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# Effects of lowering temperature and raising pressure on the spatially heterogeneous dynamics of glass-forming van der Waals liquids

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Here we study how changes in temperature and pressure affect the dynamic heterogeneity in glass formers by using dielectric, volumetric, and heat capacity experimental data for two typical supercooled van der Waals liquids, 1,1′-bis (*p*-methoxyphenyl) cyclohexane (BMPC) and *o*-terphenyl (OTP). We demonstrate that these thermodynamic variables are not equivalent. We find that changes in temperature exert a stronger influence on heterogeneous dynamics than those in pressure, and the degree of heterogeneity in different thermodynamic conditions is mirrored in some way in corresponding structural relaxation times.

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Lowering the temperature of liquid below its melting temperature $T_m$ with a cooling rate sufficiently fast to avoid the crystallization process leads to glass formation. During the vitrification process, the dynamics of the molecules enormously slows down, spanning more than 12 decades of structural relaxation times in a relatively narrow temperature range, i.e., between $T_m$ and the glass transition temperature $T_g$. The non-Arrhenius and the non-Debye behaviors are the two most distinguishable features of the dynamics of the molecules of glass-forming liquids, which are commonly observed in experimental data for various types of materials. Although the rapid cooling of liquid is probably the most natural and undoubtedly the most frequently exploited method for producing glasses, an alternative way to do that is to compress liquids in isothermal conditions. In the past decade, much effort has been put into studying the behavior of the dynamics of the molecules of real glass formers measured at an elevated pressure.[1–13] These investigations have been mainly motivated by a very general question of whether cooling and squeezing liquids has the same effect on the behavior of the dynamics of molecules.

An important aspect of the dynamics of the molecules of supercooled liquids is the heterogeneous character of molecular motions.[14–25] In supercooled liquids, there are regions in which molecules are expected to rearrange in a cooperative manner. The existence of such cooperatively rearranging regions (CRRs) was postulated by Adam and Gibbs in the mid-1960s.[26] The concept of CRRs was also implemented in their entropic model of a liquid-glass transition for a description of the temperature dependence of the structural relaxation times. As pointed out later by four-dimensional (4D) NMR measurements,[27–29] the rate of molecular rearrangements in one region of a supercooled liquid can differ by orders of magnitude from the rate of molecular rearrangements in another region, being only about a few nanometers apart. What is more, the size $\xi$ of the dynamically cooperative regions was found to grow with decreasing temperatures and it achieved a value of a few nanometers at the glass transition temperature $T_g$. The direct measurement of the length scale of dynamic heterogeneity is not an easy task, because it cannot be performed by using standard relaxation spectroscopy methods. In fact, it requires measuring the nonlinear response of a supercooled liquid. Such experiments provide similar information with that obtained from a four-point time dependent correlation function $\chi_4(t)$, called dynamic susceptibility. A four-point time dependent correlation function is sensitive to dynamic heterogeneities, because it contains information on both spatial and temporal correlations. The height of the peak in the dynamic susceptibility has been considered to directly yield the number of dynamically correlated molecules $N_c$.[30] However, there is a much simpler way to estimate quantitatively the length scale of dynamic heterogeneity, which is based on a derivative analysis of the two-point correlation function $\Phi(t)$. Recently, Berthier *et al.*[20,30] have pointed out that for real molecular systems,

$$\chi_4(t) \geqslant \frac{k_B}{\Delta c_p} T^2 \chi_T^2(t) = \frac{k_B}{\Delta c_p} T^2 \left(\frac{\partial \Phi(t)}{\partial T}\right)^2, \tag{1}$$

where $\Delta c_p$ is the change in the heat capacity between the liquid and glassy states and $\chi_T$ is the dynamic susceptibility that directly probes the range of spatial correlations between local fluctuations of the dynamics and that of the enthalpy. By assuming that the two-point linear correlation function can be parametrized by the Kohlrausch-Williams-Watts (KWW) function, $\Phi(t) = \exp[-(t/\tau_\alpha)^\beta]$, one arrives[20,30–32] at an expression for a number of dynamically correlated molecules,

$$N_c = \chi_4^{\max} \approx \left(\left.\frac{\partial \Phi(x)}{\partial x}\right|_{x=1}\right)^2 \frac{k_B}{\Delta c_p} \left(\frac{\partial \ln \tau}{\partial \ln T}\right)^2, \tag{2}$$

