Heat capacities of glass-forming molecular liquids: negative evidence for the liquid-liquid transition

LETTER TO THE EDITOR

Heat capacities of glass-forming molecular liquids: negative evidence for the liquid–liquid transition

Osamu Yamamuro, Shuichi Takahara, Akira Inaba, Takasuke Matsuo† and Hiroshi Suga‡

Department of Chemistry and Microcalorimetry Research Centre, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan

Abstract. The heat capacity of the supercooled liquid phase of 3-methylpentane has been measured with a high-precision adiabatic calorimeter. Negative evidence was obtained for the occurrence of a liquid–liquid transition currently discussed in relation to the mode-coupling theory of liquid states. A search for similar transitions in 1-butene and 1-pentene also gave negative results.

One of the current topics in amorphous materials is the dynamics of liquids and supercooled liquids near the glass transition [1, 2]. Among various theories describing molecular motion and the thermodynamics of liquids [3–5], the mode-coupling theory [6–8] has attracted much attention for the definite microscopic physical picture it presents of the dynamic processes in liquids. This theory is based on an equation for the density autocorrelation function which contains a non-linear memory term and gives predictions for dynamical processes involved in the glass transition. The most important prediction is the existence of a transition temperature T_c between the ergodic and non-ergodic states.

A neutron scattering experiment, which probes the density fluctuation directly, has been performed on various glass-forming liquids [9–24]. An unusual temperature dependence of the Debye–Waller factor has been reported as evidence for the existence of T_c [12–15, 19–21]. It has also been found that the viscosity follows a power-law temperature dependence of which the asymptotic temperature may be identified with the ergodic–non-ergodic transition temperature [25–31]. It is generally believed that the mode-coupling T_c occurs at $(1.2–1.4)$ T_g, where T_g is the calorimetric glass-transition temperature.

Another question of interest about the mode-coupling theory is whether or not any anomaly is associated with T_c in the static physical properties such as heat capacity C_p. Recently, Murthy [32] analysed previously published data on the heat capacities of several glass-forming molecular liquids and pointed out the existence of anomalies attributable to liquid-to-liquid transitions at temperatures around $T_{ll} = 1.2$ T_g. A bend in the heat capacity as a function of temperature, which he calls a third-order phase transition, was shown in the C_p curves of 3-methylpentane [33], 2-methylpentane [33], 3-methylhexane [34], and

† To whom correspondence should be addressed.

‡ Present address: Research Institute for Science and Technology, Kinki University, Kowakae, Higashi-Osaka, Osaka 577, Japan.
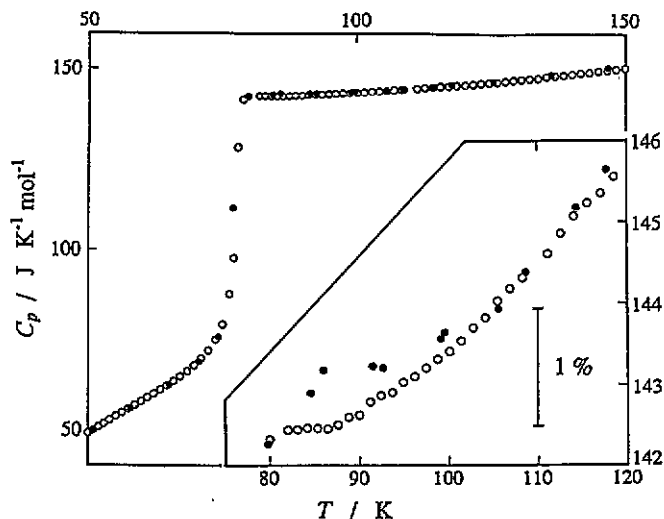
Figure 1. Heat capacities of 3-methylpentane. The open circles show the data in this study and the closed circles the data from [33].

diethylphthalate [35]. No clear anomaly was found in the heat capacity curves of six other molecular liquids cited by him.

In view of the general significance of the purported liquid-to-liquid transitions and their implication to the mode-coupling theory, we regard it as worthwhile to examine the original experimental data on which the assertion is based and to investigate whether the same conclusion can be drawn from more recent experimental data.

