

Relationship between dynamical and equilibrium characteristics of glass-forming polymeric liquids

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(Received 8 March 2001; published 26 June 2001)

A connection between measurable equilibrium thermodynamic quantities and a nonequilibrium property of supercooled polymeric liquids, namely, the fragility index, is proposed within the framework of a synthesis of generalized configurational entropy models. The theoretical predictions are compared with experimental data on five glass-forming polymers.

DOI: 10.1103/PhysRevE.64.010501

PACS number(s): 61.41.+e

INTRODUCTION

Supercooled glass-forming polymer liquids have attracted immense interest in recent years, primarily due to their implications regarding the state of matter with unusual equilibrium and dynamical characteristics [1–3]. One phenomenon in question is that of an apparent correlation between entropy and relaxation time behavior that is unique to supercooled materials [1–3]. Continuation of the supercooled liquid to low temperatures reveals the eventual intersection of the liquid entropy with that of the crystal at a temperature specific to the particular supercooled polymer [1–3]. This temperature is dubbed the Kauzmann temperature. Since an event of this nature defies much of the intuitive logic behind entropy, as one would expect to observe lower entropy in a crystalline solid than in a liquid, the supercooled liquid phenomenon gives rise to the “Kauzmann paradox.” Other unique features of glass-forming liquids are the non-Arrhenius behavior of the relaxation time and its nonlinearity, namely, the stretched exponential relaxation of various measurable quantities [1–3].

The three canonical features of glass-forming liquids are in some form related to the fragility of said liquids. Given the significance of fragility in determining and describing the characteristics of glass-forming liquids, we propose in this Rapid Communication a relationship between macroscopic equilibrium thermodynamic quantities and the fragility index.

The organization of this paper is as follows. In the next section we briefly review a generalization of the configurational entropy models [2,4–6]. The fragility index for several supercooled polymeric liquids is then evaluated within the framework of a synthesis of Adam-Gibbs and the Gibbs-DiMarzio configurational models and compared with available experimental data.

CONFIGURATIONAL ENTROPY MODELS

In essence, the theoretical model generated by Adam-Gibbs seeks to describe relaxation of supercooled liquids in an isothermal-isobaric ensemble in terms of the notion of cooperative rearranging subsystems within the macroscopic

system [4(a)]. The growth of the cooperative domains is temperature-dependent, though configurational entropy and increases dramatically as the temperature of the system decreases [4(a)]. Renormalization group analysis has established that the critical size that allows cooperative rearrangement is, instead, inversely proportional to the total entropy $S(T)$ of the supercooled liquid at temperature T [4(c)]

$$z^*(T) \approx \frac{N_A s^*}{S(T)}, \quad (1)$$

where s^* is the critical entropy of the critical rearranging region, and N_A is Avogadro’s number.

The relaxation time for cooperative rearrangements is [4(b,c)]

$$\tau(T) = A \exp\{-[\Delta\mu s^*/k_B T S(T)]\}. \quad (2)$$

where A is a constant that is weakly temperature dependent, k_B is the Boltzmann’s constant, and $\Delta\mu$ is the change in chemical potential that permits rearrangement.

The Gibbs-DiMarzio model uses lattice-based polymer statistics to describe linear polymer molecules consisting of n_x polymers of x monomers each [5]. The configurational partition function is evaluated from an approximation to the total number of ways one can arrange n_0 holes, with $f_i n_x$ molecules of conformation i , on a lattice of $x n_x + n_0$ sites [5]. By taking into account contributions to the entropy coming from vibrational degrees of freedom, DiMarzio and Dowell find that the change in heat capacity under constant pressure is [6]

$$\Delta C_p = \chi_0/T^2 + \chi_1 T - \chi_2 T^2, \quad (3)$$

where χ_0 , χ_1 , and χ_2 are functions of molecular weight M_w of the polymer, the change of heat capacity just below the glass transition temperature T_g^- , $C_p(T_g^-)$, the change of thermal expansion $\Delta\alpha$ at the glass transition temperature, the flex energy ε/k_B , and the flex f : $f(T) = 2 \exp[-(\varepsilon/k_B T)] / [1 + 2 \exp[-(\varepsilon/k_B T)]]$.