where $x$ $(=t/\tau_\alpha)$ equals 1 at $t = \tau_\alpha$ and $\Phi'(1) = \beta/e$. It should be noted that the definition exploited in Eq. (2), i.e., $N_c = \chi_4^{\max}$, for the maximum of the function $\chi_4(t)$ occurring at $t \approx \tau_\alpha$, is still fervently discussed. There are systems for which it has been shown that $N_c$ is, in general, only proportional to $\chi_4^{\max}$ (Ref. 33) and very recently it has been found even[34] that the peak of $\chi_4(t)$ before the correlation length $\xi_4(t)$ reaches its maximal value. Nevertheless, Eq. (2) remains a good estimator for many systems, including bulk samples of simple van der Waals liquids, representatives of which are examined herein.

As already mentioned, the dynamics of the molecules can be varied by changing both temperature and pressure. Temperature changes mainly affect the thermal energies of molecules whereas pressure changes modify the energy barrier heights for molecular rearrangements.[1,20,22,35–46] Taking this

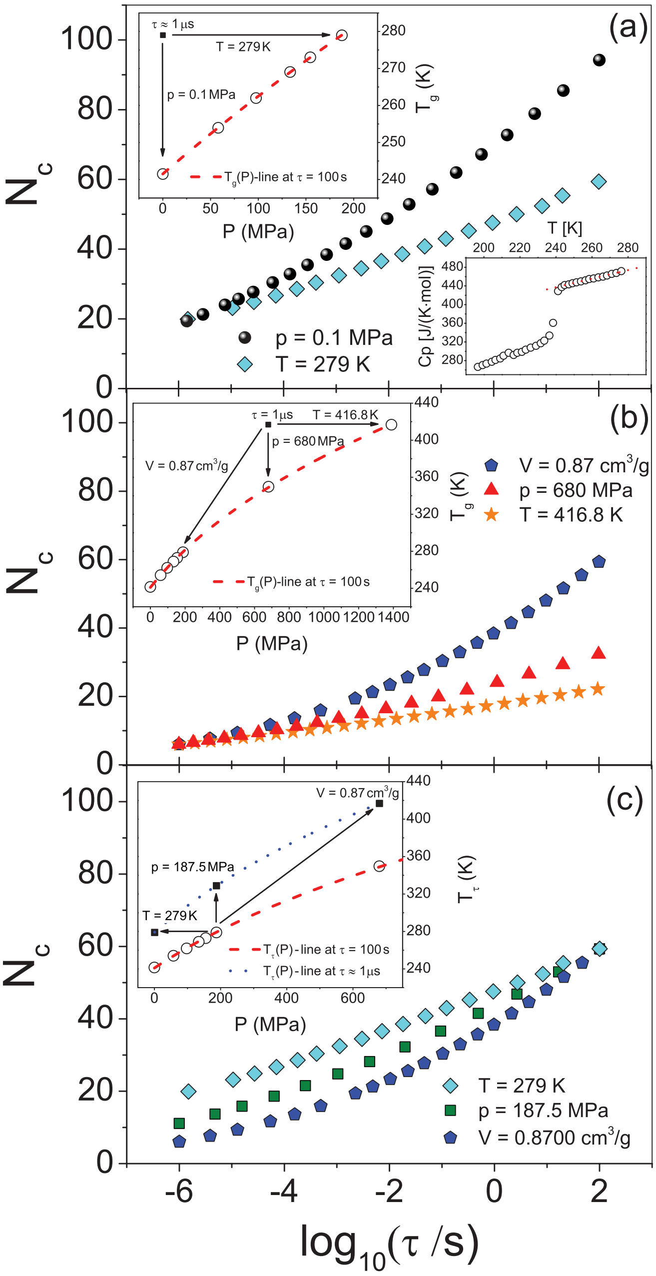

FIG. 1. (Color online) Plots of the number of dynamically correlated BMPC molecules vs the logarithm of structural relaxation times, the thermodynamic paths of which are shown in the upper inset of each panel. The bottom inset in (a) presents the temperature dependence of the heat capacity of BMPC near the glass transition at ambient pressure and its linear fit (the dashed line) found for the liquid state.

fact into account, a natural but fundamental question can be addressed: *Are there differences in the evolution of a length scale associated with the spatial correlations of the dynamics if the glass transition is approached by cooling or squeezing of liquid*? It should be stressed that this problem is especially interesting due to a previously held belief that if we transform a liquid from a dynamic state characterized by a structural relaxation time to its glass transition, the length scale of the spatial dynamic heterogeneity in the starting and glass transition states will not only depend on their structural relaxation times, but it will be independent of the thermodynamic path that is touring between these two dynamic states, e.g., it should be independent regardless of whether the liquid approaches its glass transition by isobaric cooling or isothermal compression. Such a view has been supported also by the experimental observation that the shape of the structural relaxation peak, which has been previously related to the system heterogeneity, does not depend on thermodynamic conditions at a given structural relaxation time for many glass formers.

