

Calorimetric Study of Glassy and Liquid Toluene and Ethylbenzene: Thermodynamic Approach to Spatial Heterogeneity in Glass-Forming Molecular Liquids[†]

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The heat capacities of glassy and liquid toluene and ethylbenzene were measured with an adiabatic calorimeter. Both samples were doped with about 10% of benzene to suppress crystallization. The effects of the doping were corrected for by assuming the additivity of the heat capacities of toluene (or ethylbenzene) and benzene. The configurational entropies of several glass-forming liquids, including toluene and ethylbenzene, were calculated as functions of temperature from their heat-capacity data. For these calculations, the vibrational heat capacities were determined by the least-squares fitting of the Debye and Einstein functions to the experimental values using auxiliary spectroscopic data from the literature. The size of cooperative rearranging region (CRR), which was first conceived by Adam and Gibbs, was calculated from the configurational entropy in a simplifying approximation that neglects distribution of CRR size and internal entropy of CRR. For all of the systems examined, the size of CRR increases with decreasing temperature and is frozen-in at four to eight molecules per region at the glass-transition temperature.

1. Introduction

The structural relaxation of undercooled liquids and glasses is one of the important topics of current condensed matter physics and chemistry.¹ The non-Arrhenius temperature dependence is characteristic of the α relaxation, which is the primary relaxation responsible for the glass transition. Angell² has summarized this feature by introducing a new parameter “fragility” and found a systematic relation between the bonding nature of the liquids and their fragility. A number of microscopic models have been proposed to explain the non-Arrhenius behavior of the α relaxation. One of the important models is the Adam–Gibbs theory (AG theory)³ proposed in 1965 and still influencing many current researchers in this field. This theory assumes the existence of “cooperatively rearranging regions” (CRR) of molecules (or polymer segments). This quantity is closely related to the configurational entropy (S_c), which can be evaluated from heat-capacity data. The asymptotic increase of the CRR size, which becomes infinite at the Kauzmann temperature ($S_c = 0$), is consistent with the divergence of the α relaxation time experimentally observed.

Recently, the concept of CRR, also known as “domain”, “cluster”, or “spatial heterogeneity”, is taken up in relation to the origin of the slow β (Johari–Goldstein) relaxation^{4,5} and nonexponentiality of the α -relaxation function.^{6–21} Several theoretical models also assume that the existence of some sort of heterogeneity is an essential feature of liquids.^{22–31} Recent computer-simulation studies^{32–34} also suggested the existence of spatial heterogeneity. The characteristic length of the CRR

was estimated to be 2–6 nm in some molecular^{9,14–16,20,22} and polymer glasses^{7,8,30} near the glass-transition temperatures. We have also reported the temperature dependence of the CRR size of 3-bromopentane³⁵ and cyanoadamantane (a typical plastic crystal)³⁶ on the basis of the calorimetric data. These are included in the discussion below. Despite a large number of studies listed above, there is still discussion whether the CRR exists, or whether the cooperative rearrangement is important even if the spatial heterogeneity exists. This situation occurs because the previous experiments were not direct and conclusive, and furthermore, the nonexponentiality can also be explained by the models without the spatial heterogeneity.^{37–40}

The aim of the present study is to evaluate the CRR size for several glass-forming molecular liquids and to find the general feature of the temperature dependence of the CRR size. This work assumes the existence of the CRR, which was conceived by Adam and Gibbs, and so is not intended for testing the validity of the Adam–Gibbs theory. We exclude alcohols from our analysis, since they form intermolecular hydrogen bonds and so need to be treated separately. To make an unambiguous analysis of the configurational entropy, the following properties are required of the substance examined. (1) It should have a simple molecular structure and fairly low glass-transition and fusion temperatures. (2) All of the glassy, undercooled liquid, stable liquid, and crystalline states should be realized experimentally. (3) Intramolecular vibrations should be known in sufficient detail by spectroscopic methods. In this study, we have measured the heat capacities of glassy and undercooled toluene and ethylbenzene. Both samples were doped with about 10% of benzene to suppress the crystallization, and the doping effects were subtracted by assuming the additivity of the heat capacities. Toluene is close to a rigid molecule in that the only low-frequency intramolecular vibration is that of methyl rotation. 3-Bromopentane, which was examined before, has four C–C σ bonds and so has many molecular conformations. Ethylben-

