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Spatial energy and density fluctuations and the entropy of glass

Shalom Baer and Boaz Ilan

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

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Abstract. Non-zero *spatial* energy fluctuations, $\langle(\Delta E)^2\rangle > 0$, are characteristic of an amorphous material, and can be uniquely expressed in terms of molecular distributions and interaction potentials. An approximation relating $\langle(\Delta E)^2\rangle$ to the density fluctuations, $\langle(\Delta\rho)^2\rangle$, enables us to express the former in terms of pair distribution, $g(r)$ (or scattering function, $S(k)$), data and given pair potentials.

A modelling of $g(r)$ in a form $g(r) = g(r; L, D)$, where L is an optimal virtual lattice characterizing the local configurations of atoms and D is a ‘structural diffusion’ parameter specifying the degree of spatial decay of coherence between local structures in the amorphous system, provides expressions for the energy E and for $\langle(\Delta E)^2\rangle$ in terms of L and D . This enables us to obtain the entropy function $S = S(E)$ by integrating $\partial^2 S/\partial E^2 = \langle(\Delta E)^2\rangle^{-1}$ along a (virtual) path defined in parameter space $\{L, D\}$, connecting the amorphous state to an ordered state ($L, D = 0$). The method is illustrated on a model system of ions immersed in a uniform background of opposite charge (a model ‘metal’), by calculating its entropy as a function of D in a range corresponding to typical liquid and glass structures.

1. Introduction

An amorphous material is a disordered system [1] as far as atomic structure is concerned. This statement can be based on the following observations of ordered and disordered structures.

(i) In an ordered, spatially extended (i.e. macroscopic) system the spatial atomic arrangement in a *local* domain determines uniquely the atomic positions in the entire space. (This holds for any crystal, whether periodic or ‘quasicrystal’.) On the other hand, in a disordered system it is impossible to deduce the entire spatial atomic configuration from knowledge of the atomic positions in a finite domain, no matter how large.

(ii) The experimental observation of order and disorder involves scattering experiments which produce patterns of interfering waves scattered from a macroscopic number of different localities in the bulk material. These patterns show a set of sharp peaks for a crystal, but a diffuse structure for an amorphous material [2], which indicates that in the case of an ordered system (the crystal) there is full matching (‘coherence’) between spatial atomic positions in different localities, forming a global pattern (a lattice), whereas in the disordered system we obtain only a diffuse pattern of the local order, which has to be interpreted by a statistical model.

When considering the position of atoms in a solid, it is common practice to view the atoms as arranged in one particular configuration, corresponding to some energy minimum.

However, as shown above, viewing a macroscopic system as being in a single microstate is inconsistent with our concept of disorder and with experiment, which gives us only information concerning the local arrangement of atoms. Hence a macroscopic system must be viewed always as an *ensemble of local domains* (which can be large relative to atomic dimensions but small relative to the size of the system), each possessing a particular configuration of atoms.

In a disordered system the local domains are distributed over a large number of microstates and the entropy associated with this distribution is necessarily positive. It is the 'structural' (configurational) entropy of the system, $S = S_{str} > 0$, and is positive irrespective of whether the system is in a frozen-in glass state preventing transitions between different local structures, or whether it is a liquid in internal dynamic equilibrium. It has been claimed occasionally that a glass at absolute zero, $T = 0$, can be assigned a zero entropy [3, 4], and that the system gains its full entropy content when it is heated through the glass transition temperature T_g . However, in light of the foregoing considerations this approach seems an unnecessarily restrictive interpretation of empirical evidence and of the concept of entropy as a measure of disorder (see below).

Evaluation of the entropy requires knowledge of the distribution of local domains over a set of microstates. Given the probabilities $\{p_j\}$ of microstates in the ensemble, a general expression for the entropy is

$$S = -k_B \sum_j p_j \log p_j \quad (1)$$

where the set $\{j\}$ of microstates must be defined in a way leading to correct correspondence with the quantum states of the system. To find this correspondence is not trivial even in the simple case of a microcanonical ensemble, equal probabilities for all microstates within a given narrow interval of energy E : there is no clear way of counting discrete microstates in a simple liquid or glass where the atoms are distributed continuously in configuration space [4]. (The classical statistical formulae for such systems give $S \rightarrow -\infty$ in the dense packed limit.)

In the following we choose to evaluate the entropy of a condensed amorphous system by a route which avoids the necessity of direct knowledge of the distribution of microstates of the system in a given energy interval. Instead, it is based only on experimental data of molecular distributions and on a knowledge of the molecular interaction potentials.

2. Entropy and spatial energy fluctuations

Experimentally, the entropy is determined normally by calorimetry, by following the heat capacity along a reversible path from the given state of the system to a reference state where the entropy is known, which can be either the crystalline state at $T = 0$, where $S = 0$, or the gaseous state, where exact statistical formulae for the entropy are available (taking into account the relevant internal degrees of freedom of the molecules). Heat capacity and temperature measurements involve energy exchange between the system and a heat bath. This process is related to basic statistical properties of the system. The heat capacity, C , is related directly to the energy fluctuations,

$$C = \frac{\langle(\Delta E)^2\rangle}{k_B T^2} \quad (2)$$

and the temperature, T , is expressible in terms of the entropy, given as a function of energy. We have the following relations (with S given in units of k_B):

$$S = S(E) \quad (3a)$$

$$\frac{\partial S}{\partial E} = \frac{1}{k_B T} \equiv \beta \quad (3b)$$

$$\frac{\partial E}{\partial \beta} = -\langle(\Delta E)^2\rangle \quad \frac{\partial^2 S}{\partial E^2} = -\frac{1}{\langle(\Delta E)^2\rangle}. \quad (3c)$$

