

## Does temperature fluctuate? Indirect proof by dynamic glass transition in confined geometries

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## LETTER TO THE EDITOR

**Does temperature fluctuate? Indirect proof by dynamic glass transition in confined geometries**E Donth<sup>†</sup>, E Hempel<sup>†</sup> and C Schick<sup>‡</sup><sup>†</sup> Fachbereich Physik, Universität Halle, D-06099 Halle (Saale), Germany<sup>‡</sup> Fachbereich Physik, Universität Rostock, D-18051 Rostock, Germany

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**Abstract.** The Gibbs canonical distribution,  $dw \sim \exp(-E(p, q)/k_B T) dp dq$ , seems one of the most solid pillars of statistical physics. Thermodynamics is believed to be a derivative of this distribution. Since the temperature  $T$  is introduced, *de facto*, from a heat bath by the zeroth law of thermodynamics, this distribution cannot represent a genuine temperature fluctuation; all fluctuations are derived from energy fluctuations ( $\delta E$ ). Increasingly, nanoscale problems are attacked by physics (e.g. glass transition), physical chemistry (e.g. nucleation), or biology (e.g. protein folding). The fluctuations are relatively large because the nano-subsystems are small. The fluctuations should, therefore, completely be collected. The von Laue approach [1–3] to subsystem thermodynamics via minimal work for generation of fluctuations also allows the temperature to fluctuate ( $\delta T$ ). For this alternative, statistical physics is a derivative of thermodynamics. Here we show that a decision between the alternatives is possible by a calorimetric determination of the characteristic length of dynamic glass transition in confined geometries.

The alternatives give different formulas for these lengths. From dynamic calorimetry of glass transition (for polyethylene-terephthalate (PET) in mobile layers of partially crystalline samples, for salol, and for benzoin-iso-butyl-ether (BIBE) as guests in host pores of size 2.0, 2.5, 5.0, and 7.5 nanometer diameter) we partly get lengths, if calculated from the Gibbs distribution, which are significantly larger than the morphological lengths of the host geometry. This seems impossible. Alternatively, if the lengths are calculated from the von Laue approach they are always smaller than, or of order the morphological lengths. This seems reasonable. The final consequence of these findings is that thermodynamics seems more fundamental than the Gibbs distribution, and that a new basic distribution should be derived from thermodynamics.

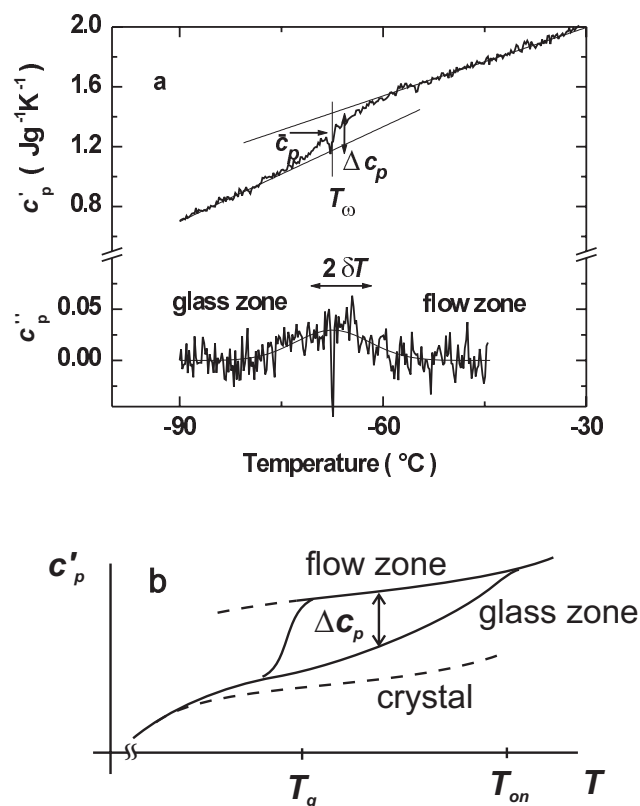
The formula derived from energy fluctuations is [4–6]

$$V_\alpha(\delta E) = \xi_\alpha^3(\delta E) = k_B T^2 / \Delta c_V \rho \delta T_g^2 \quad (1)$$

and from temperature fluctuation [7]

$$V_\alpha(\delta T) = \xi_\alpha^3(\delta T) = k_B T^2 \Delta(1/c_V) / \rho \delta T^2. \quad (2)$$