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TABLE 1: Molar Heat Capacities of Metastable Sequences of Toluene ($M = 92.141 \text{ g mol}^{-1}$, $R = 8.314 51 \text{ J K}^{-1} \text{ mol}^{-1}$)

T/K	C_p/R	T/K	C_p/R	T/K	C_p/R	T/K	C_p/R	T/K	C_p/R	T/K	C_p/R	T/K	C_p/R
5.71	0.1353	13.06	0.9129	29.95	3.263	50.97	5.273	81.41	7.269	114.44	9.536	155.73	16.30
5.85	0.1444	14.10	1.054	31.68	3.466	53.21	5.439	84.42	7.444	116.11	10.18	158.25	16.29
6.30	0.1745	15.28	1.220	33.41	3.670	55.55	5.622	87.45	7.610	117.66	13.70	160.77	16.29
6.87	0.2180	16.60	1.408	35.13	3.865	58.07	5.818	90.50	7.781	118.97	16.31	163.30	16.29
7.45	0.2651	17.98	1.608	36.89	4.056	60.69	5.993	93.58	7.946	120.28	16.64	165.84	16.30
8.09	0.3238	19.48	1.828	38.69	4.236	63.49	6.176	96.69	8.123	121.60	16.62	168.38	16.30
8.78	0.3911	21.19	2.076	40.57	4.419	66.46	6.360	99.83	8.305	122.93	16.60	170.94	16.31
9.50	0.4688	22.94	2.325	42.50	4.592	69.55	6.556	103.01	8.492	124.27	16.57	173.50	16.32
10.25	0.5533	24.68	2.568	44.46	4.768	72.52	6.744	106.22	8.693	125.62	16.56	176.08	16.33
11.11	0.6573	26.43	2.797	46.57	4.940	75.47	6.921	109.47	8.928	150.74	16.31	178.66	16.35
12.06	0.7783	28.20	3.026	48.75	5.119	78.43	7.097	112.77	9.248	153.23	16.30		

zene lies between these two with respect to the rigidity of the molecule. The heat capacities of crystalline and stable liquid toluene have been measured by Scott et al.,⁴¹ while those of ethylbenzene have not. Therefore, we also measured the heat capacities of the crystal and liquid of pure ethylbenzene. We also calculated the CRR size of 1-butene and *o*-terphenyl by using the previous data^{17,42} to make a comparison for as many molecules as possible.

2. Experimental Section

Commercial reagents of toluene (purity: >99%) and ethylbenzene (purity: >99%) were purchased from Tokyo Kasei Kogyo Inc. The samples were first dehydrated with molecular sieves (3 Å, $1/16$, Wako Pure Chemical Ind., Ltd.) and then fractionally distilled with a concentric-type rectifier (HC-5500-F, Shibata Kagakukikai Kogyo Co., Ltd.). The main distillates were degassed and distilled in vacuo in a homemade vacuum line. Both samples subsequently showed no trace of organic impurity as detected by gas chromatography (F21, Perkin-Elmer). Karl Fischer tests were also carried out, and the amount of water contained in each sample was found to be negligible (<0.007 wt %). Toluene and ethylbenzene were then doped with about 10% of benzene purified by the similar method. The respective mole fractions of these samples were determined by the gravimetric method to be the following: 0.9003 for toluene and 0.0997 for benzene; 0.9023 for ethylbenzene and 0.0977 for benzene.