To answer this question, we used herein the high pressure dielectric measurements of structural relaxation process of low molecular glass-forming liquid 1,1′-bis ($p$-methoxyphenyl) cyclohexane (BMPC)[47] and $o$-terphenyl (OTP),[48] because this relaxation is commonly considered to reflect the dynamics of the molecules related to the glass transition. At first, we consider the dielectric relaxation data of BMPC combined with its *PVT*, and specific heat capacity measurements allowed us to determine both the temperature and pressure dependences of $N_c$. According to Eq. (2), the temperature and pressure evolution of $N_c$ for BMPC can be calculated only if the temperature dependences of three quantities, $\beta$, $\tau_\alpha$, and $\Delta c_p$, at various pressures are known. The $\beta(T,P)$ and $\tau_\alpha(T,P)$ data have been determined from high pressure dielectric relaxation measurements and are taken from Ref. 47. Since we have found that the structural dielectric relaxation peaks of BMPC at a given structural relaxation time, similarly to some other van der Waals liquids,[49] possess the same shape for different pairs $(T,P)$ in the measurement range, the values of $\beta$ can be treated as dependent only on $\tau_\alpha$. Consequently, within the temperature-pressure range considered to estimate $N_c$ in BMPC, we have determined a slowly varying, linear function $\beta(\tau_\alpha)$ and applied it to Eq. (2). To facilitate calculations performed for different thermodynamic conditions by means of Eq. (2), we exploited the previous fit of $\tau_\alpha(T,V)$ for BMPC (Ref. 43) to the temperature-volume version[50] of the Avramov entropic model[51] and described[52] the earlier reported[53] volumetric data $V(T,P)$ by the recently derived equation of state (EOS) for supercooled liquids.[54–56] Since measurements of the specific heat capacity at an elevated pressure are very difficult, such data for BMPC are needed. However, it is still possible to calculate $\Delta c_p(T,P)$ from the *PVT* measurements, using the well known Maxwell's thermodynamic relations. Based on the temperature dependence of heat capacity data measured at ambient pressure by means of the adiabatic calorimetry method [see the bottom inset in Fig. 1(a)] and the *PVT* data, we finally estimated also the temperature and pressure dependence of $\Delta c_p$:

$$\Delta c_p(T,P) = \Delta c_p(T,P_0) - T\int_{P_0}^{P}\left(\frac{\partial^2 V}{\partial T^2}\right)dP, \qquad (3)$$

where $\Delta c_p(T,P_0)$ at ambient pressure $P_0$ is a linear increasing temperature function found from experimental heat capacity data on the assumption that the heat capacity of the glassy state depends neither on temperature nor pressure.

As a starting point we consider the case [see the upper inset in Fig. 1(a)] when the liquid-glass transition line $T_g(P_g)$ is achieved by lowering temperature at ambient pressure and by compression of the liquid at constant $T = 279$ K. Note that $T_g(P_g)$ is the isochronal line defined as $T_g = T(\tau_\alpha = 100\text{ s})$