These equations follow from a representation of the macroscopic system by a canonical ensemble. The latter is derived [5] by choosing in (1) for the microstates $\{j\}$ eigenstates of the energy, and maximizing S by varying the $\{p_j\}$, subject to the constraint of a given average energy E ,

$$E = \sum_j p_j E_j.$$

The canonical ensemble can be viewed as representing a compound system consisting of a large number of subsystems which are themselves macroscopic, i.e. the total energy of the system is a sum of the energies of the subsystems. This is valid whether the subsystems are in mutual thermal equilibrium or not, as is the case in glass. If the subsystems are in complete internal equilibrium, each can be represented by a microcanonical ensemble with equal weights assigned to all states within a narrow energy interval $E < E_j < E + \Delta$ (for Δ small compared to E). The canonical ensemble then leads to the Boltzmann distribution $p(E) \propto \Omega(E) e^{-\beta E}$, with β a corresponding Lagrange multiplier. Since the system is macroscopic, the number of states, $\Omega(E)$, in the energy interval (Δ) increases exponentially with E , from which it follows that S is an extensive and β an intensive property of the system.

Similarly, a glass can be represented by a microcanonical ensemble which is *restricted by additional constraints*. Although the nature of these constraints is not well understood, it is expected that they can be represented by a set of parameters, say g , characterizing the states of the system in addition to the energy. Hence a *restricted* canonical ensemble can be derived by the same variational procedure as applied to the equilibrium system, but now keeping g constant, leading to the Boltzmann distribution $p_g(E) \propto \Omega(E, g) e^{-\beta E}$, with $\Omega(E, g)$ the number of *accessible* states (smaller than $\Omega(E)$), and a corresponding Lagrange multiplier $\beta = \beta(E, g)$.

Thus, equations (3) are general relations which hold for any statistical ensemble representing a macroscopic physical system, whose energy is a sum of the energies of its subsystems and whose entropy is defined by (1) [5]. For glass, the derivatives in (3b) and (3c) are taken along a path of constant g through the point in (E, g) space.

In glass, the frozen-in state prevents transitions between different local structures, and thus no energy fluctuations can be monitored by a heat bath exchanging energy with the glass system. Consequently no ‘structural’ temperature or heat capacity can be measured directly and no quasireversible path through a sequence of glass structure states can be followed by calorimetry. Yet, a structural temperature $T = T_{str}$ and a heat capacity $C = C_{str}$ are now defined, via (3b) and (2) respectively, by the ensemble representing the glass in its particular frozen-in structure. Both quantities are obtained directly from the entropy function (3a).

We shall take (3c) as a starting point for the evaluation of the entropy. As will be shown below, $\langle(\Delta E)^2\rangle$ can be computed from pair distribution data and a given pair potential. This leads to an expression for $\langle(\Delta E)^2\rangle$ as a function of E , which enables in principle the integration of (3c).

3. Spatial energy fluctuations: an explicit expression

Viewing the macroscopic system as an ensemble of macroscopic subsystems, an expression for the spatial fluctuations of a local energy can be obtained in terms of molecular interaction potentials and low-order molecular distributions. In particular, when the molecules interact via a pair potential, $\varphi(r)$, the average interaction energy of N molecules is

$$E = \frac{1}{2} \left\langle \sum_{i \neq j} \varphi_{ij} \right\rangle = \frac{1}{2} \rho^2 \int \varphi(12) g(12) d1 d2 \quad (4)$$

and the energy fluctuations are given by [6]

$$\langle (\Delta E)^2 \rangle = \overline{E^2} - \bar{E}^2$$

where

$$\overline{E^2} = \frac{1}{4} \left\langle \sum_{i \neq j} \varphi_{ij} \sum_{k \neq l} \varphi_{kl} \right\rangle = \frac{1}{4} \left\langle \sum_{i \neq j \neq k \neq l} \varphi_{ij} \varphi_{kl} \right\rangle + \left\langle \sum_{i \neq j \neq l} \varphi_{ij} \varphi_{il} \right\rangle + \frac{1}{2} \left\langle \sum_{i \neq j} \varphi_{ij}^2 \right\rangle \quad (5a)$$

$$\bar{E}^2 = \frac{1}{4} \left\langle \sum_{i \neq j} \varphi_{ij} \right\rangle \left\langle \sum_{k \neq l} \varphi_{kl} \right\rangle. \quad (5b)$$

Hence

$$\begin{aligned} \langle (\Delta E)^2 \rangle &= \frac{1}{4} \rho^4 \int \varphi(12) \varphi(34) [g^{(4)}(1234) - g(12)g(34)] d1 d2 d3 d4 \\ &\quad + \rho^3 \int \varphi(12) \varphi(13) g^{(3)}(123) d1 d2 d3 + \frac{1}{2} \rho^2 \int [\varphi(12)]^2 g(12) d1 d2. \end{aligned} \quad (5c)$$

The summations in (4) and (5a, b) are over the N particles of the system and the different terms of the rhs of (5a) result from selection according to coincidence between different summation indices. A shorthand notation numbering the respective molecular coordinates and volume elements has been used: g , $g^{(3)}$ and $g^{(4)}$ are respectively, pair, triplet and quadruplet correlation functions, and ρ is the average molecular density.

In summary, both the energy E and the energy fluctuations $\langle (\Delta E)^2 \rangle$ in a macroscopic system are uniquely determined by the pair potential φ and low-order molecular distributions $g^{(k)}$ ($k \leq 4$) characteristic of the system, which can be frozen in or in dynamic internal equilibrium.