The masses of the pure ethylbenzene, doped toluene, and doped ethylbenzene loaded in the sample cell were 4.0242 g (0.037 903 mol), 3.6242 g (0.039 939 mol), and 2.7352 g (0.026 445 mol), respectively. The dead volume of the cell (about 1 cm³) was filled with helium gas at room temperature and atmospheric pressure in order to enhance thermal equilibration at low temperatures.

The heat capacities were measured using an adiabatic calorimeter⁴³ in the temperature range between 5 and 300 K. The heat-capacity measurement was carried out using a standard intermittent heating method, i.e., repetition of equilibration and energizing intervals. The temperature increment for each measurement was between 0.3 and 2.5 K. It took about 30 s for the sample to reach thermal equilibrium in the cell after each energy input at 10 K and about 3 min at 300 K. The accuracy of the heat-capacity measurement was better than 1% at $T < 10$ K, 0.5% at $10 < T < 20$ K, 0.2% at $20 < T < 30$ K, and 0.1% at $T > 30$ K. The effect of the vaporization enthalpy on the heat-capacity data was estimated to be less than 0.1% even at 300 K. This favorable situation resulted because the dead space inside the cell was small (ca. 1 cm³).

The temperature of the sample was measured with a precision of 100 μ K using Rh-Fe resistance thermometers (27 Ω at 273 K, purchased from Oxford Instruments Company) calibrated on

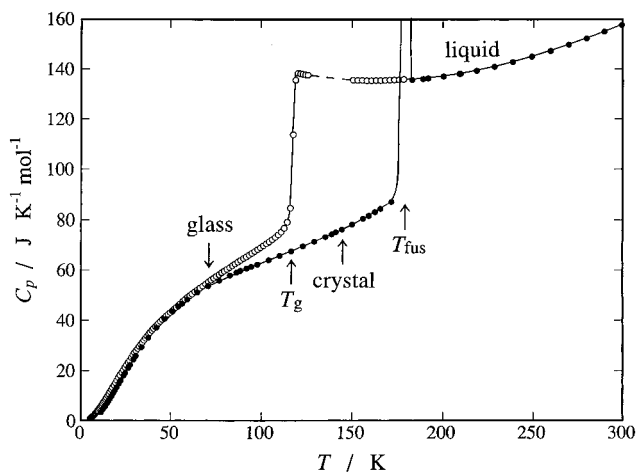


Figure 1. Molar heat capacities of toluene in the stable (●) and metastable (○) states. The data for the stable states are from ref 41.

the temperature scales EPT76 ($T < 30$ K) and IPTS68 ($T > 30$ K). The heat-capacity difference caused by the conversion to the new temperature scale ITS90⁴⁴ was estimated to be smaller than 0.05% over the 13–300 K temperature range.

