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Entropy–structure relations in amorphous materials

S Baer

Department of Physical Chemistry, The Hebrew University, Jerusalem 91904, Israel

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Abstract. It is suggested that a generalisation of a variational relation between the equilibrium free energy and the pair potential also holds for changes of the system along paths of non-equilibrium states. Combined with a parametrised model for the radial distribution function, this relation leads to an expression for the configurational entropy of an amorphous phase in terms of empirically determined radial distributions and a given pair potential. It is applied in combination with the 'structural diffusion' model to computer simulated amorphous aluminium, using recently determined model parameters from the normal liquid down to the amorphous solid at 273 K. The entropy difference between the liquid at melting point and the amorphous solid is estimated to be of the order of the entropy of melting, implying a negligible residual entropy. The temperature dependence of the structural diffusion coefficient, as determined from structural data, exhibits a glass transition of the amorphous system.

1. Introduction

All non-crystalline materials are expected to possess a positive ('residual') entropy in the low temperature limit $T \rightarrow 0$. This follows from general statistical mechanical considerations if we accept the assumption that such materials can be represented by a fixed distribution of systems over a large number of different 'frozen-in' disordered states (Mazo 1963, Jäckle 1981, 1984; for an early application to spin glasses, see e.g. Brout 1959).

Experimentally, the existence of a residual entropy has been verified for glasses where calorimetric measurements of entropy change can be performed by heating the material along a path of macroscopic states from a low T up to a state of internal thermodynamic equilibrium, say up to the melting point T_m . More correctly, such a path is not well defined over a small temperature interval around the glass transition temperature T_g , but in all studied cases this ambiguity has been found to cause only a small error in the measured entropy change (Jäckle 1981, 1984). However, calorimetric measurements are not always applicable to amorphous materials such as metal glasses obtained by methods such as splat cooling, chemical and vapour deposition or sputtering (see e.g. Chaudhari and Turnbull 1978), where the material cannot be heated reversibly through a glass transition temperature.

A theoretical evaluation of the residual entropy is possible in principle provided the distribution of the frozen-in states of the system is known. In practice, such a distribution—compatible with an ensemble over a complete orthonormal set of quantum states—can be calculated only for lattice systems where an enumeration of different

configurations can be obtained by actual counting of all possible ‘occupation states’ for each site or elementary unit of the lattice. Known examples are the calculated entropy of disordered mixed crystals (Einstein 1914), ice Ih (Pauling 1935), network models of vitreous silica (Bell and Dean 1968), lattice models of polymeric glasses (Gutzow 1962), etc.

However, calculation of the entropies of systems such as assemblies of hard- or soft-core spheres, which have a continuous configuration space, presents considerable difficulties. Nevertheless, we will show in the following how experimental structure data are related to the distribution of frozen-in states in a way that provides a basis for the calculation of the residual (configurational) entropy of amorphous materials.

2. Constraints and variational relations

Formally, a system in a non-equilibrium state can always be viewed as a system in equilibrium under the constraint of certain fictitious external forces (Morita 1965). This follows from the principle of maximum entropy with constraints, which by the method of Lagrange multipliers produces the corresponding external potentials. Thus, let ξ enumerate the sets of frozen-in states or configurations, given with probabilities p_ξ , and let s enumerate the states of the system within each configuration, with $E_{\xi s}$ the corresponding energies. The p_ξ being fixed but the states s being otherwise in thermal equilibrium we have

$$p_\xi = (Q_\xi/Q) e^{-\beta\psi_\xi} \quad \beta = (k_B T)^{-1}$$

where the ψ_ξ are the external potentials of the fictitious constraining forces

$$Q_\xi = \sum_s \exp(-\beta E_{\xi s})$$

and

$$Q = \sum_{\xi, s} \exp[-\beta(\psi_\xi + E_{\xi s})] \quad (1)$$

is the generalised partition function of the system, related to the free energy of the system, F , by $\beta F = -\log Q$.

