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Glass phase and other multiple liquid-to-liquid transitions resulting from two-liquid phase competition

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Abstract: Melt supercooling leads to glass formation. Liquid-to-liquid phase transitions are observed depending on thermal paths. Viscosity, density and surface tension thermal dependences measured at heating and subsequent cooling show hysteresis below a branching temperature and result from the competition of two-liquid phases separated by an enthalpy difference depending on temperature. The classical nucleation equation of these phases is completed by this enthalpy saving existing at all temperatures. The glass phase thermodynamic parameters and their thermal variation have already been determined in such a two-liquid model. They are used at high temperatures to predict liquid-to-liquid transitions in some metallic glass-forming melts.

1-Introduction

Phenomena of branching thermal properties of melts measured at heating and subsequent cooling have been observed for a long time and explained by the irreversible breakdown of a metastable micro-heterogeneous state of melts inherited from the original crystal sample or appearing in the process of melting [1-3]. This breakdown happens when heating up to the homogenizing temperature of the melts, which is often close to the branching temperature. The recent observations of liquid-to-liquid phase transitions (LLPT) in well-known metallic glass-forming melts raise the question of the competition between two homogeneous liquid phases numbered 1 and 2 separated by an enthalpy difference depending on the temperature [4-10]. The glass phase formation is often viewed as being due to a true thermodynamic transition. Various microscopic models and experiments prove its existence at T_g [11-22]. The classical nucleation equation has been completed by introducing enthalpy savings $\epsilon_{ls} \times \Delta H_m$ and $\epsilon_{gs} \times \Delta H_m$, respectively associated with growth nucleus formation giving rise to crystallization in Phase 1 above T_g and Phase 2 below T_g , where ΔH_m is the melting heat per g-atom [22]. The enthalpy saving $\Delta \epsilon_{lg} \times \Delta H_m$ associated with the glass formation is then equal to $(\epsilon_{ls} - \epsilon_{gs}) \times \Delta H_m$. The energy saving coefficients ϵ_{ls} and ϵ_{gs} are linear functions of $\theta^2 = (T - T_m)^2 / T_m^2$, as shown by a study of supercooling rate maxima of liquid elements [23] and are equal to ϵ_{ls0} and ϵ_{gs0} at T_m . The minimum value 0.217 of ϵ_{ls0} and ϵ_{gs0} determined in many liquid elements at their melting temperature T_m corresponds to the Lindemann coefficient 0.103 [24]. The first-order transition to an ultrastable glass of confined liquid helium under pressure has been successfully described using $\epsilon_{ls0} = \epsilon_{gs0} = 0.217$ [25]. The transformation temperature of glasses in ultrastable phases having higher density has been defined as a function of an excess of frozen enthalpy $\Delta \epsilon$. The enthalpy of the ultrastable phase attains the minimum and the density the maximum when $\Delta \epsilon$ is equal to $\Delta \epsilon_{lg0} = \epsilon_{ls0} - \epsilon_{gs0}$ at T_m . The time dependence of T_g is explained by a weak excess enthalpy increasing T_g and relaxing after cooling [26].

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