No *ad hoc* assumptions (besides the decision whether temperature can fluctuate or not) are necessary for their derivation. All calorimetric variables needed are well defined by fully reproducible (for a given sample) experiments with dynamic scanning calorimetry (DSC) corrected by partial freezing-in [8], or heat capacity spectroscopy (figure 1) [9–11].  $V_\alpha$  is the volume of a cooperatively rearranging region (CRR) as defined by Adam and Gibbs [12] via statistical independence, from the environment, of fluctuations in the dispersion zone of dynamic glass transition. In any case, the CRR size is microscopically small, since all quantities in equations (1) and (2) do not depend on the macroscopic sample size. The walls



**Figure 1.** Method: calorimetry for determination of characteristic length for glass transition. (a) Real ( $c'_p$ ) and imaginary ( $c''_p$ ) part of dynamic heat capacity  $c_p^* = c'_p + ic''_p$  as a function of temperature  $T$  for a given frequency in the equilibrium liquid.  $\bar{c}_p$  is the average  $c'_p$  value between the glass zone and the flow zone,  $\Delta c_p$  the step at the glass transition between these zones, and the temperature fluctuation  $\delta T$  is calculated from the  $c''_p$  peak width or the  $c'_p$  step width. The example [16] is temperature modulated DSC (TMDSC) for BIBE in  $D = 2.5$  nm glass pores coated with dimethyl amino-triethyl silane. The dielectrical BIBE mass fraction is 0.15. The curves are for cooling with a rate  $dT/dt = -0.5$  K  $\text{min}^{-1}$ , a modulation amplitude  $\Delta T = 0.2$  K, and a period time  $\tau_p = 60$  s corresponding to a frequency  $\omega = 0.10$  rad  $\text{s}^{-1}$ . The parameters from the  $c'_p(T)$  and  $c''_p(T)$  curves are:  $\Delta c_p = 0.25$  J  $\text{g}^{-1}\text{K}^{-1}$ ,  $\delta T = 4.85 \pm 0.65$  K using a Gauss fit for  $c''_p(T)$ ,  $\bar{c}_p = 1.3$  J  $\text{g}^{-1}\text{K}^{-1}$ ;  $T_\omega = -67.4$  °C,  $\xi_\alpha(\delta T) = 1.6$  nm (total uncertainty [14]:  $\pm 15\%$ ),  $N_\alpha(\delta T) = 9$  (total uncertainty:  $N_\alpha$  between 5 and 18). This example corresponds to the highest cross  $\xi_\alpha(\delta E)$  and circle  $\xi_\alpha(\delta T)$  at  $D = 2.5$  nm in figure 3(b). Only  $\Delta c_p$  (no  $\bar{c}_p$ ) is needed for the crosses  $\xi_\alpha(\delta E)$ . The spreading of the three crosses from independent experiments for the 2.5 nm pores is practically collapsed in one point for  $\xi_\alpha(\delta T)$ , because the  $\Delta c_p$  differences are compensated by the different  $\bar{c}_p$  values needed additionally for  $\xi_\alpha(\delta T)$ . Such a data collapse for  $\xi_\alpha(\delta T)$  is rather frequent according to our experience. For salol (figure 3(a)), the upper crosses and circles are from DSC at  $T_g$ , the lower ones from TMDSC at  $T_\omega > T_g$ . Note that different  $D$  in figure 3(a) and (b) correspond to different  $T_g$  or  $T_\omega$  (confinement effect) and different kinetics of structure formation [16] near the walls (surface effect). The coatings were also partly varied. (b)  $c'_p$  behaviour as a function of temperature for a scenario similar to poly(*n*-hexyl)methacrylate [22].  $\Delta c_p$  is defined between the flow and the glass zone of the liquid state, not between the flow zone and the crystal (schematically).

of the confinement do not disturb the statistical independence, as long as no slow Fourier components are contained in the molecular mobility of confining materials. The symbol  $\Delta c_V$

in equation (1) corresponds to a compliance step of linear energy response, and  $\Delta(1/c_V)$  in equation (2) corresponds to a modulus step of temperature response. Linear response including the fluctuation dissipation theorem (FDT) is considered as a partition of the Gibbs or the von Laue fluctuation formulas in the time or frequency domains. The difference symbol  $\Delta$  means the difference between the flow zone (large times) and the glass zone (short times) of the equilibrium liquid, not between different states as liquid and glass, nor between liquid and crystal (configurational quantities), nor between particle-property subsystems such as spin and lattice in other cases.