The purpose of the present letter is to demonstrate that the previous conclusion cannot be supported in our closer examination. We will present the heat capacities of three simple molecular liquids which could be studied both in the supercooled and glassy states without being hindered by crystallization. The heat capacity of 3-methylpentane, which gave the clearest T_{ll} anomaly in Murthy's paper [32], was re-measured for the present purpose, while those of 1-butene [36] and 1-pentene [37] have already been reported. The heat capacities were measured with high-precision adiabatic calorimeters [38, 39] constructed in our group. The precision and accuracy of the data are normally 0.05% and 0.1%, respectively, in the temperature range (50–150 K) of the present interest. The heat capacities were determined by the standard intermittent-heating method, i.e. repetition of equilibration and energizing intervals. In the temperature region above T_g, the equilibration in the sample was carefully checked by recording the temperature for long times (ca. 30 min). The heat capacities thus obtained are therefore those of equilibrium (supercooled) liquid including the contributions from both fast-responding vibrational degrees of freedom and a slow-relaxing configurational part. Near and below T_g, non-equilibrium heat capacities are obtained even if one takes a long equilibration time. It is, however, an important feature of adiabatic calorimetry that one can know whether one is measuring an equilibrium or non-equilibrium heat capacity simply by following the temperature as a function of time: non-linear variation of the temperature with time is a signature of a sample slowly approaching the equilibrium.

Figures 1, 2 and 3 show the heat capacities of 3-methylpentane, 1-butene and 1-pentene, respectively. They undergo glass transitions at 78, 59 and 71 K. In the insets of the figures the heat capacities in the temperature range between T_g and $1.5T_g$ are given. In the framework of the mode-coupling theory, T_c has been located in this relative temperature range for other glass-forming substances such as orthoterphenyl [12, 13] and 1, 2, 5-tri-α-naphthylbenzene [11]. The closed circles in figure 1 represent the data reported by Douslin and Huffman [33] in 1946. Murthy pointed out that the data of Douslin and Huffman bend
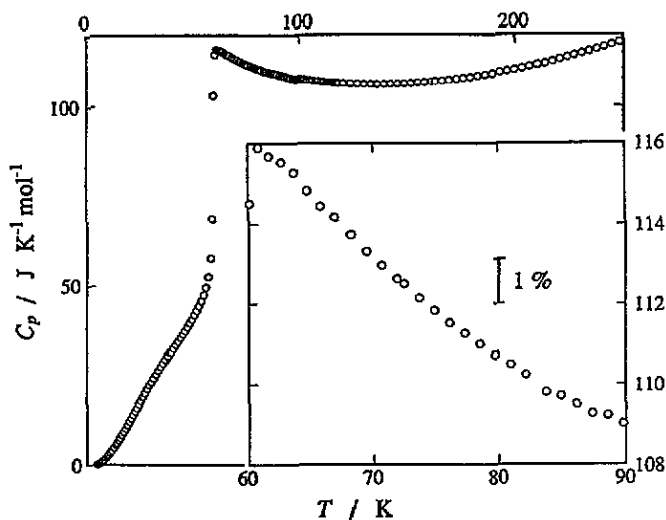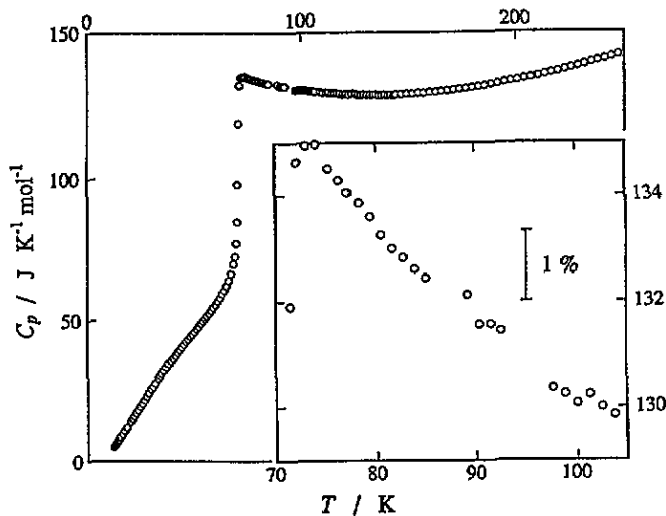
Figure 2. Heat capacities of 1-butene ([36]).

Figure 3. Heat capacities of 1-pentene ([37]).

upwards at 100 K, and took it as evidence for a third-order phase transition. However, our data are smooth as a function of temperature within the scattering (0.05%) of the points. Above 100 K the two sets of data agree excellently. Between 100 K and T_g the data of Douslin and Huffman are larger than ours and have a small hump but the difference is 0.7% at most.

It is our experience in adiabatic calorimetry that thermal equilibrium in a supercooled liquid is reached sluggishly even at temperatures considerably higher than T_g where one expects normal equilibration behaviour. The reason for this slow relaxation is not understood. In the 1940s when thermometry and adiabatic control techniques had not been sufficiently refined, unexpected slow relaxation effects probably escaped detection and could not be properly taken into account in the computation of the molar heat capacity from the experimental temperature data. We suspect that the discrepancy between the previous and present data below 100 K arises from this relaxational effect overlooked in the former experiment.