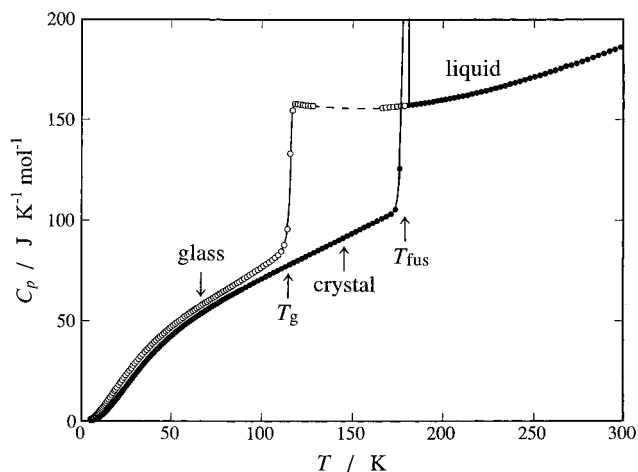
3. Results and Discussion

A. Heat Capacities of Toluene and Ethylbenzene. The doped toluene and doped ethylbenzene were cooled from the room temperature to the base temperature (ca. 5 K) as rapidly as possible to avoid crystallization and to obtain their glassy states. The cooling rate was about 10 K min⁻¹ around their glass-transition temperatures. The crystalline sample of pure ethylbenzene was prepared by annealing it at temperatures several Kelvin lower than its fusion temperature. The effect of the dopant (benzene) was corrected by assuming the additivity of heat capacities by using the previously measured heat capacity of benzene.⁴⁵ For the correction in the glassy states, the heat capacity of solid benzene was used, since that of glassy benzene is not available. For both toluene and ethylbenzene, the additivity of heat capacity was found to be a good approximation by comparing the corrected heat capacities and the experimental heat capacity of the pure sample in the equilibrium liquid states. The corrected molar heat capacities of glassy and undercooled liquid toluene and ethylbenzene are collected in Tables 1 and 2, respectively. Table 2 also includes the molar heat capacities of crystalline and equilibrium liquid ethylbenzene.

Figures 1 and 2 show the heat capacities of toluene and ethylbenzene, respectively. The open circles denote the heat capacities in the metastable states (glass and undercooled liquid) and the closed circles those in the stable states (crystal and equilibrium liquid). The glass-transition temperatures (T_g) of toluene and ethylbenzene were 117 and 115 K, respectively. The heat capacity increases (ΔC_p) at T_g were 64 J K⁻¹ mol⁻¹

TABLE 2: Molar Heat Capacities of Ethylbenzene ($M = 106.17 \text{ g mol}^{-1}$, $R = 8.314 51 \text{ J K}^{-1} \text{ mol}^{-1}$)

T/K	C_p/R	T/K	C_p/R	T/K	C_p/R	T/K	C_p/R	T/K	C_p/R	T/K	C_p/R	T/K	C_p/R
Metastable Sequences													
5.64	0.1378	14.13	1.114	32.12	3.737	53.38	5.933	75.70	7.566	102.66	9.418	123.94	18.91
5.88	0.1505	15.54	1.327	34.35	4.025	55.51	6.105	78.05	7.727	105.88	9.663	126.80	18.87
6.51	0.1953	17.18	1.578	36.54	4.286	57.67	6.287	80.42	7.881	109.17	9.965	128.26	18.88
7.30	0.2612	18.87	1.838	38.69	4.525	59.85	6.446	82.84	8.043	110.85	10.19	166.36	18.75
8.15	0.3420	20.22	2.047	40.83	4.753	62.05	6.610	85.29	8.210	112.54	10.56	170.33	18.79
9.00	0.4326	22.12	2.341	42.94	4.968	64.27	6.769	87.83	8.377	114.22	11.52	174.52	18.84
9.84	0.5302	24.07	2.631	45.03	5.177	66.51	6.928	90.55	8.565	115.73	16.01	178.80	18.89
10.74	0.6440	26.04	2.916	47.11	5.378	68.78	7.091	93.43	8.766	117.06	18.60		
11.77	0.7801	27.99	3.187	49.18	5.577	71.06	7.248	96.41	8.967	118.41	18.99		
12.90	0.9368	29.99	3.471	51.27	5.755	73.37	7.409	99.50	9.182	121.14	18.96		
Stable Sequences													
5.90	0.04459	22.76	1.754	50.18	5.112	84.06	7.598	142.43	10.85	181.06	18.92	250.54	20.61
6.62	0.06193	24.50	2.006	52.45	5.320	86.67	7.760	147.04	11.11	185.39	18.98	256.21	20.80
7.64	0.09599	26.44	2.282	54.74	5.527	89.25	7.913	151.69	11.36	189.94	19.05	261.97	21.00
8.69	0.1440	28.40	2.564	57.05	5.724	93.61	8.168	156.37	11.62	194.54	19.12	267.81	21.23
9.69	0.2021	30.26	2.822	59.39	5.909	97.97	8.419	161.13	11.88	199.17	19.22	273.74	21.41
10.62	0.2650	32.10	3.073	61.75	6.094	102.32	8.662	166.09	12.14	203.84	19.31	279.76	21.63
11.51	0.3374	34.01	3.330	64.13	6.275	106.69	8.905	171.11	12.41	208.61	19.42	285.86	21.87
12.50	0.4275	35.87	3.569	66.53	6.450	111.07	9.148	177.47	190.9	213.50	19.51	292.04	22.12
14.14	0.5959	37.74	3.797	68.96	6.621	115.47	9.385	177.71	216.2	218.49	19.65	298.29	22.36
15.32	0.7319	39.65	4.021	71.41	6.789	119.89	9.621	177.98	616.4	223.58	19.79	301.45	22.45
16.65	0.8968	41.61	4.238	73.89	6.955	124.33	9.866	178.05	1535	228.78	19.93		
18.18	1.099	43.68	4.462	76.39	7.117	128.81	10.11	178.08	2281	234.08	20.09		
19.73	1.314	45.79	4.680	78.92	7.281	133.32	10.35	178.10	2426	239.47	20.26		
21.22	1.529	47.94	4.893	81.48	7.439	137.86	10.60	178.13	1621	244.96	20.44		