4. Reduction of molecular distributions to a set of parameters

If we can find a path (a sequence of closely neighbouring states) along which we can follow molecular distributions, and if this path connects the glass state with a state of known entropy, then, given the potential φ , both E and $\langle (\Delta E)^2 \rangle$ can be evaluated along the path and it is possible in principle to evaluate S for the glass by integrating (3c). A modelling of molecular distributions by parametrized analytic functions has suggested how such a path can be constructed.

The model used here is the structural diffusion model (SDM [7]), based on viewing the variations in the atomic configurations at different localities as a random *spatial* process. In its simplest version the model relates the local atomic configurations to a lattice L subject to random displacements, $s = s(\mathbf{r})$, in space. The local density, which for a given configuration of N particles, $\mathbf{r}^N \equiv (\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$, is given by

$$\rho(\mathbf{r}) \equiv \rho(\mathbf{r}; \mathbf{r}^N) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) \quad (6)$$

is now approximated by

$$\rho(\mathbf{r}) = \rho(\mathbf{r}; \mathbf{s}) = \sum_{\mu, \sigma} \delta(\mathbf{r} - \mathbf{a}_{\mu, \sigma} - \mathbf{s}) \tag{7}$$

where the double sum runs over all lattice points, $\mathbf{a}_{\mu, \sigma} = \mathbf{a}_{\mu} + \mathbf{a}_{\sigma}$, of L ; the μ -sum counts the position vectors \mathbf{a}_{μ} of all unit cells of L , and $\sigma = 1, \dots, n$ counts the points \mathbf{a}_{σ} inside one unit cell. The average density $\rho = \langle \rho(\mathbf{r}; \mathbf{s}) \rangle$ is obtained by applying the operation $(1/v) \int_v d^3s$ to (7), with v being the volume of the unit cell of L . The random process $\mathbf{s}(\mathbf{r})$ is chosen to be a radially evolving diffusion in ‘structure’ space $\{\mathbf{s}\}$. Considering a pair of points in space, $\mathbf{r}_1, \mathbf{r}_2$, and the respective random displacements, $\mathbf{s}_1, \mathbf{s}_2$, the conditional probability density function, $P(\mathbf{s}|\mathbf{r})$, $r = |\mathbf{r}_1 - \mathbf{r}_2|$, $\mathbf{s} = \mathbf{s}_1 - \mathbf{s}_2$, is assumed to obey for large r a diffusion type equation,

$$\frac{\partial P}{\partial r} = D \nabla_s^2 P \tag{8}$$

where D is a ‘structural diffusion’ coefficient. Solving (8), $P(\mathbf{s}|\mathbf{r})$ is obtained as an analytic function (a theta-type series), depending parametrically on L and D , which can be applied directly to evaluate the average

$$\langle \rho(\mathbf{r}_1)\rho(\mathbf{r}_2) \rangle = \rho^2 g(r)$$

with the resulting radial pair distribution $g(r)$ given by

$$g(r) = g(r; L, D) = \sum_{\nu} C_{\nu} e^{-W b_{\nu}^2} \langle e^{i\mathbf{b}_{\nu} \cdot \mathbf{r}} \rangle_0 \quad C_{\nu} = \left| \frac{1}{n} \sum_{\sigma} e^{i\mathbf{b}_{\nu} \cdot \mathbf{a}_{\sigma}} \right|^2. \tag{9}$$

Here the ν -sum extends over all points, \mathbf{b}_{ν} , of the reciprocal lattice L^* , and the σ -sum runs over all points in the unit cell of L . The brackets $\langle \rangle_0$ denote averaging over all orientations of L , or of \mathbf{r} . $W = W(r)$ has the asymptotic forms $W \sim Dr$, $r \rightarrow \infty$, and $W'(r) \rightarrow 0$, $r \rightarrow 0$. For practical reasons of convergence at small r the particular form

$$W = W_0 + D \left(\sqrt{r^2 + r_0^2} - r_0 \right) \tag{10}$$

is used. Using (9), all functionals of $g(r)$ considered in the present discussion can be easily evaluated.

It has been shown [7] that L and D can be chosen optimally so as to reproduce $g(r)$ data for liquids to a high degree of accuracy. Moreover, the optimization is asymptotically exact: the fitting $g(r) = g(r; L, D)$ should improve with increasing complexity of L (i.e. increasing n), accompanied by a decreasing optimal value of D . In the limit of $L = L_N$ with a large number N (say ≈ 1000) of points in the unit cell, and $D \approx 0$, the optimal $g(r; L, D)$ coincides with $g(r)$ obtained by the reverse Monte Carlo method [8]. Yet, even with a low complexity $L = L_n$, with $n = 1, 2, 4$, very good fits [7] to given $g(r)$ data are obtained.

Consequently, the structure of a system in any given state can be represented by a point in parameter space $\{L, D\}$. Given an optimal L and $D = D_g$, we can define a path in the $\{L, D\}$ space, connecting the glass state to an ordered state L ($D = 0$), by the interval (see figure 1)

$$0 \leq D \leq D_g \quad L \text{ fixed.} \tag{11}$$

This path need not be realized by an actual quasistatic process, but can be considered as a virtual path. For any value of D within the interval (11) the energy can be evaluated by substituting $g(r; L, D)$ for $g(r)$ in (4). Thus,

$$E = E(L, D) = \frac{1}{2} \rho^2 V \int \varphi(r) g(r; L, D) d^3r. \tag{4'}$$

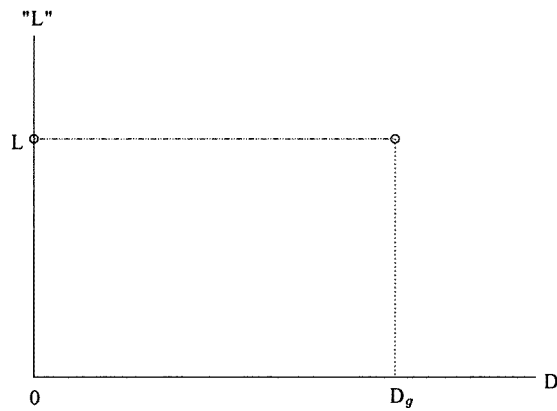


Figure 1. A path in $\{L, D\}$ parameter space connecting an amorphous state with a virtual crystalline state.