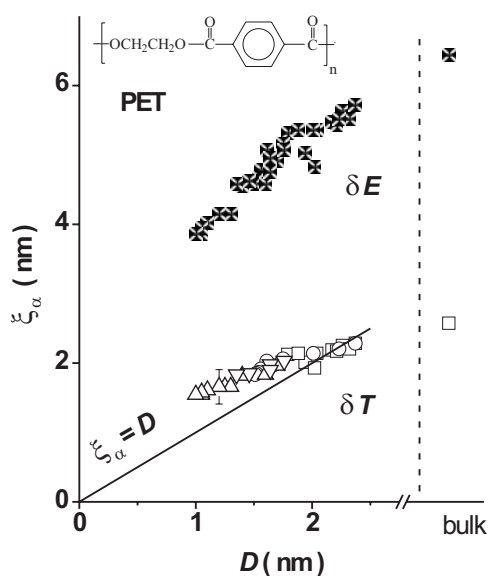
The CRR size from equations (1) and (2) can even be measured in bulk, without confinements, because the spectral density for entropy fluctuation of one single CRR is not deformed by the transfer from nanoscopic to macroscopic samples. The FDT frequencies, transmitted [13] between the representative subsystem and the measuring device, are not changed so that the macroscopic linear response signal is a representative for the smallest, statistically independent functional subsystem, the CRR. Briefly,  $V_\alpha$  can be determined from the temperature property being a thermodynamically intensive variable,  $(\delta T)^2 \sim 1/V_\alpha$ , after calibrating by the step of a specific (per gram) extensive variable,  $\Delta c_V$  or  $\Delta(1/c_V)$ .

At present, a direct proof by pointer fluctuations of a nano thermometer seems technically also possible. The decision, however, which size of a subsystem then is really measured—necessary for the decision between  $\delta E$  and  $\delta T$  fluctuation—seems difficult.

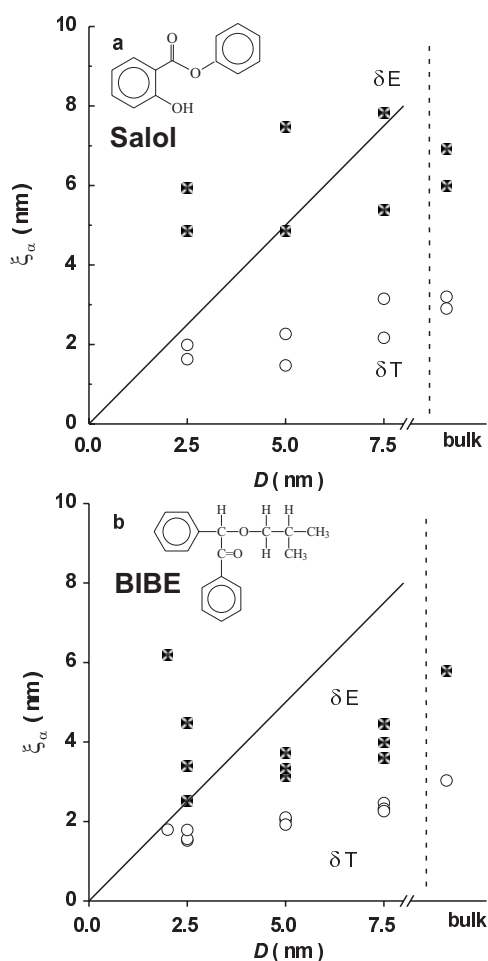
The existence of a temperature fluctuation is equivalent to the inclusion of the entropy-temperature pair as a compliance-modulus pair in the linear response theory including the FDT. The temperature fluctuation  $\delta T$  for equations (1) and (2) is calculated from the dispersion of the imaginary part of dynamic heat capacity,  $c_p''(T; \omega)$ , as a function of  $T$  for given frequency  $\omega$ . It was proved by means of linear response theory, that this  $\delta T$  quantity from the entropy compliance  $c_p^*/T$  is exactly equal to the average temperature fluctuation from the temperature modulus  $T/c_p^*$  via the FDT [14]. The temperature fluctuation  $\delta T$  is functional, i.e. it is only attached to the Fourier components that correspond to the slow mobility of dynamic glass transition;  $\delta T$  is the step height resulting from the integration of the spectral density of temperature fluctuation over the dispersion zone of this transition. The glass-transition length of a few nanometers is not appropriate for a hydrodynamic [15] treatment. (In the latter, temperature fluctuation is no problem for a spatio-temporal temperature field which can also be constructed from the Gibbs distribution for the larger volume elements of this field.) In the energy-fluctuation formula equation (1),  $\delta T_g$  is interpreted as a glass-temperature distribution of differently frozen CRRs. After correction of nonlinear influence of fictive temperature we obtain  $\delta T_g = \delta T$ . Furthermore, we approximated [14]  $c_V$  by  $c_p$ .