**Figure 2.** Molar heat capacities of ethylbenzene in the stable (●) and metastable (○) states.

(46% of $C_p(\text{liquid})$ at T_g) and $76 \text{ J K}^{-1} \text{ mol}^{-1}$ (48% of $C_p(\text{liquid})$ at T_g), respectively. Such large ΔC_p 's indicate that toluene and ethylbenzene are both fragile liquids as 3-bromopentane (ΔC_p is 46% of $C_p(\text{liquid})$ at T_g). Crystallization occurred at about 10 K higher than T_g in both samples. The temperature, enthalpy, and entropy of the fusion of ethylbenzene were $(178.08 \pm 0.02) \text{ K}$, $(9.166 \pm 0.009) \text{ kJ mol}^{-1}$, and $(51.47 \pm 0.05) \text{ J K}^{-1} \text{ mol}^{-1}$, respectively.

B. Calculation of Vibrational Heat Capacity. To evaluate the configurational entropy as described in the next section, the vibrational heat capacity of the glass is required above T_g . To make this extrapolation as precisely as possible, we fitted a model function (eq 1) to the experimental heat capacities of glassy toluene and ethylbenzene.

$$C_p^{\text{gl}} = C(\text{lat}) + C(\text{lib}) + C(\text{Me}) + C(\text{vib}) + \Delta C(\text{corr}) \quad (1)$$

$C(\text{lat})$, $C(\text{lib})$, $C(\text{Me})$, $C(\text{vib})$, and $\Delta C(\text{corr})$ are the heat capacities due to the translational lattice vibration, rotational vibration (libration), methyl-group rotation, intramolecular vibration, and

the $C_p - C_v$ correction, respectively. The last term is approximately given by