This equation has been used to evaluate numerically [10] the energy $E(L, D)$ along (11). It was found that $E(L, D)$ is a smooth function of D which can be accurately represented by a simple rational ($[1/2]$ or $[2/3]$) approximant [10] over the entire interval. It was used to evaluate lattice sums (Coulomb energies in particular) by extrapolation to $D \rightarrow 0$.

The structural diffusion process as defined by (8) can be generalized to a multi-theta process, from which analytic expressions similar to (9) can be obtained [9] for the higher-order correlation functions $g^{(k)} = g^{(k)}(r^{(k)}; L, D)$, $k > 2$. These involve $(k - 1)$ -fold sums over lattice points. In the same way that a multi-Gaussian process is uniquely determined by the pair distribution, the single Gaussian, so a multi-theta process can be fully expressed in terms of the parameters (L, D) determining the single theta-type pair distribution.

Using the appropriate $g^{(k)}$ functions, an expression corresponding to (4') can be obtained for $\langle(\Delta E)^2\rangle = \langle(\Delta E)^2\rangle(L, D)$ from (5). However, to avoid using higher-order $g^{(k)}$, which are increasingly cumbersome to evaluate for $k > 2$, use is made in the following of an approximate expression for $\langle(\Delta E)^2\rangle$ depending only on $g(r)$.

5. Approximate $\langle(\Delta E)^2\rangle$ in terms of $\langle(\Delta\rho)^2\rangle$

Given a particular configuration of N particles, $\mathbf{r}^N \equiv (\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$, the interaction energy can be decomposed formally into a sum of single-particle terms

$$E \equiv E(\mathbf{r}^N) = \sum_i e_i(\mathbf{r}^N) \quad (12)$$

where

$$e_i(\mathbf{r}^N) = \frac{1}{2} \sum_{j(\neq i)} \varphi(\mathbf{r}_{ij}). \quad (13)$$

Defining the local energy density by

$$e(\mathbf{r}) = \sum_i \delta(\mathbf{r} - \mathbf{r}_i) e_i(\mathbf{r}^N) \quad (14)$$

we now make the approximation

$$e(\mathbf{r}) = \rho(\mathbf{r}) \bar{e} \quad (15)$$

where $\bar{e} = E/N$ is an average energy per particle. This approximation implies that $e_i(\mathbf{r}^N) = \bar{e}$ for all i , irrespective of the particular configuration (\mathbf{r}^N). Thus, fluctuations in the energy density at a point \mathbf{r} result only from fluctuations in the particle density at \mathbf{r} , ignoring structural fluctuations in a more distant neighbourhood. Hence, with $\langle e(\mathbf{r}) \rangle = \rho\bar{e}$, we have

$$\Delta e(\mathbf{r}) = e(\mathbf{r}) - \langle e(\mathbf{r}) \rangle = \Delta\rho(\mathbf{r})\bar{e} \quad (16)$$

$$\begin{aligned} \langle (\Delta E)^2 \rangle &= \int \langle \Delta e(1)\Delta e(2) \rangle d1 d2 = \bar{e}^2 \int \langle \Delta\rho(1)\Delta\rho(2) \rangle d1 d2 \\ &= N(E/N)^2 \int [G(r) - \rho] d^3r \end{aligned} \quad (17)$$

where $G(r) = G(r, t = 0) = \delta(r) + \rho g(r)$ is the van Hove correlation function at $t = 0$. Using the structure factor (scattering function),

$$F(k) = 1 + \rho \int [g(r) - 1] e^{ik \cdot r} d^3r \quad (18)$$

we can write (17) in the form

$$\langle (\Delta E)^2 \rangle = N(E/N)^2 F(0). \quad (17')$$

(17) shows how the spatial energy fluctuations in a glass can be obtained directly from scattering data. Making use of the analytic form (9) of $g(r) = g(r; L, D)$, the integration in (18) can be performed analytically, and an accurate evaluation of $F(k) = F(k; L, D)$ for small k values, including $F(0) = F(k \rightarrow 0)$, is possible. Hence, (17) together with (4') gives an estimate of $\langle (\Delta E)^2 \rangle$.

The density fluctuations are related to macroscopic properties of the system by $F(0) = k_B T \partial\rho/\partial P$. This relation holds provided a structural temperature, T_{str} , is substituted for T . Estimating $T_{str} \sim T_g$, a glass transition temperature, and given the compressibility, $\kappa = \rho^{-1} \partial\rho/\partial P$, of the glass, the following relation should hold between experimentally obtainable quantities:

$$k_B T_g = F(0)/\kappa\rho \quad (19)$$

which implies that $F(0)/\kappa\rho$ remains constant for all thermally measured $T \leq T_g$, provided the approximation (15) does not involve a large error. Experimentally (19) might be difficult to check since $F(0)$ and κ are small and large errors are involved in particular in the determination of $F(0)$ by extrapolation from scattering data.