and $P_g = P(\tau_\alpha = 100\,\text{s})$. To be able to compare the temperature and pressure dependences of $N_c$ on the same figure, we plotted $N_c$ as a function of $\log_{10}\tau_\alpha$ [Fig. 1(a)]. From this comparison, two conclusions can be drawn. First, the dramatic slowing down of the dynamics of the molecule is accompanied by a much stronger increase in $N_c$ when the liquid-glass transition is approached by lowering the temperature of the liquid than by increasing the pressure. Second, the number of dynamically correlated molecules can be expected to decrease with pressure at a constant relaxation time. For instance, $N_c = 95$ at $T_g = 241.5$ K and $P = 0.1$ MPa, whereas it is reduced to a value of 60 at $T_g = 279$ K and $P = 187.5$ MPa. This behavior will be analyzed more thoroughly below. Now, it is worth noting that the value $N_c$ found from dielectric data in the glass transition at ambient pressure is quite close to $N_c = 110$ calculated from the heat capacity data by using the method described in Ref. 57. This satisfactory result confirms Eq. (2) as a proper tool to evaluate $N_c$, in particular, the use of $\Delta c_p$ instead of $c_p$ in Eq. (2). Next, we return to the general question about the relative contributions of thermal energy and local density fluctuations to dynamic correlations. Lowering the temperature of a liquid exerts an influence on both types of fluctuations. To isolate the effect of only the thermal energy fluctuations, it is necessary to determine the temperature dependence of $N_c$ at a constant volume. Obviously, it cannot be done at ambient pressure because it requires applying negative pressures to satisfy the constant volume condition during cooling of a liquid. Therefore, to overcome this problem, we repeated our analysis at higher isobaric ($p = 680$ MPa) and isothermal ($T = 416.8$ K) conditions. The results of this analysis are displayed in Fig. 1(b). The isobaric and isothermal dependences of $N_c$ exhibit the same qualitative behavior as previously observed for the data presented in Fig. 1. In the pressure and temperature range considered it is now possible to calculate the number of dynamically correlated molecules in the isochoric condition at $V = 0.87\ \text{cm}^3/\text{g}$. These isochoric data are also shown in Fig. 1(b). Surprisingly, the most pronounced increase in $N_c$ is just observed in the isochoric conditions. It becomes obvious now that thermal fluctuations alone exert a stronger effect on dynamic correlations than do density fluctuations. In other words, taking into account the origin of the fluctuations in all the thermodynamic cases considered in Fig. 1(b), one can conclude that the most considerable growth of $N_c$ is caused by thermal fluctuations, and the density fluctuations make the smallest impact on the dynamic heterogeneity. However, at constant pressure, a competition between thermal and density fluctuations is observed, which results in a middle effect on the size of the heterogeneous regions.

It is also very instructive to have a look at the isobaric, isothermal, and isochoric dependences of $N_c$ when we start from the same point on the $T_g(P_g)$ line. Again the same pattern of behavior can be found [see Fig. 1(c)]. The number of dynamically correlated molecules is more influenced by temperature than by pressure. Of course, the largest effect can be achieved when the sample is heated at constant volume. The isobaric and isochoric data from Figs. 1(c) and 1(a) (supplemented with the isochor at $V = 0.886\ \text{cm}^3/\text{g}$, which meets the atmospheric isobar at $\tau_\alpha = 100$ s) but plotted in Fig. 2(a) as a function of inverse temperature can be compared now with the analogous dependences for their structural relaxation times [see the inset in Fig. 2(a)]. The results of this comparison are interesting. It clearly follows from the data presented in the inset in Fig. 2(a) that the rapidity of the change of $\tau_\alpha$ with temperature is significantly larger at constant pressure than that at constant volume. This is the general rule which underlies the relationship between the commonly used measures of the sensitivity to the temperature changes of the systems approaching the glass transition, which are the isobaric, $m_P = \partial \log_{10}(\tau)/\partial(T_g/T)|_{P=\text{const},\,T=T_g}$, and isochoric, $m_V = \partial \log_{10}(\tau)/\partial(T_g/T)|_{V=\text{const},\,T=T_g}$, fragilities that obey the inequality $m_p > m_V$. The same pattern of behavior is found for the isobaric and isochoric dependences of $N_c$ [Fig. 1(a)]. Thus, the larger the change in $N_c$, a larger deviation from the Arrhenius law is observed, which has been expected from a discussion of Eq. (2) (Ref. 20) in terms of

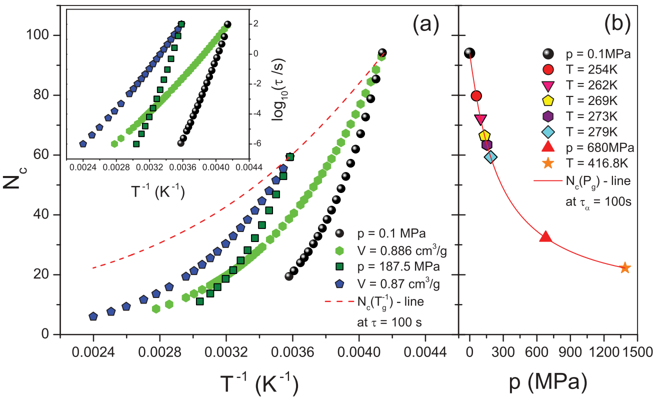

FIG. 2. (Color online) (a) Plot of the inverse temperature dependences of the number of dynamically correlated BMPC molecules for two chosen pairs of isobaric and isochoric conditions. The inset in (a) shows the corresponding dependences for structural relaxation times. (b) Plot of the isochronal pressure dependence of the number of dynamically correlated BMPC molecules at $\tau_\alpha = 100$ s.