$$\Delta C(\text{corr}) = A[C(\text{lat}) + C(\text{lib})]^2 T \quad (2)$$

where A is a constant and T the temperature. $C(\text{lat})$ was approximated by a Debye function and $C(\text{lib})$ by an Einstein function, each having three degrees of freedom. $C(\text{vib})$ and $C(\text{Me})$ were represented by a combination of Einstein functions. For both toluene and ethylbenzene, all of the frequencies of the intramolecular vibrations are known from the Raman and infrared spectra.^{46–48} The Debye temperature θ_D for the lattice vibration, Einstein temperatures $\theta_E(\text{lib})$ for the libration and $\theta_E(\text{Me})$ for the methyl rotation, and the correction coefficient A were determined by the least-squares fitting of the model functions to the experimental heat capacities in the temperature range 5–89 K for both toluene and ethylbenzene. The optimum values were $\theta_D = 100.7 \text{ K}$, $\theta_E(\text{lib}) = 151.6 \text{ K}$, $\theta_E(\text{Me}) = 39.9 \text{ K}$, and $A = 4.19 \times 10^{-5} \text{ mol J}^{-1}$ for toluene and $\theta_D = 72.4 \text{ K}$, $\theta_E(\text{lib}) = 142.1 \text{ K}$, $\theta_E(\text{Me}) = 94.9 \text{ K}$, and $A = 3.45 \times 10^{-5} \text{ mol J}^{-1}$ for ethylbenzene. The fitting was satisfactory for both samples and is illustrated in Figure 3 for toluene. The contribution from each part is also shown in Figure 3. A similar calculation was performed also for 1-butene ($T_g = 60 \text{ K}$, $T_{\text{fus}} = 88 \text{ K}$, ΔC_p is 58% of $C_p(\text{liquid})$ at T_g)¹⁷ and *o*-terphenyl ($T_g = 240 \text{ K}$, $T_{\text{fus}} = 329 \text{ K}$, ΔC_p is 35% of $C_p(\text{liquid})$ at T_g)⁴² by using the heat-capacity data measured before. The uncertainty of the present extrapolations would be smaller than 5% of the total heat capacity, considering our previous analyses for the various baseline problems.

C. Calculation of Configurational Entropy. The temperature dependence of the configurational entropy $S_c(T)$ was calculated by the equation

$$S_c(T) = \Delta_{\text{fus}} S - \int_T^{T_{\text{fus}}} \frac{[C_p^{\text{dq}}(T') - C_p^{\text{gl}}(T')]}{T'} dT' - \int_0^{T_{\text{fus}}} \frac{[C_p^{\text{gl}}(T') - C_p^{\text{cr}}(T')]}{T'} dT' \quad (3)$$

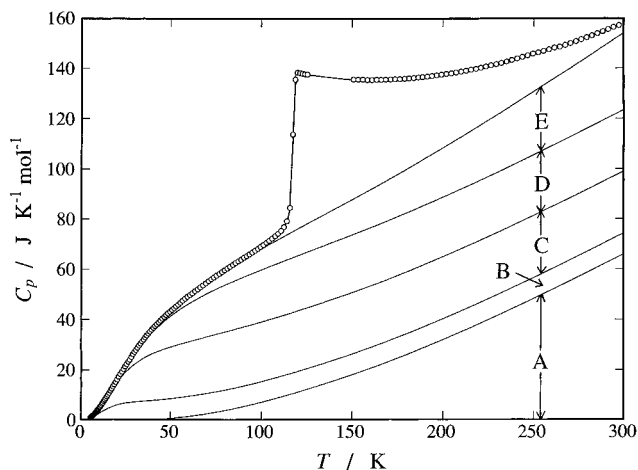


Figure 3. Molar heat capacities of glassy, undercooled liquid, and stable liquid toluene, where the vibrational heat capacities determined from the least-squares fitting are shown by parts A–E (see text for the details): (A) intramolecular vibration; (B) methyl rotation; (C) lattice vibration; (D) libration; (E) $C_p - C_v$ correction.

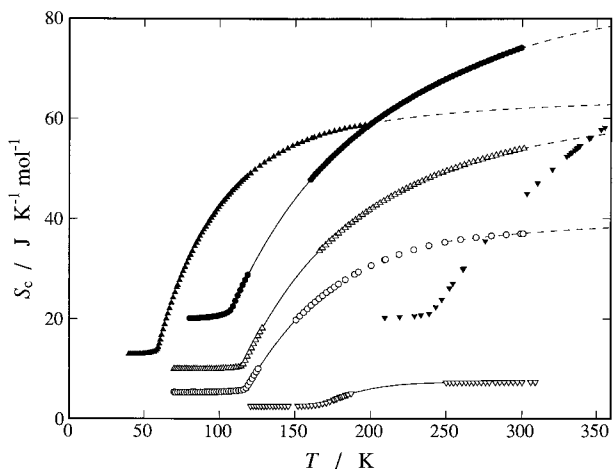


Figure 4. Temperature dependence of the configurational entropy of several glass-forming molecular liquids (○, toluene; △, ethylbenzene; ●, 3-bromopentane; ▲, 1-butene; ▼, *o*-terphenyl) and a glass-forming plastic crystal (▽, cyanoadamantane).