Making use of (17') and (19) one can obtain from (2) the structural heat capacity,

$$C_{str} = N \left(\frac{E}{N} \right)^2 \frac{\rho\kappa}{T_g}. \quad (20)$$

(20) is probably a somewhat low estimate of C_{str} because of the approximation (15) involved, which omits certain contributions of fluctuations in positions of triplets and quartets of molecules to the energy fluctuations.

6. Particular solutions of (3c), $\partial^2 S/\partial E^2 = -\langle (\Delta E)^2 \rangle^{-1}$

In order to evaluate the entropy $S(E) = S(L, E)$ by integrating (3c) along the path (11), the following boundary conditions at the end point $D = 0$ are required:

$$\lim_{E \rightarrow E_0} S(E) = 0 \quad (21a)$$

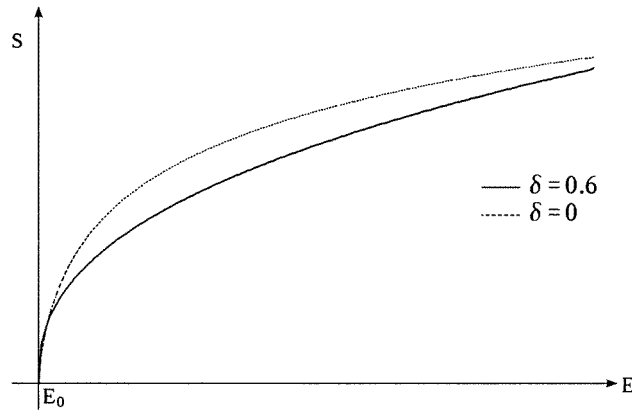


Figure 2. Particular solutions $S = S(E)$ of (23).

$$\lim_{E \rightarrow E_0} \frac{\partial S}{\partial E} = \lim_{E \rightarrow E_0} \beta(E) = \infty \quad (21b)$$

$$\lim_{E \rightarrow E_0} \frac{\partial^2 S}{\partial E^2} = - \lim_{E \rightarrow E_0} \frac{1}{\langle (\Delta E)^2 \rangle} = -\infty \quad (21c)$$

where $E_0 = E(L, D = 0)$. Conditions (21a) and (21b) are a restatement of the third law. The condition $\lim_{E \rightarrow E_0} \langle (\Delta E)^2 \rangle = 0$ follows from the condition on the heat capacity, $\lim_{E \rightarrow E_0} C = 0$. Moreover, from (2) it follows that $\langle (\Delta E)^2 \rangle \rightarrow 0$ faster than $\beta^{-2} \sim T^2$.

Thus, by (21), $S(E)$ has an infinite slope and an infinite negative curvature at the ground level limit. Hence, integrating (3c) we expect $S(E)$ to have qualitatively the form of the curves given in figure 2.

Assuming a simple power law

$$\langle (\Delta E)^2 \rangle \sim (E - E_0)^{1+\delta} \quad (22)$$

the following functional form of $S(E)$ results:

$$\frac{\partial^2 S}{\partial E^2} = - \frac{a}{(E - E_0)^{1+\delta}} \quad (23a)$$

$$\frac{\partial S}{\partial E} = \frac{a}{\delta(E - E_0)^\delta} \quad (23b)$$

$$S = a \frac{(E - E_0)^{1-\delta}}{\delta(1-\delta)} \quad (23c)$$

$$0 < \delta < 1 \quad a > 0.$$

The case of $\delta = 0$ can be included as well in (22) (see figure 2), but to ensure in this case $\partial S / \partial E > 0$ for all allowed energies $E_0 < E < \infty$ we must add to (23a) a positive term which goes to zero in the limit $E \rightarrow \infty$ and preserves $\partial^2 S / \partial E^2 \sim -(E - E_0)^{-1}$ for $E \rightarrow E_0$. A simple choice is

$$\frac{\partial^2 S}{\partial E^2} = \frac{1}{E - E_0 + B} - \frac{a}{E - E_0} \quad B > 0 \quad (24)$$

which by (3c) gives

$$\langle (\Delta E)^2 \rangle = - \left(\frac{\partial^2 S}{\partial E^2} \right)^{-1} = (aB)^{-1} (E - E_0)(E - E_0 + B). \quad (25)$$

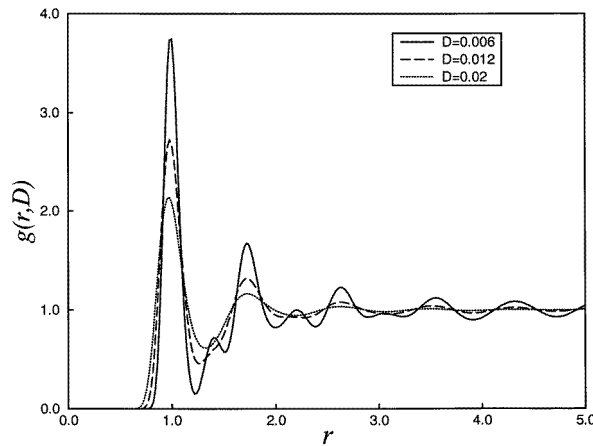


Figure 3. $g(r; L, D)$ a function of r for three D values (see the inset). $L = \text{fcc}$ ($r_0 = 1.0$, $W_0 = 10^{-4}$, see (10)).