For 1-butene and 1-pentene, the heat capacity curves are smooth functions of temperature as shown in figures 2 and 3. The latter curve has a few irregular points. But they barely exceed 0.1% of the molar heat capacity and cannot be regarded as a systematic deviation from the normal behaviour.

We conclude that, for the substances investigated here, no heat capacity anomaly exists in the supercooled liquids beyond the scattering of the experimental data. This does not, of course, exclude the possibility of an ergodic–non-ergodic transition, for possible effects of this transition on the static properties have not been predicted in a way amenable to an experimental test.

References

[1] Ngai K L and Wright G B (ed) 1991 *Relaxation in Complex Systems, J. Non-Cryst. Solids* **131–133**
[2] Hansen J-P, Levesque D and Zinn-Justin J (ed) 1989 *Liquids, Freezing and Glass Transition* (Amsterdam: North-Holland)
[3] Fredrickson G H 1988 *Ann. Rev. Phys. Chem.* **39** 149
[4] Klinger M I 1988 *Phys. Rep.* **165** 275
[5] Hunt A 1993 *J. Non-Cryst. Solids* **160** 183
[6] Leutheusser E 1984 *Phys. Rev.* A **29** 2765
[7] Götze W 1984 *Z. Phys.* **56** 139; 1986 *Phys. Scr.* T **34** 415
[8] Götze W and Sjögren L 1992 *Rep. Prog. Phys.* **55** 241
[9] Mezei F, Knaak W and Farago B 1987 *Phys. Rev. Lett.* **58** 571
[10] Knaak W, Mezei F and Farago B 1988 *Europhys. Lett.* **7** 529
[11] Fujara F and Petry W 1987 *Europhys. Lett.* **4** 921
[12] Bartsch E, Fujara F, Kiebel M, Sillescu H and Petry W 1989 *Ber. Bunsenges. Phys. Chem.* **93** 1252
[13] Petry W, Bartsch E, Fujara F, Kiebel M, Sillescu H and Farago B 1991 *Z. Phys.* B **83** 175
[14] Frick B, Richter D, Petry W and Buchenau U 1988 *Z. Phys.* B **70** 73
[15] Frick B, Farago B and Richter D 1990 *Phys. Rev. Lett.* **64** 2921
[16] Richter D, Frick B and Farago B 1988 *Phys. Rev. Lett.* **61** 2465
[17] Frick B, Zorn R, Richter D and Farago B 1991 *J. Non-Cryst. Solids* **131–133** 169
[18] Richter D, Zorn R, Farago B and Frick B 1992 *Phys. Rev. Lett.* **68** 71
[19] Floudas G, Higgins J S, Kremer F and Fischer E W 1992 *Macromolecules* **24** 4955
[20] Kanaya T, Kawaguchi T and Kaji K 1992 *Physica* B **192** 403
[21] Börjesson L and Howells W S 1991 *J. Non-Cryst. Solids* **131–133** 53
[22] Kanaya T, Kawaguchi T and Kaji K 1993 *J. Chem. Phys.* **98** 8262
[23] Kiebel M, Bartsch E, Debus O, Fujara F, Petry W and Sillescu H 1992 *Phys. Rev.* B **45** 10301
[24] Frick B and Richter D 1993 *Phys. Rev.* B **47** 14795
[25] Cukierman M, Hane J W and Uhlmann D R 1973 *J. Chem. Phys.* **59** 3637
[26] Laughlin W T and Uhlmann D R 1972 *J. Phys. Chem.* **76** 2317
[27] McLaughlin E and Ubbelohde A R 1958 *Trans. Faraday Soc.* **54** 1804
[28] Gruver T and Kraus G 1964 *J. Polym. Sci.* A **2** 797
[29] Bondeau A and Huck J 1985 *J. Physique* **46** 1717
[30] Taborek P, Kleiman R N and Bishop D J 1986 *Phys. Rev.* B **34** 1835
[31] Rossler E 1990 *J. Chem. Phys.* **92** 3725
[32] Murthy S S N 1993 *J. Polym. Sci. Polym. Phys. Edn* **31** 475
[33] Douslin D R and Huffman H M 1946 *J. Am. Chem. Soc.* **68** 1704
[34] Parks G S, Thomas S B and Light D W 1936 *J. Chem. Phys.* **4** 64
[35] Chang S S, Horman J A and Bestul A B 1967 *J. Res. NBS* A **71** 293
[36] Takeda K, Yamamuro O and Suga H 1991 *J. Phys. Chem. Solids* **52** 607
[37] Takeda K, Yamamuro O and Suga H 1994 *J. Phys. Chem.* submitted
[38] Yamamuro O, Oguni M, Matsuo T and Suga H 1987 *Bull. Chem. Soc. Japan* **60** 1269
[39] Moriya K, Matsuo T and Suga H 1982 *J. Chem. Thermodynam.* **14** 1143