where T_{fus} and $\Delta_{\text{fus}}S$ denote the temperature and entropy of the fusion, respectively, and C_p^{gl} , C_p^{liq} , and C_p^{cr} the heat capacities of the glass, liquid, and crystal, respectively. This equation gives the configurational entropy by using entropy of fusion as a reference point. The second term of eq 3 corresponds to the configurational-entropy decrease caused by a temperature decrease and the third term for the correction due to the difference in vibrational entropy between the glassy and crystalline states (usually smaller than 5%). The calculated configurational entropies of toluene, ethylbenzene, 1-butene, and *o*-terphenyl are plotted in Figure 4 together with the previous results for 3-bromopentane³⁵ and cyanoadamantane.³⁶ Cyanoadamantane is a plastic crystal, which is positionally (for the center of mass) ordered and orientationally disordered. The plastic phase is quenched by rapid cooling and immobilized into a glassy crystal ($T_g = 163$ K). It is a useful peculiarity of cyanoadamantane among glass-forming substances that it has no intramolecular rotational modes such as a methyl rotation and thus is a rigid molecule. As shown in Figure 3, the configurational entropy decreases with decreasing temperature and becomes constant at each glass-transition temperature. The configurational entropy frozen at T_g is the residual entropy of a glass.

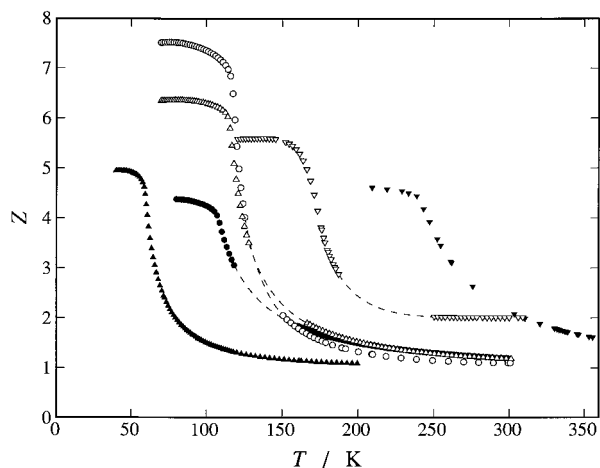


Figure 5. Temperature dependence of the number of the molecules in CRR of several glass-forming molecular liquids (○, toluene; △, ethylbenzene; ●, 3-bromopentane; ▲, 1-butene; ▼, *o*-terphenyl) and a glass-forming plastic crystal (▽, cyanoadamantane).

D. Temperature Dependence of CRR. By assuming that the entropy within the CRR is zero, the average CRR size $Z(T)$ (the number of the molecules in a CRR) is related to $S_c(T)$ by the equation

$$Z(T) = s_c^* N_A / S_c(T) \quad (4)$$

Here, s_c^* is the configurational entropy of a single molecule and N_A is the Avogadro constant. The value of s_c^* is determined by extrapolating the $S_c(T)$ curve in Figure 4 to infinite temperature. The extrapolation was made by fitting the following function to the available S_c data in the highest 50 K temperature range for each sample.

$$S_c(T) = s_c^* N_A - C/T^2 \quad (5)$$

Here, $s_c^* N_A$ and C are fitting parameters. This equation is derived from the high-temperature form of the Schottky heat-capacity function. The fittings were quite satisfactory as shown by the dashed lines in Figure 4. The $s_c^* N_A$ values obtained are as follows, in $\text{J K}^{-1} \text{mol}^{-1}$: toluene, 40.8; ethylbenzene, 64.0; 1-butene, 64.5; *o*-terphenyl, 93.7; 3-bromopentane, 88.4. The present method for the determination of s_c^* may cause an inaccuracy of 10% in the absolute value of $Z(T)$ for most of compounds. The inaccuracy is estimated to be larger (20–40%) for *o*-terphenyl, since $C_p^{\text{liq}} - C_p^{\text{gl}}$ is still large at the maximum temperature of the heat-capacity measurement (355 K). For cyanoadamantane, it is known from the X-ray diffraction study⁴⁹ that the molecule is disordered among six equivalent orientations so that s_c^* is unambiguously $k_B \ln 6$.