Thus, the case $\delta = 0$ requires adding also a term quadratic in $E - E_0$ to (22). Integrating now (24) twice, taking into account the boundary conditions (21), we obtain

$$\frac{\partial S}{\partial E} = a \log \frac{E - E_0 + B}{E - E_0} \quad S = a\epsilon \log \frac{(M + J)^{M+J}}{M^M J^J} \quad M = \frac{E - E_0}{\epsilon}$$

$$J = \frac{B}{\epsilon}. \quad (26)$$

Having introduced the additional constant ϵ , we choose $\epsilon = k_B/a$ and approximate M and J by integers. This enables us to express $S(E)$ by a simple combinatorial formula,

$$S = k_B \log \binom{M + J}{J} \quad (26')$$

which suggests an interpretation in terms of boson statistics. Let ϵ be a quantum of excess (structural) energy, M the number of quanta and J the number of local groups of atoms which can sustain such quanta. Then the binomial coefficient in (26') is the total number of quantum states of the system. Clearly, such an interpretation can serve only as a hint to a possible connection between glass structure and energy, which takes into account the quantum constraint of a discrete state space.

7. Estimate of the entropy of a model liquid and glassy metal

As a more concrete example for evaluation of the entropy consider a system of charged particles, neutralized by a uniformly distributed opposite charge, interacting in addition to the Coulomb potential by an inverse power potential Ar^{-n} . We choose $L = \text{fcc}$ for the virtual lattice in $g(r; L, D)$ and make use of the representations of the Coulomb energy $E_a = E_a(D)$ and the inverse power repulsive energy $E_r = E_r(D)$ by rational approximants [10] in the range $0 < D < 0.02$, which corresponds to typical structures of liquid and amorphous metals (see figure 3). In addition we have constructed a rational approximant representation for the zero-scattering structure factor $F(0, D)$ (see table 1).

With the notation

$$E_{a0} = E_a(0) \quad E_{r0} = E_r(0) \quad e_0 = E_0/N \quad e_{a0} = E_{a0}/N \quad e_{r0} = E_{r0}/N$$

Table 1. Coefficients of rational approximants $y(D) = (p_0 + p_1D + p_2D^2)/(q_0 + q_1D + q_2D^2)$.

	p_0	p_1	p_2	q_0	q_1	q_2
e_a	-1.620 995	0.460 019	0.0	1.0	-0.283 564	5.452 831
e_r ($n = 6$)	14.451 106	107.139 6	0.0	1.0	-11.110 731	49.426 576
F	0.0	0.035 879	1.974 872	1.0	-18.914 906	0.0

$$u = (E - E_0)/N \quad u_a = (E_a - E_{a0})/N \quad u_r = (E_r - E_{r0})/N$$

and with the nearest-neighbour distance chosen to minimize the total lattice energy E_0 , we have

$$e_0 = e_{a0} + \gamma e_{r0} \quad u = u_a + \gamma u_r \quad \gamma = \frac{|e_{a0}|}{ne_{r0}} \quad (27)$$

and introducing the notation $f = \langle(\Delta E)^2\rangle/N$ for the reduced energy fluctuations, we have from (17')

$$f = (e_0 + u)^2 F(D). \quad (28)$$

Since $F(D) \equiv F(0, D)$ must be zero in the ordered system limit, $D \rightarrow 0$, we can put

$$f(D) = D\psi(D) \quad \psi(0) \neq 0. \quad (29)$$

Writing $s = S/k_B N$ for the reduced entropy, we have by (3c)

$$\frac{\partial^2 s}{\partial u^2} = -\frac{1}{f} \quad s = s(u). \quad (30)$$

Changing variables, (30) can be written in the form

$$\frac{\partial}{\partial D} \left(\frac{s'}{u'} \right) = -\frac{u'}{f} \quad s = s(D) \quad u = u(D). \quad (30')$$

Hence

$$\frac{s'}{u'} = -\int \frac{u'}{f} dD \quad s = -\int dD u' \int \frac{u'}{f} dD \quad (31)$$

where primes denote derivatives with respect to D . Substituting the given rational approximants for u and f , the integrations in (31) are straightforward. The two constants of integration of (31) can be determined from the zero-entropy condition at $u = 0$ and from the boundary condition

$$\beta \equiv s'(u) = s'(D)/u'(D) \rightarrow 0 \quad u \rightarrow \infty \quad (D \rightarrow \infty) \quad (32)$$

which is the limit of 'maximum disorder' (infinite temperature). However, the presently applied rational approximants for u and f have been designed to fit small- u data and are not consistent with (32). Neither do they comply with the condition (3c), $\beta'(u) = -[f(u)]^{-1}$, which implies that $\beta(u)$ is monotonically decreasing, nor with the stronger condition that $f(u)$ itself be monotonically increasing, possibly becoming infinite at the maximum-disorder limit. Nevertheless, we shall assume that practically $\beta \approx 0$ at some limit point $D = D_\infty$, where $f(D)$ reaches its maximum, and require instead of (32),

$$\beta = \beta(u) = s'(u) \rightarrow 0 \quad u \rightarrow u_\infty = u(D_\infty). \quad (32')$$

(For the high-temperature limit, see however the comments in section 9.)