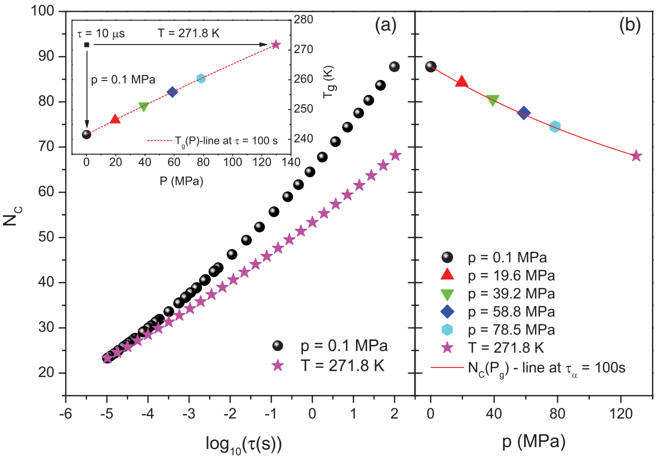

FIG. 3. (Color online) (a) Plot of the number of dynamically correlated OTP molecules vs the logarithm of structural relaxation times in isothermal and atmospheric isobaric conditions, the thermodynamic paths of which are shown in the inset. (b) Plot of the isochronal pressure dependence of the number of dynamically correlated OTP molecules at $\tau_\alpha = 100$ s.

the Arrhenius equation $\tau = \tau_0 \exp(E/k_B T)$, in which $E$ is the activation energy for a relaxation process and $\tau_0$ is its relaxation time in the high temperature limit. This finding explains on a molecular level the dramatic slowdown in the values of dynamic quantities such as structural relaxation time and viscosity near the glass transition.

It has been already noted[28,32] that the number of dynamically correlated molecules is smaller at higher $T_g$ and $P_g$. Thus, it is of interest to analyze the dependence of $N_c$ as a function of pressure at constant $\tau_\alpha = 100$ s, i.e., along with the $T_g(P_g)$ line. This dependence for BMPC is depicted in Fig. 2(b) and also marked auxiliarly in Fig. 2(a). The observed drop in the number of dynamically correlated molecules with increasing pressure in isochronal conditions can be considered as an intrinsic behavior of van der Waals liquids. The straightforward conclusion that can be drawn from this behavior is that the compression of a liquid in isochronal conditions brings about a decrease in the heterogeneity degree of the dynamics of the molecules. The immediate practical consequence of this finding may be the enhancement of the liquid's ability to crystallize at an elevated pressure. In fact, a stronger tendency for liquids to crystallize in high pressure conditions has been already observed by us in the case of a few low molecular van der Waals liquids.

A similar analysis has been performed also for OTP by using earlier reported dielectric,[48] heat capacity,[58] and *PVT* (Ref. 59) data describe by the Tait EOS.[60] In calculations based on Eq. (2), we exploited the previous fit of $\tau_\alpha(T,V)$ for OTP (Ref. 43) to the temperature-volume version[50] of the Avramov model.[51] As a result we can draw the same conclusions as those for BMPC. It means that the isothermal compression of OTP has a lower effect on its dynamic heterogeneity than the isobaric cooling of the liquid [Fig. 3(a)], and the number of dynamically correlated OTP molecules decreases with increasing pressure at $\tau_\alpha = \text{const}$ [Fig. 3(b)], although the pressure range for OTP is much smaller than that for BMPC in Fig. 2(b).

To sum up, we found that temperature exerts a stronger influence on $N_c$ than pressure if the effects of $T$ and $P$ are compared as functions of structural relaxation time. In this context, pressure and temperature cannot be treated as equivalent thermodynamic variables. Although the degree of heterogeneity in different thermodynamic conditions is reflected in some way in corresponding structural relaxation times, the system compression in isochronal conditions causes the system homogenization, i.e., a decrease in $N_c$.

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