Without knowing the ψ_ξ explicitly, we can make certain general assumptions about their nature. If we view the quenching from a liquid to a glass as a process producing constraints on molecular pair geometries, or more generally, bounds on pair potential energies relative to the thermal energy $k_B T$, we can suggest that the configurational part of the energies of the system be presented as a sum of pair contributions

$$\beta(\psi_\xi + E_{\xi s}) \rightarrow \sum_{i < j} \varphi(r_{ij}) \quad (2)$$

where the pair function $\varphi(r)$ can be related to an effective pair potential $u(r)$ by

$$\varphi(r) = \beta u(r). \quad (3)$$

Assuming (2), we have disregarded possible contributions of many body terms to the constraining field and have dumped all constraints into the pair function $\varphi(r)$, or effective pair potential $u(r)$.

It follows from (2) that the configurational partition function, written in the classical form

$$Q = (N!)^{-1} \int \dots \int \exp\left(-\sum_{i<j} \varphi(r_{ij})\right) d\mathbf{r}_1 \dots d\mathbf{r}_N \quad (4)$$

has the same functional dependence on the pair potential, whether the system is in free or in constrained thermal equilibrium. Furthermore, this holds also for the variational relation (see e.g. Stell 1976)

$$\delta(\beta F) = \frac{1}{2}N \int \rho g(r, [\varphi]) \delta\varphi(r) d^3r \quad (5)$$

where $[\varphi]$ denotes the functional dependence of the radial distribution $g(r)$ on φ .

Relation (5) holds necessarily for any variation $\delta\varphi$ corresponding to a variation in the external field ψ_{ξ} or in T or in both. Thus, we can determine the variation of βF along any path traversed by the system, whether in or out of equilibrium, provided we know the effective pair potential and can follow $g(r)$ along this path. This becomes feasible in particular if we can construct a model of $g(r)$, parametrised with a small set of parameters, and express the constrained functional variation $\delta\varphi$ in terms of variations of these parameters.

3. The structural diffusion model

The structural diffusion model (Baer 1977, 1978, 1987) provides a very useful example of a concise parametrisation of $g(r)$. In this model the radial distribution is given explicitly in terms of a virtual lattice L in a 3-dimensional (or higher-dimensional (Baer 1987)) 'structure space' associated with the local atomic structure and a 'width' function $W(r)$ characterising the loss of coherence between local structures at different points in space. In the simplest version of the model it is given by

$$W(r) = \begin{cases} D(r - r_0) & r > r_0 \\ 0 & r < 0 \end{cases} \quad (6)$$

where r_0 is an exclusion diameter and D is a 'structural diffusion' coefficient measuring the radial evolution of a diffusion-like process in structure space. The derived radial distribution function has two equivalent representations. One is a sum over the points of the reciprocal lattice to L

$$g(r) = \sum_{\nu} C_{\nu} e^{-W b_{\nu}^2} (\sin b_{\nu} r) / b_{\nu} r. \quad (7)$$

The other is a sum over the points of L

$$\rho g(r) = (4\pi W)^{-1/2} \sum_{\mu} (4\pi r a_{\mu})^{-1} \{\exp[-(r - a_{\mu})^2 / 4W] + \exp[-(r + a_{\mu})^2 / 4W]\}. \quad (7a)$$

From (7a) it is clear that the short-range peaks of $g(r)$, positioned around the a_{μ} each have a dispersion of order $2W(a_{\mu})$. The transformation between (7) and (7a) is given by the Poisson sum formula (Baer 1977).