In the following we adopt an integration procedure which enables also numerical integration of (31). We handle first the singularity in the integrand on the rhs of (31) by performing an integration over the interval (δ, D) :

$$s(D) = \lim_{\delta \rightarrow 0} \left\{ u(D) \frac{s'(\delta)}{u'(\delta)} - \int_{\delta}^D d\bar{D} u'(\bar{D}) \int_{\delta}^{\bar{D}} \frac{u'(\bar{D})}{f(\bar{D})} d\bar{D} \right\}. \tag{33}$$

Integrating (33) by parts,

$$s(D) = \lim_{\delta \rightarrow 0} \left\{ u(D) \frac{s'(\delta)}{u'(\delta)} - u(D) \int_{\delta}^D \frac{u'(\bar{D})}{f(\bar{D})} d\bar{D} + \int_{\delta}^D \frac{u(\bar{D})u'(\bar{D})}{f(\bar{D})} d\bar{D} \right\}. \tag{34}$$

The first term on the rhs of (34) has a singularity in the limit $\delta \rightarrow 0$, which must cancel with the singularity contained in the integral in the second term. Extracting this singularity from the integral and adding to the first term, we have, introducing the notation $\chi(D) = u'(D)/\psi(D)$,

$$s(D) = -\chi(0)u(D) \log D + cu(D) - u(D) \int_0^D [\chi(\bar{D}) - \chi(0)] \frac{d\bar{D}}{D} + \int_0^D u(\bar{D})\chi(\bar{D}) \frac{d\bar{D}}{D} \tag{35}$$

with

$$c = \lim_{\delta \rightarrow 0} \left\{ \frac{s'(\delta)}{u'(\delta)} + \chi(0) \log \delta \right\}. \tag{36}$$

Differentiating (35) and dividing by $u'(D)$, we have

$$\beta(u) = s'(u) = \frac{s'(D)}{u'(D)} = -\chi(0) \log D + c - \int_0^D [\chi(\bar{D}) - \chi(0)] \frac{d\bar{D}}{D} \tag{37}$$

and applying (32')

$$c = \chi(0) \log D_{\infty} + \int_0^{D_{\infty}} [\chi(\bar{D}) - \chi(0)] \frac{d\bar{D}}{D}. \tag{38}$$

Thus, substituting c from (38) into (35), we have

$$s(D) = u(D) \int_D^{D_{\infty}} \chi(\bar{D}) \frac{d\bar{D}}{D} + \int_0^D u(\bar{D})\chi(\bar{D}) \frac{d\bar{D}}{D}. \tag{35'}$$

The resulting numerical evaluation of the entropy from (35') is represented in figure 4. It shows e.g. that the entropy for a typical liquid structure ($D = 0.02$) is $s = 8.99$, whereas for a typical amorphous solid structure ($D = 0.006$) it is $s = 4.84$, i.e. almost half the liquid value. For comparison, the entropy of liquid Na is [12] $s = 8.70$ ($T = 473$ K).

8. The dependence of S and E on the complexity of L

Using two alternative model representations of $g(r)$, namely $g(r) = g(r; L_1, D_1)$ and $g(r) = g(r; L_n, D_n)$, where L_1 is a simple lattice choice while L_n is a complex one, i.e. having a larger unit cell with a larger base, L_n consists of a more densely spaced sequence of shells and correspondingly requires a smaller D in order to achieve the same dispersion of the peaks in $g(r)$, i.e. $D_n < D_1$. In the limit of L_n with a very large unit cell, D_n is expected to be very small. Although the model states (L_n, D_n) and (L_1, D_1) are macroscopically practically the same, the two ordered states $(L_n, 0)$ and $(L_1, 0)$ are macroscopically different, representing two different lattice structures. The total entropy change for both systems is the same:

$$S(L_n, 0) = S(L_1, 0) = 0 \quad S(L_n, D_n) \approx S(L_1, D_1)$$

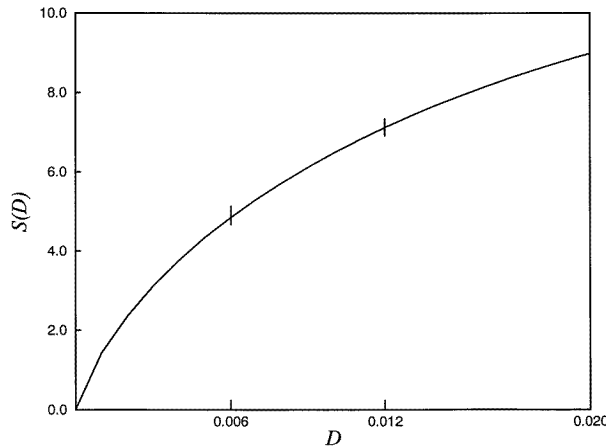


Figure 4. $S = S(L, D)$ as function of D from (35) for a model metal ($D_\infty = 0.052$). The bars on the curve delimit the section of the curve ($0.006 < D < 0.012$) to which the Chebyshev interpolation formula has been applied (see the text).

(see figure 5(a)). The entropy rise with increasing D is much faster in the complex system (L_n) than in the simple one (L_1). (A more complex L corresponds to a larger local domain (unit cell), and hence is closer to a globally ordered view of the system.) On the other hand, the energy $E(L) \equiv E(L, 0)$ approaches E_g with increasing complexity of L_n , thus differs little from $E(L, D)$ at high complexity ($E(L_n, D_n) \approx E(L_1, D_1)$) (see figure 5(b)).

The above considerations imply that all parameters appearing in the expression (23) for the entropy depend on the model choice of L . This includes in particular the exponent δ and a in (23), and B and a (or ϵ) in (25).