The temperature dependence of the total entropy is

$$S(T) = S(T_2) + [\chi_0/T^2 T_2^2 - \chi_2] \{T - T_2\} \{T + T_2\} / 2 + \chi_1 (T - T_2). \quad (4)$$

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TABLE I. Literature values of various parameters for the glass-forming polymer liquids needed to theoretically evaluate the fragility index. Values given in the second and fourth rows are from Ref. [6]. Values given in the first, third, and fifth rows were obtained from Ref. [7], while those in the sixth through ninth rows were obtained from Refs. [4(a)] and [3]. The last row is the “effective” activation energy Q for various polymers from Ref. [8]. From Q one obtains the experimental fragility index as compiled in Table II. $\Delta C_V/R$ is the heat capacity at constant volume, $\Delta\alpha$ is change in thermal expansion at T_g , and C'_1 is the William-Landel-Ferry (WLF) parameter with T_s as the reference temperature.

	PVAc	PMMA(c)	PS	PVC	PIB
ϵ/k_B	532	660	842	595	455
M_w (g/mol) molecular weight	86	100	104	62.5	56
$\Delta\alpha$ (10^{-4} K $^{-1}$)	4.3	3.1	2.9	3.7	4.7
$C_P(T_g^-)$ (J/gm K)	1.45	1.7	1.49	1.14	1.13
$\Delta C_V/R$	0.57	0.57	0.75	0.57	0.74
C'_1	16.19	20.18	15.90	17.11	14.85
T_s (K)	351	435	418	396	243
T_g (K)	305	378	373	347	202
T_2 (K)	244	332	311	320	132
Q (kcal/mol)	134.9	246.5	238.4	307	42.3

For temperatures below the glass transition temperature, contributions to the total entropy come from the vibrational degrees of freedom [6]

$$S(T) = 3 \frac{R}{M_w} \left(\frac{X \exp(-X)}{1 - \exp(-X)} - \ln[1 - \exp(-X)] \right), \quad (5)$$

where $X = h\omega/2\pi k_B T$, ω is the oscillation frequency, R is the gas constant, and h is the Planck's constant. X is determined as described in Ref. [6].

RESULTS AND DISCUSSION

The fragility index m of five polymers polyvinyl acetate (PVAc), polymethyl methacrylate (PMMA), polyvinyl chloride (PVC), polystyrene (PS), and polyisobutylene (PIB) were evaluated from the relation [1]

$$m = \left(\frac{d \log \tau(T)}{d(T_g/T)} \right)_{T=T_g}. \quad (6)$$

Three approximations for the dependence of the relaxation time on entropy discussed above were employed to evaluate

TABLE II. Theoretical predictions of the fragility for five polymers are compared with experimental data.

	PVAc	PMMA(c)	PVC	PS	PIB
m_{AG}	88.7	176	228	103	49.8
m_{DD}	79	139	138	82.6	42.1
m_{DD}^C	86.7	175	224	101	42.7
Experimental values of m	96.5 ^a 101 ^b 95 ^c	142 ^a 172 ^b 160 ^c	193 ^a 281.6 ^b	93 ^b 139 ^c 127 ^c	45.7 ^a

^aReference [8].

^bReference [3].

^cReference [9].

the fragility index. In the first approximation, the entropy is approximated by that given by Adam-Gibbs, namely, [4(a),4(b)].

$$S \approx S_c = \Delta C_p \ln(T/T_2). \quad (7)$$

Here T_2 is the temperature where the configurational entropy S_c vanishes and ΔC_p is the change of heat capacity at T_g . The corresponding fragility index is denoted by m_{AG} . In the second approximation, we make use of only the configurational entropy part of the total entropy as predicted by DiMarzio-Dowell [see Eq. (4)]; the corresponding fragility index is denoted by m_{DD}^C . In the last approximation, the total entropy as predicted by the Gibbs-DiMarzio model is employed to calculate the relaxation time as a function of temperature. In this case, the fragility index is denoted by m_{DD} .

The various parameters [7,8] needed to evaluate the entropy in the Gibbs-DiMarzio and the Adam-Gibbs models are given in Table I. The quantity $\Delta\mu_s^*$ is related to T_g , $S(T_g)$, and k_B WLF parameter C'_1 [4(c)]. Table II shows a comparison of the theoretical prediction of the fragility index for the five polymers with various experimental data. Note that the experimental measurements of the fragility index of some polymers vary due to the diverse techniques used for the measurement of the relaxation time. The theoretical predictions fall within the bounds of the experimental variations [3,8,9].

The connection between the slope of the relaxation time and macroscopic thermodynamic properties of supercooled polymer liquids is considerable more general than the results presented here suggests [10–12]. In fact, by starting from Eq. (6) we find that the ratio of heat capacity and entropy changes at the glass transition temperature is directly related to fragility [10]. The predictions are in accord with experimental data on strong and fragile molecular as well as organic liquids [10].

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