Some methodical details [16] are quoted in the caption of figure 1(a). The total uncertainty of bulk length  $\xi_\alpha(\delta T)$  was estimated [14] to be about  $\Delta\xi_\alpha \approx \pm 15\%$ . Inclusion of possible interfaces in confined geometries adds a maximal uncertainty of the confining layer thickness or pore diameter of  $\Delta D \approx \pm 20\%$ . The total uncertainty is less than the ratio of the two lengths: The volume ratio is  $V_\alpha(\delta E)/V_\alpha(\delta T) \approx (\bar{c}_p/\Delta c_p)^2$ , i.e. a factor 15 for  $\Delta c_p \approx 0.25\bar{c}_p$  as for PET. The length ratio is then about 2.5.

The calorimetric  $\delta E$  lengths (equation (1)) of the mobile amorphous fraction between the immobile and crystalline layers in PET are much larger than its morphological thickness  $D$  determined from x-ray scattering and calorimetry, whereas the alternative  $\delta T$  lengths (equation (2)) are [17], in the framework of the uncertainties, nearly equal to  $D$  (figure 2). The  $D$  thickness was varied by systematic changes of crystallization regimes and parameters. The large  $\delta E$  volume of about  $V_\alpha(\delta E) = 100 \text{ nm}^3$  at  $D = 1.5 \text{ nm}$  would correspond to an unreasonably oblate disc with a diameter of about  $d' \approx 9.2 \text{ nm}$  (from  $V_\alpha = Dd'^2\pi/4$ ), whereas the small positive deviations from  $\xi_\alpha(\delta T) = D$  of the  $\xi_\alpha(\delta T)$  lengths could be explained by a small



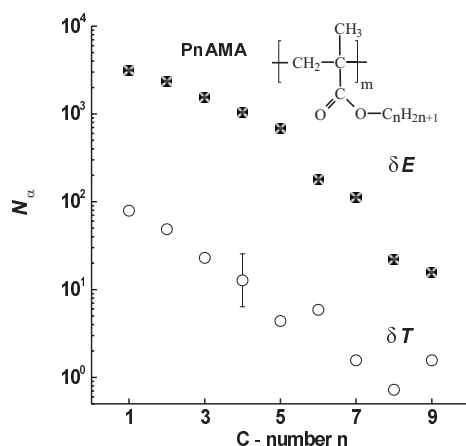
**Figure 2.** Calorimetrically (DSC) determined characteristic length  $\xi_\alpha$  from the energy fluctuation  $\delta E$  formula equation (1) ( $\blacksquare$ ) and from the temperature fluctuation  $\delta T$  formula equation (2) ( $\Delta$ ,  $\nabla$ ,  $\circ$ ,  $\square$  for different crystallization regimes) in amorphous mobile layers of partially crystalline PET, as a function of layer thickness from morphology,  $D$ .