The parameters implied in W and L can be varied so as to achieve a good fit of (7) with empirically obtained radial distribution functions of any condensed system. In

principle (7) becomes asymptotically exact in the limit of L having a very large unit cell (encompassing the entire bulk system) and D becoming very small (reducing $g(r)$ to a sum of δ -functions). In practice, a good fit is obtained with very simple lattices. An example of such a fit is given by Lopez and Silbert (1989) who used one and the same L (a distorted FCC lattice) and a fixed r_0 together with a variable $D = D(T)$ to obtain a good fit of (7) to empirical $g(r)$ data from aluminium over a range of 1000 K, from the normal liquid down through the supercooled liquid to a quenched amorphous phase (Smolander 1985, Waseda 1980). Over this range they find

$$\log(D/D_0) = \alpha T. \quad (8)$$

4. Entropy change and variation of $g(r)$

The variation of D over the given range of temperatures defines a path from the stable liquid to the metastable amorphous phase. Along this path we can set $g(r) \equiv g(r, D)$, $\varphi(r) \equiv \varphi(r, D)$ and performing the variation (5) between two states (1 and 2) on the path, we obtain

$$\begin{aligned} (\beta F)_2 - (\beta F)_1 &= \frac{1}{2}N \int_1^2 dD \int \rho g(r, D) \frac{\partial \varphi(r, D)}{\partial D} d^3r \\ &= \frac{1}{2}N \left[\int \rho g(r, D) \varphi(r, D) d^3r \right]_1^2 \\ &\quad - \frac{1}{2}N \int_1^2 dD \int \varphi(r, D) \frac{\partial \rho g(r, D)}{\partial D} d^3r. \end{aligned} \quad (9)$$

The second equality in (9) follows through integration by parts. The first term on the RHS of this equality is seen by (3) to be $(\beta E)_2 - (\beta E)_1$ (E —a configurational energy) and comparing with the LHS we obtain for the configurational entropy change

$$\frac{\Delta S}{k_B} = \frac{1}{2}N \int_1^2 dD \int \varphi(r, D) \frac{\partial \rho g(r, D)}{\partial D} d^3r. \quad (10)$$

Note that (10) holds for both a constant volume and a constant pressure change with negligible error, because of the negligible difference between energy and enthalpy changes in a condensed system at low pressures.

The path defined in (10) by variation in D can be understood in a more general sense as including possible simultaneous variations of the lattice L or even of the effective pair potential. Thus, in addition to the path leading to the supercooled liquid–quenched solid regime, (10) can also include, for example, the isothermal change of freezing at T_m , where D changes from $D = D_1 > 0$ to $D = 0$ and L changes from the virtual lattice L_1 of the liquid to the true crystalline lattice, L_c . For this process, which is free of any external constraints, we can put $\varphi(r) = u(r)/k_B T_m$. Hence the entropy change at melting becomes

$$\Delta S_m = \frac{\Delta E_m}{T_m} = \frac{1}{2T_m} N \int u(r) [\rho_l g_l(r) - \rho_c g_c(r)] d^3r \quad (11)$$

where the subscripts l and c refer to the liquid and crystalline phase, respectively. We see that here, given separate data for $g(r)$ in both phases, the parametrisation of $g(r)$ becomes redundant.

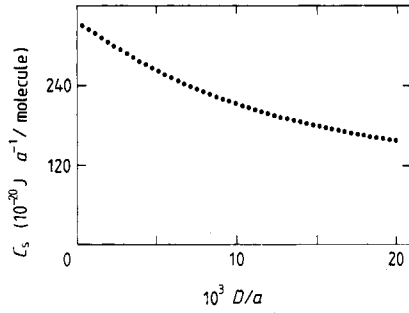


Figure 1. Plot of $C_s(D)$ ($J a^{-1}/\text{molecule}$) versus D/a (equation (12)) for amorphous Al (see § 4): L , D data from Lopez and Silbert (1989), pair potential from Rautioaho (1982). a is the unit length of L .

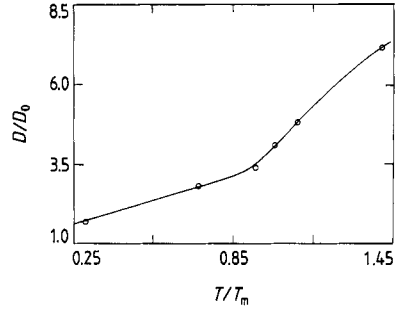


Figure 2. Plot of D/D_0 versus T/T_m : open circles data from Lopez and Silbert (1989); full curve, equation (15).