Figure 5 shows the temperature dependence of the CRR size calculated by using eq 4. The uncertainty of Z at T_g , which arises mainly from the uncertainties of the extrapolations of C_p^{gl} using eq 3 and S_c using eq 5, is estimated to be 20–40% for *o*-terphenyl and 10–20% for other compounds. For all of the molecules examined, the CRR size increases with decreasing temperature and becomes constant at about four to eight molecules at T_g . It is interesting to compare this number of the CRR size with the previously reported characteristic length of the spatial heterogeneity.^{7–9,14–16,20,22} These two quantities should be related to each other but are not necessary to be identical. The CRR size obtained here (four to eight molecules) are consistent with the characteristic length (2–6 nm) obtained by other methods if one takes the van der Waals diameters of

the presently examined molecules (0.5–1 nm) into consideration. Only for *o*-terphenyl can we compare more directly (using the same molecule) our present result ($Z = \text{ca. } 4$ at T_g) with the previous data by $^2\text{H NMR}^9$ (5.6 nm in length of the rigid cluster) and optical spectroscopy using probe molecules with a photobleaching technique (2.5 nm in the characteristic length of heterogeneity).¹⁵ *o*-Terphenyl is quasi-planar molecule (phenyl groups are twisted by $40\text{--}60^\circ$)⁵⁰ with the largest van der Waals diameter of 1.4 nm and thickness of 0.5 nm. Our result agrees with the data by the photobleaching method;¹⁵ i.e., there are various ways to make a linear dimension of 2.5 nm by combining four molecules.

It is noteworthy that toluene and ethylbenzene have Z values larger than those of the nonaromatic molecules with similar T_g (1-butene and 3-methylpentane). A neutron-diffraction study⁵¹ reported that benzene rings tend to make a definite local structure. It is plausible that the molecules with a benzene ring tend to form a larger CRR than chain molecules around T_g .

There exists an additional factor that need be considered for ethylbenzene, 1-butene, and 3-bromopentane. If the intramolecular configurational entropy changes significantly in the temperature range of our interest (this will be the case if the energy differences among various intramolecular configurations are comparable with the thermal energy and if the barrier height is low enough), our result on $Z(T)$ need be corrected for this effect. At present, it is difficult to estimate this effect quantitatively, since the intramolecular configurational change will affect both s_c^* and $S_c(T)$ in complicated ways and effectively change the number of molecules in a CRR. Toluene, *o*-terphenyl, and cyanoadamantane are free from this effect. The methyl group of toluene is almost freely rotating, and *o*-terphenyl and cyanoadamantane have no intramolecular conformational change.

4. Concluding Remarks

We have shown that the CRR size increases with decreasing temperature and becomes frozen at four to eight molecules per region at T_g . The size derived agrees with other experimental evidence. Specifically, the CRR size of *o*-terphenyl at T_g is consistent with the results from optical spectroscopy using probe molecules.

Heat-capacity data of liquids have been accumulated, but they have seldom been analyzed from microscopic viewpoints. The calorimetric method has played a minor role in the recent development of the science of the liquid state compared with diffraction and spectroscopic methods. This is because the calorimetric data represent all the degrees of freedom of the substance under study with a equal weight, making it difficult to extract microscopic information from them. For the study on the CRR, however, the heat-capacity data can provide important microscopic information, since the configurational heat capacity is directly related to the short-range ordering (CRR growth) and they are easily related to the CRR size with simple assumptions.

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