Non-Universality of the Specific Heat in Glass Forming Systems

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We present new simulation results for the specific heat in a classical model of a binary mixture glass-former in two dimensions. We show that in addition to the formerly observed specific heat peak there is a second peak at lower temperatures which was not observable in earlier simulations. This is a surprise, as most texts on the glass transition expect a single specific heat peak. We explain the physics of the two specific heat peaks by the micro-melting of two types of clusters. While this physics is easily accessible, the consequences are that one should not expect any universality in the temperature dependence of the specific heat in glass formers.

The thermodynamic properties of glass-formers near the glass transition have been a subject of intensive and far from settled research for more than half a century [1–4]. The temperature dependence of the entropy and how the entropy extrapolates to low temperatures gave rise to the so-called Kauzmann paradox [1] that remains confusing to the present time. Important to the understanding of these issues is the specific heat, either at a constant volume or at a constant pressure, since its integral over a temperature path provides the entropy. Experimental measurements of the specific heat in glass-forming systems are obtained from the linear response to either slow cooling (or heating) or to oscillatory perturbations with a given frequency about a constant temperature. The latter method gives rise to a complex specific heat with a given frequency about a constant temperature. The former method should be identified with thermodynamic measurements.

Experimental measurements reveal anomalies in the temperature dependence of the specific heat, including the so-called “specific heat peak” in the vicinity of the glass transition. In fact, throughout the literature on the glass transition one finds references to the so-called Kauzmann paradox [1] that remains confusing to the present time. Important to the understanding of these issues is the specific heat, either at a constant volume or at a constant pressure, since its integral over a temperature path provides the entropy. Experimental measurements of the specific heat in glass-forming systems are obtained from the linear response to either slow cooling (or heating) or to oscillatory perturbations with a given frequency about a constant temperature. The latter method gives rise to a complex specific heat with a given frequency about a constant temperature. The former method should be identified with thermodynamic measurements.

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In short, the system consists of an equimolar mixture of two types of point-particles, “large” with interaction range $\sigma_2 = 1.4$ and “small” with interaction range $\sigma_1 = 1$, respectively, but with the same mass $m$. In general, the three pairwise additive interactions are given by the purely repulsive soft-core potentials

$$\phi_{ab}(r) = \epsilon \left( \frac{\sigma_{ab}}{r} \right)^n, \quad a, b = 1, 2,$$  \hspace{1cm} (1)

where $\sigma_{aa} = \sigma_a$ and $\sigma_{ab} = (\sigma_a + \sigma_b)/2$. The cutoff radii of the interaction are set at $4.5\sigma_{ab}$. The units of mass, length, time and temperature are $m$, $\sigma_1$, $\tau = \sigma_1 \sqrt{m/\epsilon}$ and $\epsilon/k_B$, respectively, with $k_B$ being Boltzmann’s constant. In numerical calculations the stiffness parameter of the potential (1) was chosen to be $n = 12$.

The isochoric specific heat is determined by the fluctuations of the energy of the system at a given temperature:

$$\frac{C_V}{N} = \frac{d}{2} + \frac{(U_2^2 - \langle U \rangle^2)}{N T^2}. \hspace{1cm} (2)$$

The specific heat of our binary mixture model was measured at constant volume in [7, 11] and by us. We have used the last equation which allows one to estimate the specific heat in a single run of the canonical ensemble Monte Carlo simulations. At each temperature the density was chosen in accordance with the simulation results in an NPT ensemble as described in [7] with the pressure value fixed at $P = 13.5$. As the initial configuration in the Monte Carlo process the last configuration of the molecular dynamics run for this model at given temperature after $1.3 \times 10^8$ time steps was used. After short equilibration the potential energy distribution functions were measured during $2 \times 10^6$ Monte Carlo sweeps. The acceptance rate was chosen to be 30%. Simulations were performed with $N = 1024$ particles in a square cell with periodic boundary conditions. Our simulations appear to provide trustable values of $C_V$ down to lowest temperatures where the value of the specific heat coincides with that of two-dimensional solid, i.e. $C_V = 2$. What could not be seen in earlier simulations is that there is a smaller second peak of the specific heat at lower temperatures. To resolve it to the naked eye we present in Fig. 1 a blow-up of the region of lowest temperatures where the second peak is more obvious.

To understand the nature of the specific heat anomalies one must understand the physics that is behind the glassy behavior of this model in general and the existence of the two specific heat peaks in particular. When the temperature is lowered at a fixed pressure this system [12] (as well
As many other glass-formers [13–18] tends to form micro-clusters of local order. In the present case large particles form hexagonal ordering first (starting at about $T = 0.5$, and at lower temperatures (around $T = 0.1$) also the small particles form hexagonal clusters. The clusters are not that huge, with at most $O(100)$ particles, (cf. Fig. 2), depending on the temperature and the aging time. But we have shown that the long time properties of correlation functions are entirely carried by the micro-clusters [12]. Below we will refer to the micro-clusters as curds and the liquid phase as whey. We will argue that the specific heat responds to the micro-melting of the clusters - those of small particles at the lowest temperatures and those of the larger particles at higher temperatures. The large increase in the number of degrees of freedom when a particle leaves a crystalline cluster and joins the liquid background is the basic reason for the increase in entropy that is seen as a specific heat peak.