To obtain the value of the residual entropy of an amorphous material, we now substitute (7) (or (7a), depending on rates of convergence of the series) into (10) and obtain $\partial g(r, D)/\partial D$ analytically. Then, given L , r_0 and the parameters D_0 , α determining $D(T)$, the integrations in (10) can be performed numerically. Putting $\varphi(r) = \beta u(r)$ and performing the spatial integration first, we can define a generalised heat capacity $C_s(D)$ which is the differential increase in the energy (heat) content of the system per unit increase in D along the path connecting the amorphous and liquid state. Thus we have for the generalised specific heat per particle

$$C_s(D) = 2\pi \int_0^\infty u(r) \frac{\partial \rho g(r, D)}{\partial D} r^2 dr. \quad (12)$$

The values of this function, obtained for aluminium by numerical integration of the RHS of (12), using $u(r)$ obtained by Rautioaho (1982) from calculations based on pseudo-potential theory, are plotted in figure 1 for a range covering the entire set of simulation data from the amorphous solid to the liquid well above melting. We see here that $C_s(D)$ changes smoothly throughout this range.

Using (12) and (10) we now write the entropy change per particle in the form

$$\Delta S = \int_{D_1}^{D_2} \frac{C_s(D)}{T} dD. \quad (13)$$

We expect that on cooling an amorphous material down to $T = 0$, we still have $D(T = 0) \equiv D_0 > 0$ and correspondingly $C_s(D_0) > 0$. (From the particular method of parametrisation—the structural diffusion model—we also have $C_s(D = 0) \neq 0$, as can be seen from figure 1. (It is not clear whether this has any physical meaning or is an artefact of the model). Nevertheless, the true specific heat $C(T)$ must approach zero at $T \rightarrow 0$. By the relation

$$C(T) = C_s(D) dD/dT \quad (14)$$

we see that $C(T) \rightarrow 0$ provided $dD/dT \rightarrow 0$, and this implies that (8) cannot hold down to $T = 0$. Indeed $D(T)$ must level off near this limit, as was also noted by Lopez and Silbert. Moreover, examining the $D(T)$ data one can recognise two distinct sets of points fitting a smooth curve obtained by combination of two different functions of T (see figure

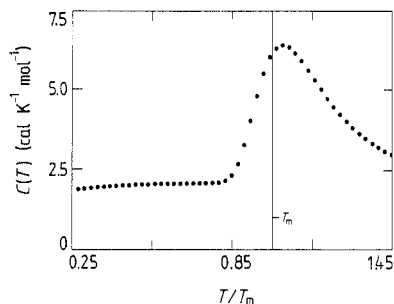


Figure 3. Plot of $C(T)$ ($\text{cal K}^{-1} \text{mol}^{-1}$) versus T/T_m for amorphous Al (see § 5). The vertical line is at $T = T_m$.

2) representing, respectively, a liquid and a solid-like branch. We have chosen as a fitting formula

$$D/D_0 = 1 + c(T/T_m)^{1.2} + A \exp[-bT_m/\Theta_\delta(T - T_g)] \quad (15)$$

where $D_0/a = 1.9 \times 10^{-3}$, $c = 2.2$, $A = 5.4$, $b = 0.4$, $T_g = 0.86 T_m$, given that the unit length of L is $a = 2.8 \text{ \AA}$ and the melting temperature $T_m = 933 \text{ K}$. $\Theta_\delta(x)$ is an integrated 'rounded' step function, obtained by integration of a Fermi-type distribution, and is defined by