**Figure 3.** The same for salol (DSC and TMDSC, (a)) and BIBE (TMDSC [16], (b)) as guest substances in porous glasses as hosts with a series of pore diameters  $D$ .  $\blacksquare$  from the  $\delta E$  formula equation (1),  $\circ$  from the  $\delta T$  formula equation (2).

oblateness. A similar situation [18] is obtained for salol in the pores of sol-gel-glass hosts from GELTECH (figure 3(a)). If the  $\delta E$  volume of  $V_\alpha(\delta E) = 170 \text{ nm}^3$  for  $D = 2.5 \text{ nm}$  would be attached to a pore volume of  $V_{\text{pore}}(\delta E) = \pi D^2 L/4$ , we would obtain a corresponding pore length  $L = 35 \text{ nm}$ . Such an extreme prolongation is not reasonable for a CRR with diameter of 2.5 nm. The differences are not so extreme for BIBE, with its large  $\Delta c_p$  step, in the larger pores [16] (figure 3(b)). The BIBE  $\delta E$  length for the small pore ( $D = 2 \text{ nm}$ ) in a porous glass from spinodal decomposition [16], however, is still three times larger than  $D$  which would correspond to a prolonged length of about  $L \approx 60 \text{ nm}$ .

As an example for application, we think that the inclusion of temperature fluctuation is necessary for an analysis of the crossover region [19, 20] of dynamic glass transition. This region is systematically shifted [21] to the glass temperature  $T_g$  in the homologous series of



**Figure 4.** Logarithm of cooperativity,  $N_\alpha$  = number of particles (monomeric units with molecular mass  $M_0$  here) in a cooperatively rearranging region (CRR), as a function of the length of normal-alkane side chain (e.g. C-number  $n = 1$ : methyl, PMMA,  $n = 6$ : hexyl) in a homologous series of atactic x-ray amorphous poly( $n$ -alkyl-methacrylates).  $\blacksquare$  from the  $\delta E$  formula equation (1),  $\circ$  from the  $\delta T$  formula equation (2).

poly( $n$ -alkyl-methacrylates). Starting with the methyl member, PMMA, where the crossover temperature is 70 K above,  $T_g$  is arrived at the hexyl member [22], see also figure 1(b). The  $\delta T$  length becomes small, below one nanometer, corresponding to small cooperativities  $N_\alpha = V_\alpha \rho / M_0$  there, whereas the  $\delta E$  cooperativity would remain large (figure 4). For the crossover region (the C-number region from 5 to 7 in figure 4), the average cooperativity ratio is about  $N_\alpha(\delta E) / N_\alpha(\delta T) \approx 70$  (!), the length ratio  $\xi_\alpha(\delta E) / \xi_\alpha(\delta T) \approx 4.1$ , and the temperature fluctuation of order  $\delta T = 20$  K. The physical pictures derived from the alternatives would be very different.

In summary, the calorimetric experiments of glass transitions in confined geometries significantly exclude the Gibbs distribution from a treatment of characteristic lengths, whereas the von Laue treatment gives always reasonable results (figures 2 and 3). We suggest, therefore, to analyse older [23, 24] and newer [25–29] indications for a dynamic heterogeneity of dynamic glass transition with distributions that include temperature fluctuations. The crossover region of dynamic glass transition seems to be a region where analytical or computer-aided theoretical methods should not be based on the Gibbs distribution alone. Theoretically, an analysis where the weak point of the derivation of Gibbs distribution from the quantum-mechanical (qm) microcanonical distribution is, will be published elsewhere. From a dynamic point of view, the large fluctuation of subsystem entropy,  $\ln \Delta \Gamma(t)$ , and of subsystem energy,  $\Delta E(t)$ , must both be considered as stochastic functions of time so that their quotient,  $\ln \Delta \Gamma(t) / \Delta E(t)$ , cannot be identified with the derivation of an ‘exact’ function,  $d \ln \Gamma / dE(E) \sim 1/T$ , as required by the zeroth law. A positive argument for the von Laue approach could be to consider the FDT as dynamic equation for a qm measuring process where both the qm object and the classical apparatus are identified with a representative subsystem [30], with a CRR here.

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