We will calculate the specific heat at constant volume per particle from the exact expression that can be derived [19] for any system with inverse power law potential $r^{-n},$

$$\frac{C_V}{N} = 1 + 4 \frac{K^\infty - K}{n^2 \rho T}. \quad (3)$$

For our system $n = 12$, $K$ is the bulk modulus and $K^{\infty}$ [20, 21] is given by:

$$K^\infty = \rho T + \frac{n(n + 2)}{4} \langle U \rangle. \quad (4)$$

The bulk modulus requires an equation of state for its calculation. In the rest of this Letter we will therefore derive an approximate equation of state and compute the specific heat, exposing the origins of the two peaks.

To start we define $v^c_{\ell}$, $v^s_{\ell}$, $v^c_{w}$ and $v^s_{w}$ respectively as the volume of large particle in the whey, small particle in the whey, large particle in the solid and small particle in the solid. Similarly we denote by $\epsilon^c_{\ell}$, $\epsilon^s_{\ell}$, $\epsilon^c_{w}$ and $\epsilon^s_{w}$ the energy of a large and small particle in the in the whey and in the crystalline phase respectively. Needless to say, all these quantities are temperature and pressure dependent; we will therefore explicitly use our low temperature knowledge concerning $v^c_{\ell}$ and $v^s_{\ell}$ in the crystalline phase, but treat the difference $v^c_{\ell} - v^s_{\ell}$ and $v^c_{w} - v^s_{w}$ as constants that we estimate below from our simulation knowledge. Similarly we estimate $\epsilon^c_{\ell}$ and $\epsilon^c_{w}$ from our knowledge of the hexagonal lattices at $T = 0$. We assume that $\epsilon^c_{w} \approx \epsilon^c_{\ell}$ and similarly $\epsilon^s_{w} \approx \epsilon^s_{\ell}$ since our simulations indicate a very small change in these parameters, see Table I. It should be stressed that the enthalpy change at these pressures is almost all due to the $PV$ term. This will result in a semi-quantitative theory ascribing the important changes in specific heat to the changes in the fraction of particles in curds and whey. In other words the number of particles in the whey and the number of clusters are all explicit functions of temperature and pressure.

| $\epsilon^c_{\ell}$ | $\epsilon^c_{w}$ | $\epsilon^s_{\ell}$ | $\epsilon^s_{w}$ | $v^c_{\ell}$ | $v^s_{\ell}$ | $v^c_{w}$ | $v^s_{w}$ | $N^c_{\ell}$ |
|---------------------|------------------|---------------------|------------------|-------------|-------------|-------------|-------------|-------------|
| 3.69                | 3.27             | 2.76                | 2.16             | 1.43        | 0.92        | 1.58        | 0.94        |

**Table I:** Parameters used in the calculation of the specific heat

As the condensed phase consists of clusters of large and small particles, we use the notation $N^c_{\ell}$ for the number of
clusters of $n$ large particles and $N_w^s$ for the clusters of $m$ small particles. Here we only need the intensive variables $p_w^c = 2 \sum_m N_w^s / N, p_w^s = 2 \sum_m N_w^s / N$ and $p_w = 2N_w^s / N$ which stand for the fraction of large particles and small particles in the curds, and large particles and small particles in the whey, such that $p_w^c + p_w^s = 1$ and $p_w^c + p_w^s = 1$. Using these variables we can write an expression for the volume per particle $v \equiv V / N$:

$$v = \frac{v_w^c + v_w^s}{2} + \frac{v_w^c - v_w^s}{2} p_w^c + \frac{v_w^c - v_w^s}{2} p_w^s. \quad (5)$$

At this point we need to derive expressions for $p_w^c$ and $p_w^s$. To do so we need to remember that in the relevant range of temperatures the large particles in the whey can occupy either hexagonal or heptagonal Voronoi cells, whereas small particles can occupy only pentagonal or hexagonal cells [8, 9, 12]. Accordingly there are $g_w^c \approx (26^0 - 1)/6 + 2^7 / 7$ ways to organize the neighbours of a large particle in the whey (neglecting the rare large particle in heptagonal neighbourhood), but only one way in the cluster. Similarly, there are $g_w^s \approx (26^0 - 1)/6 + 2^5 / 5$ ways to organize a small particle in the whey. We note that this estimate assumes that the relative occurrence of the different Voronoi cells is temperature independent. While reasonable at higher temperatures [12], at lower temperature one should use the full statistical mechanics as presented in [9] to get more accurate estimates of $g_w^c$ and $g_w^s$. This is not our aim here; we aim at a physical understanding of the specific heat peaks rather than an accurate theory. We thus end up with the simple estimates

$$p_w^c(P, T) \approx \frac{1}{1 + g_w^c e[|v_w^c - v_w^s| + p(v_v^c - v_w^s)] / T}, \quad (6)$$

$$p_w^s(P, T) \approx \frac{1}{1 + g_w^s e[|v_w^c - v_w^s| + p(v_w^c - v_w^s)] / T}. \quad (7)$$

