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Universality in Glass Transitions

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Abstract

The Vogel-Fulcher-Tammann equation is exposed as a particular example of the mean field theory. It is generalized by taking into account an arbitrary critical exponent of susceptibility, discriminating between different classes of universality. The Bell-Evans-Polanyi principle is employed to estimate the difference between the activation energies of flows in crystals and glasses, which appears to coincide with the excess Gibbs energy of the glass compared to the crystal.

Keywords: glass transitions, universality, Bell-Evans-Polanyi principle

It is known that the dynamic viscosity η of many complex liquids is well described by the empirical Vogel-Fulcher-Tammann (VFT) equation[1]

$$\ln(\eta / \eta_0) = B / (T - T_0) \tag{1}$$

where η_0, B and T_0 are specific constants. When temperature T approaches T_0, the viscosity increases dramatically, thus leading to glass formation. On the other hand, the temperature dependence of the viscosity defines the activation energy $E_A = RT \ln(\eta / \eta_0)$ via the rigorous Arrhenius law. Introducing here Eq. (1) results in temperature dependent activation energy[2]

$$E_A = RB / (1 - T_0 / T) = \varepsilon_A (1 + C) \tag{2}$$

where $\varepsilon_A \equiv RB$ is the constant activation energy of a single molecule. The flow in condensed matter is a collective phenomenon and that is why the quantity $C \equiv (T / T_0 - 1)^{-1}$ can be interpreted as the cooperative number. It shows how many additional molecules should move in the

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liquid to absorb the external force per unit molecule. This definition is normalized by the obvious limit $C(T \to \infty) = 0$, since at infinite temperature no correlations between the fluid molecules are present.

According to the theory of critical phenomena, T_0 appears to be the critical temperature of the viscosity and one can generalize the expression above by introduction of the critical exponent of susceptibility γ

$$C \equiv (T / T_0 - 1)^{-\gamma} \tag{3}$$

The cooperative number is related also to the Kohlrausch exponent,[3] which can be generalized by using Eq. (3) to

$$n = \frac{C(T_m)}{C(T)} = (\frac{T - T_0}{T_m - T_0})^{\gamma} \tag{4}$$

where T_m is the melting temperature. The VFT equation (1) corresponds in particular to the mean field theory with $\gamma = 1$. There are, however, many other possibilities.[4] For instance, 3D systems can follow the self-avoiding walk ($\gamma = 1.1575$), the Ising model ($\gamma = 1.2373$), the classical XY model ($\gamma = 1.3177$), the Heisenberg model ($\gamma = 1.3955$), the percolation model ($\gamma = 1.7933$), etc. Thus, one can relate the universality class of the liquid to a macroscopic model for the dynamic viscosity

$$RT \ln(\eta / \eta_0) = \varepsilon_A [1 + (T / T_0 - 1)^{-\gamma}] \tag{5}$$

The activation energy ε_A for the viscous flow in glasses is lower than the activation energy ε_K of the viscous flow in crystals, due to the positive enthalpy of melting Δh_m. Following the Bell-Evans-Polanyi (BEP) principle,[5] one can write the relation

$$\varepsilon_A = \varepsilon_K - \alpha \Delta h_m \tag{6}$$

where $\alpha = 0 \div 1$ is the BEP coupling parameter. Since the liquid can flow only at temperature above the melting point T_m, one expects the height of the barriers of flow in crystals to be proportional also to the heat of melting, i.e. $\varepsilon_K \approx \Delta h_m$. On the other hand, the activation energy in glasses should be proportional to the critical temperature, $\varepsilon_A \approx T_0 \Delta s_m$, where $\Delta s_m = \Delta h_m / T_m$ is the positive entropy of melting. Thus, Eq. (6) acquires the elegant form $T_0 = (1-\alpha) T_m$ and the BEP parameter can be expressed now as

$$\alpha = 1 - T_0 / T_m \qquad (7)$$

It is amazing that the decrease of the activation energy $\varepsilon_K - \varepsilon_A = \alpha \Delta h_m = \Delta s_m (T_m - T_0)$ equals exactly to the excess of Gibbs energy in the glass as compared to the corresponding crystal. Since the glass transition temperature $T_g \approx T_0$ in metals and alloys is usually half of the melting temperature, it follows from Eq. (7) that the BEP parameter is $\alpha \approx 1/2$. Interestingly, the cooperative number at the melting point is one for such systems, $C(T_m) \approx 1$. For organic materials, however, it is known that $T_g / T_m \approx 3/4$, which implies $\alpha \approx 1/4$ and $C(T_m) \approx 3^\gamma$.

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