9. Comments

The energy E considered in sections 3–5 and 7, as well as the explicit calculation of its fluctuations, refer strictly to the potential energy U , but the systems considered are at such low temperatures that the thermal energy E_{th} of vibrations is assumed negligible compared to U . However, at higher temperatures the contribution of the thermal motion to the energy dispersion must be taken into account in all foregoing applications to the evaluation of $S(E)$. In the classical limit one can put for the total energy fluctuations

$$\langle (\Delta E)^2 \rangle = \langle (\Delta U)^2 \rangle + \langle (\Delta E_K)^2 \rangle \quad (39)$$

where $\langle (\Delta U)^2 \rangle$ and $\langle (\Delta E_K)^2 \rangle$ are the dispersion of the potential energy as calculated above in (17') and of the kinetic energy, respectively. Strictly, with

$$E = U + E_K \quad \Delta E = \Delta U + \Delta E_K \quad \Delta U = U - \langle U \rangle \quad \Delta E_K = E_K - \langle E_K \rangle$$

we have

$$\langle (\Delta E)^2 \rangle = \langle (\Delta U)^2 \rangle + \langle (\Delta E_K)^2 \rangle + \langle \Delta U \Delta E_K \rangle + \langle \Delta E_K \Delta U \rangle. \quad (40)$$

In the ordered ground state ($\langle E \rangle_0 \equiv E_0$) $\langle E^2 \rangle_0 = \langle E \rangle_0^2$, hence $\langle (\Delta E)^2 \rangle_0 = 0$. Thus the sum of the cross terms in (40) must be negative. In the classical limit they drop out, resulting in (39). Moreover, the cross terms seem to be negligible in disordered systems, where some

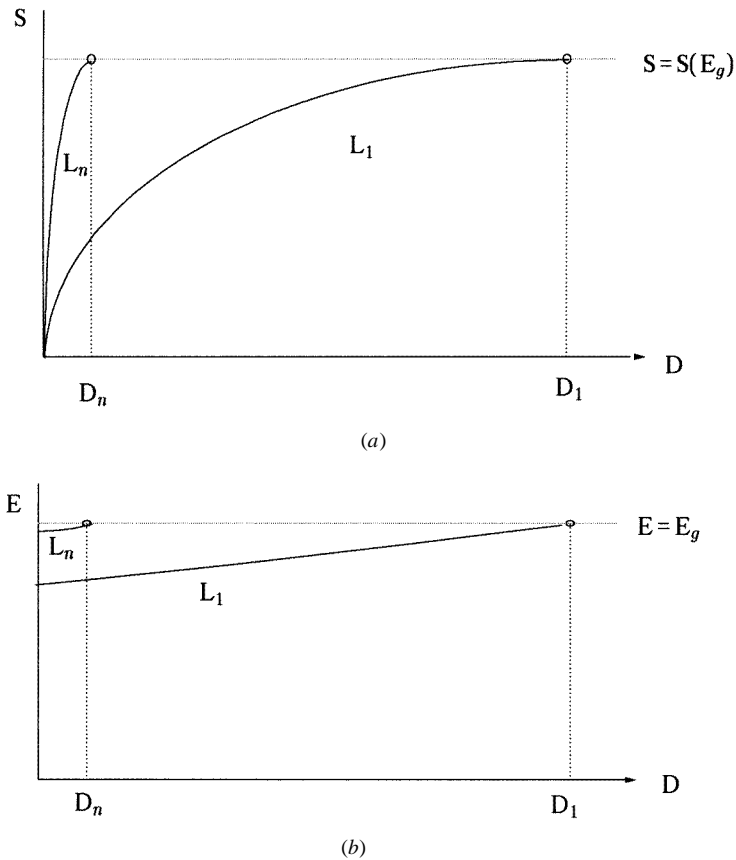


Figure 5. (a) $S = S(L, D)$ as function of D , connecting a glass state with an ordered state ($L, D = 0$), for a low and a high complexity L . (b) $E = E(L, D)$, as in (a).

kind of ‘random phase’ approximation is expected to hold. Note that in the classical gas limit the kinetic energy dispersion is given by

$$\langle(\Delta E)^2\rangle/N = \frac{2}{3}(E/N)^2$$

which, up to the factor $\frac{2}{3}$, coincides with (17’).

In the solid a distinction must be made between E_K and E_{th} . Strictly, the potential energy is split into two terms, $U = U_{str} + U_{th}$, where U_{str} is a local minimum of U (or just a reference potential for several minima as in tunnelling states) and $U_{th} = U - U_{str}$ is the deviation from this local minimum. The total energy associated with atomic motion, i.e. the energy above U_{str} , is then $E_{th} = E_K + U_{th}$. In the amorphous system we have a distribution of U_{str} values corresponding to a distribution of U surfaces. Thus, the ground vibrational energy, E_{th}^0 above the minimum, U_{str} , of the potential energy, becomes ensemble dependent in the glass. The same holds for the total energy $E^0 = E_{th}^0 + U_{str}$ at the zero *thermometric* $T = T_{th} = 0$, while still $T_{str} > 0$.

In classical statistical mechanics the entropy can be obtained directly from structure data through [11]

$$S = S^{id} + \sum_{n \geq 2} S_n \quad S^{id} - 3Nk_B \left\{ \frac{5}{2} - \log(\rho \Lambda^3) \right\} \quad \Lambda = \frac{h}{\sqrt{2\pi mkT}}. \quad (41)$$

Here S^{id} is the ideal gas entropy, and the S_n , $n \geq 2$, are functionals of the density ρ and of the molecular distributions $g^{(k)}$, $2 \leq k \leq n$. Taking only the first two terms, S_2 being evaluated directly from $g(r)$ data, an estimate of S for liquid Na near the melting point has been obtained within 2% of the calorimetric measurement value [12]. These results do not require knowledge of the potentials. In the classical limit (41) should be consistent with (5) and (3), provided the correct $T = T(E)$ is substituted into Λ in S^{id} . However, it seems that in the glass regime (41) cannot apply, since the translational temperature entering S^{id} is lower than the unknown 'structural' temperature which remains practically constant for measured T below T_g . It is not clear either how (41) should be modified to account for quantum effects.

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