It is important to note that the combination of Eq. (5) together with Eqs. (6) and (7) provides a mechanical equation of state. We will now compute $C_v$ directly from Eq. (3). The peaks in the specific heat are determined by the temperature dependence of $p_w^c(P, T)$ and $p_w^s(P, T)$ each which has a temperature and pressure derivatives that peaks at a different temperature, denoted as $T^c(P)$ and $T^s(P)$. As said above we take $\Delta v^c \equiv v_w^c - v_w^s$ and $\Delta v^s \equiv v_w^c - v_w^s$ as approximately constants (as a function of temperature and pressure). The constants are estimated from the condition that the second temperature derivative of $p_w^c(P, T)$ and $p_w^s(P, T)$ should vanish. From this conditions we find

$$\Delta v^c \approx T^c(P^*) \ln g_w^c / P^*, \quad \Delta v^s \approx T^s(P^*) \ln g_w^s / P^*. \quad (8)$$

where $P^*$ is the pressure for which the peaks in the derivatives are observed (13.5 in our simulations). This is equivalent to a linear dependence of the specific heat peaks as a function of pressure, $T^c(P) / T^c(P^*) = P / P^*$ and similarly for the small particles.

![FIG. 3: Specific heat at constant volume as predicted by the simple theory which is based on the mechanical equation of state supplied by Eqs. (5) and (6) and (7). Note that the theory predicts the two peaks which are associated with the micro-melting or micro-freezing of the clusters of large and small particles respectively. The magnitude of the peaks is too high, reflecting terms missing in the simple approach, like the effect of anharmonicity at the lowest temperatures which are negative, tending to decrease the height of the low-temperature peak.](image)

In terms of these objects we can rewrite

$$v = v_c(P, T) + \Delta v^c(1 - p_w^c) + \Delta v^s(1 - p_w^s) \quad (9),$$

$$\left(\frac{\partial v}{\partial P}\right)_T = \left(\frac{\partial v_c}{\partial P}\right)_T - \Delta v^c \left(\frac{\partial p_w^c}{\partial P}\right)_T - \Delta v^s \left(\frac{\partial p_w^s}{\partial P}\right)_T. \quad (10)$$

To compute the temperature dependence of $\left(\frac{\partial v}{\partial P}\right)_T$ we need first to determine its $T \rightarrow 0$ limit, which is determined by the first term on the RHS of Eq. (9) as the other terms on the RHS decay exponentially fast when $T \rightarrow 0$. Since we have already exact results for the bulk modulus for the present model, we return to Eqs. (3) and (4). We know on the one hand that $\lim_{T \rightarrow 0} C_v = 2$ and that $\langle U \rangle / N \approx 2.94$ over the whole interesting temperature range, cf. [19]. The compressibility $\kappa$ is related to the bulk modulus via $\kappa = -\left(\frac{\partial v}{\partial P}\right)_T / v = 1 / K$ and therefore $\left(\frac{\partial v}{\partial P}\right)_T \approx -1/(123.5 - 35T)$ is easily estimated as $T \rightarrow 0$. For simplicity we will use this approximation up to $T \approx 0.5$.

Having all the ingredients we can compute $C_v / N$. The parameters used were estimated from the numerical simulation and are summarized in Table I. Since the aim of this subsection is only semi-quantitative, we do not make any attempt of parameter fitting, and show the result of the calculation in Fig. 3.

Indeed, the theoretical calculation exhibits the existence of two, rather than one, specific heat peaks. We can now explain the origin of the peaks as resulting from the derivatives $\left(\frac{\partial p_w^c}{\partial P}\right)_T$ and $\left(\frac{\partial p_w^s}{\partial P}\right)_T$. These derivatives change most abruptly when the micro-clusters form (or dissolve), each at a specific temperature determined by
(\frac{h_w^s - h_s^c}{\ln g_w^c} \quad \text{and} \quad \frac{h_w^l - h_c^l}{\ln g_w^l}). \ Note\ that\ there\ can\ be\ pressures\ (both\ upper\ and\ lower\ boundaries)\ where\ the\ the\ sign\ of\ \( (h_w^s - h_s^c) \) or \( (h_w^l - h_c^l) \) change sign and the peak can be lost.

In summary, we have presented a simulational discovery of an unexpected second peak in the temperature dependence of the specific heat of a popular model of glass-formation. This discovery means that the universal expectation of seeing a single “specific heat peak” should be seriously revised. As there are two peaks in this examples, other examples may have multiple peaks or one peak. Even in this system at a different pressure the two peaks may merge, giving the appearance of a single peak. We have also presented a detailed explanation of the existence of the two peaks, based on an approximate equation of state that we have derived on the basis of statistical mechanics. Indeed, it is not difficult to explain the two peaks in terms of the effects of micro-melting of clusters of small and than of large particles when the temperature is increased. The important consequence is, however, that no universality is expected for the thermodynamics properties of different glass formers.

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