$$\Theta_\delta(x) = \delta \log(1 + e^{x/\delta}). \quad (16)$$

5. Results and discussion

As seen from figure 2, a certain structural change is recognisable in the temperature range around $T = T_g$, and we can identify it with some kind of glass transition. This transition (corresponding also to a gradual change from supercooled liquid to amorphous solid) is characterised by a pronounced change in the slope dD/dT . This change can serve as a criterion for a glass transition. Compared with the Wendt–Abraham (WA) criterion (Wendt and Abraham 1978) of change of the slope of g_{\min}/g_{\max} , the ratio of the minimum to the maximum of $g(r)$, as a function of T , we see that both criteria are based on characteristics of the temperature dependence of $g(r)$. However, whereas the WA criterion is based on a very restricted, though pronounced feature of $g(r)$, the one offered here is based on the properties of the entire set of $g(r)$ values as expressed by the function $D(T)$.

Using (15) we obtain dD/dT analytically and hence, from (14), the numerically evaluated $C(T)$; these are plotted in figure 3 in the temperature range of the available $D(T)$ data. Having obtained $C(T)$, we integrate (13) between $T = 273 \text{ K}$ to $T = T_m$ so as to obtain the configurational entropy change of aluminium from the amorphous solid to the liquid melt. We find $\Delta S = 2.9 \text{ cal K}^{-1} \text{mol}^{-1}$, which is of the order of the entropy of melting $\Delta S_m = 2.73 \text{ cal K}^{-1} \text{mol}^{-1}$. This result is based on limited $D(T)$ data and the interpolation formula (15). If we could ignore the errors involved in our estimate, as well as the differences between the contribution of vibrations in the amorphous and crystalline phases, we could obtain the absolute entropy of amorphous aluminium at $T = 273 \text{ K}$ from $\Delta S_m - \Delta S$. However, this gives a negative value which is an indication of the magnitude of the errors involved.

One source of these errors may lie in the inaccuracy of our parametrisation, which does not reproduce $g(r)$ sufficiently faithfully over the wide range of temperatures

covered by the given data. This can be seen also from the obtained $C(T)$ curve (figure 3). Although a rise in the heat capacity with decreasing T is a general feature of supercooled liquids, we have here a rise of $C(T)$ to its maximum already around $T = T_m$. We believe that such errors could be rectified by a more refined treatment of the parametrisation of $g(r)$, which should take into account a possible change of the virtual lattice L and include also an r -independent but T -dependent Debye-Waller-type contribution to the width function $W(r)$ (equation (6)), due to the vibrational motion of the atoms.

Another possible error could arise from the fact that all foregoing calculations are based on a single effective pair-potential $u(r)$ used for both the liquid and amorphous phase (see (12)). However, by definition (3) the effective potential must include the effect of constraints imposed by the quenching process on the amorphous phase. It has been suggested by Jäckle (1989) that a 'constrained' effective potential can be related to an unconstrained potential via a certain fictive temperature T^* (Jäckle 1981): for $T \geq T^*$ an unconstrained potential $u(r)$ is effective while for $T \leq T^*$ a constrained potential (to be denoted by $\bar{u}(r)$) is effective and should correspond to a practically frozen configuration. By (4) and (5) this implies that $\varphi(r)$ should remain fixed in this temperature range. Thus, by (3)

$$\bar{u}(r) = k_B T \varphi(r) = (T/T^*)u(r) \quad T \leq T^*. \quad (17)$$

In terms of the parameter D we should have $D = D^* \equiv D(T^*)$ for $T \leq T^*$. Although not strictly correct, figure 2 confirms the trend towards a more slowly varying D in the low- T range. Similarly, even if (17) is not strictly correct, our findings conform with a constrained effective potential whose magnitude is smaller than that of the unconstrained $u(r)$. Substitution of $\bar{u}(r)$ from (17) for $u(r)$ in (12) will produce a smaller value for $C_s(D)$ in the low- T range and correspondingly (13) will produce a smaller value for ΔS , or equivalently a larger value for the absolute entropy at $T = 273$ K.

Nevertheless, we conclude from our result for ΔS of amorphous aluminium that its residual entropy (and possibly that of all close-packed one-component metal glasses) is negligibly small in comparison to the entropy of melting.

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