacity $c_p(T)$.

As a result of scaling, the following dependencies are obtained:

for $n = 1$

\[
\ln \left[ -T^2 \left( \frac{\partial \ln \tau(T)}{\partial T} \right) \right] = \ln A' - 2 \ln \left( \frac{T - T_K}{T} \right),
\]

(3)

and for $n \neq 1$

\[
\ln \left[ -T^2 \left( \frac{\partial \ln \tau(T)}{\partial T} \right) \right] = \ln A' + (-n - 1) \ln \left( \frac{T - T_K}{T} \right),
\]

(4)
Fig. 2 shows the performed scaling of the primary relaxation time described by the Adam-Gibbs equation (2) for the tested liquid crystal systems and glycerol. Because of linearisation, it was possible to determine the exponent \( n = b - 1 \) from the slope of the data. The obtained results are consistent with the values obtained on the basis of specific heat data with the accuracy of the error resulting from the numerical calculation methods. It is worth mentioning that this is the first attempt of this type to combine the dynamic description (relaxation time) and the thermodynamic description (configuration entropy) in glass-forming systems.

\[
\ln\left[-T^2\frac{\partial \ln \tau}{\partial T}\right] = \ln(1 - T_K/T)
\]

**Fig. 2** Scaling the Adam-Gibbs relation (1) by the use of critical-like configurational entropy expression (2).

Conclusions

- The description of the configuration entropy \( S_c(T) \) calculated from the specific heat capacity \( c_p(T) \) is possible using the critical-like relationship with the parameter \( n \) corresponding to the parameter value calculated on the basis of dynamic data (relaxation time) \([1,13]\), which allows for an accurate estimation of the Kauzmann temperature. The parameter \( n \) is related to the symmetry of the system.
- The scaling of the Adam-Gibbs relation allows to determine the dynamic parameter $\eta$ from the slope of the straight line, a value equals to that obtained from the thermodynamic data.

- The above conclusions suggest the thermodynamic nature of the transition to the glass state.

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