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Letter of Guest Editor

Remark on the interpretation of the imaginary part C'' of the complex heat capacity

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In some papers of this issue, e.g. Refs. [1–3], the imaginary part of complex heat capacity is connected with the entropy. In particular, it is interpreted as an entropy exchanged [1], or produced [2] during one cycle. The authors use the following definition for entropy:

$$\Delta S_{b-a} \equiv \oint_{a\to b} \frac{\mathrm{d}Q}{T(t)} = \int_a^b \mathrm{d}t \frac{1}{T}\frac{\mathrm{d}Q}{\mathrm{d}t} \qquad (1)$$

Where Q is the heat of the process along a certain path from state a to b, and T the temperature. In the case of temperature-modulated DSC (TMDSC), the following periodic time dependences of temperature and heat flow rate are used:

$$T(t) = T_0 + T_\mathrm{A} \sin \omega t \qquad (2)$$

and

$$\begin{aligned}\frac{\mathrm{d}Q(t)}{\mathrm{d}t} &\equiv T_\mathrm{A}\omega C \cos(\omega t - \delta) \\ &= T_\mathrm{A}\omega(C' \cos \omega t + C'' \sin \omega t) \qquad (3)\end{aligned}$$

with ω the angular frequency, T_A the temperature amplitude, C' and C'' the real and imaginary parts, respectively, of the complex heat capacity. The temperature is controlled to follow the time course of Eq. (2), causing a heat flow from and to the sample which corresponds to Eq. (3). With these quantities, the authors calculate the entropy exchanged of the sample during one cycle:

$$\Delta S_\mathrm{cycl} = \pi \frac{T_\mathrm{A}^2}{T_0^2} C'' \qquad (4)$$

As the process in question is a time-dependent one, Eq. (1) (which originally is only valid for quasi-static, namely reversible processes) must be replaced by the Clausius inequality:

$$\Delta S_{b-a} \geq \oint_{a\to b} \frac{\mathrm{d}Q_\mathrm{ex}}{T} \qquad (5)$$

which implies that the total entropy change may be larger than that connected to the exchanged heat. ΔS_cycl is calculated from the exchanged heat and does not say very much about the total entropy production of the process in question without further assumptions. Furthermore Eq. (4) may suggest that entropy production during a process can always be determined from C''. This is, however, not true as there are time-dependent processes which produce entropy but do not influence C''. The heat and, thus, entropy exchanged may be rather large and it may only be visible, say, in the underlying signal. In other words, every exchanged heat is coupled with an exchanged entropy, but this must not necessarily yield a non-zero C'' signal.

There are additional problems arising: Time-dependent (irreversible) thermodynamics is a rather com-

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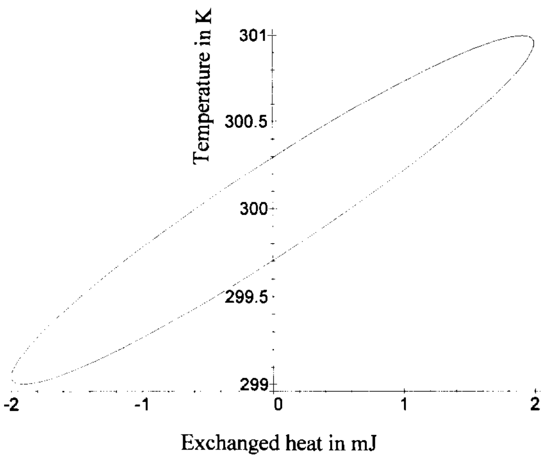

Fig. 1. Temperature-heat hysteresis

plicated theory which is not yet finalized. Whether the common entropy definition is valid or not is, strictly speaking, a matter of controversial discussion. One point of view is, that the Eq. (1) is only valid in irreversible thermodynamics, if *a* and *b* denote ***equilibrium*** states [4], which obviously is not the case for TMDSC. Hence, the validity of evaluations using Eq. (1) or Eq. (4) may be restricted to a narrow region of pathways in the very neighbourhood of equilibrium. To cut the matter short, in my opinion, the entropy term is not very helpful for interpretation of the imaginary part of the complex heat capacity.

There is another interpretation of C'' which I would like to present in what follows. If we plot the temperature change (Eq. (2)) and the resulting exchanged heat (from Eq. (3)) in one parametric plot in the T-Q-plane, we get (for linear response) an ellipse (Fig. 1). Its area can be calculated from the following integral:

$$A_{\mathrm{ell}} = \oint Q(t)\mathrm{d}T(t) = \oint T(t)\mathrm{d}Q(t) = \int_{\mathrm{period}} \mathrm{d}t T(t)\frac{\mathrm{d}Q(t)}{\mathrm{d}t} = \pi T_{\mathrm{A}}^2 C'' \qquad (6)$$

Comparing this result with that from Eq. (4) yields $A_{\mathrm{ell}}/T_0^2 = \Delta S_{\mathrm{cycl}}$, where T_0 is the average temperature of one cycle. So the result is not very different in principle, but the interpretation varies: The area of the ellipse (Fig. 1) is only different from zero if there is a non-zero phase shift δ between the temperature perturbation and the resulting heat flow rate. For $\delta = 0$, the ellipse collapses to a straight line. The larger δ is, the broader the ellipse and the larger the area. In this way, A_{ell} is closely connected with the time constant(s) of the relaxation process involved.

More precisely speaking, within the framework of linear response behaviour the real $C'(\omega)$ and the imaginary $C''(\omega)$ parts together denote the Fourier transform of the impulse response (the transfer function) of the system in time, which can be determined from the step response by differentiation. This is the very heat flow rate function which the sample exchanges with the surroundings on a step-like perturbation of its temperature. Any perturbation of the temperature causes a 'field' with a certain energy within the sample. This energy, the driving force of the process in question, dissipates during the relaxation. In this sense, the area of the ellipse in the T-Q-plane (and thus C'') reflects the dissipated energy, namely that of the driving force, during one cycle.

Hence, the situation is similar to that of dielectric, mechanic or other measurements, where the imaginary part of the respective generalized susceptibility (i.e. ε'', G'') is proportional to the area of the hysteresis in the plane of the generalized force and flux which, in turn, is proportional to the dissipated energy during one cycle [1,5]. The latter is mostly delivered to the surroundings in the form of heat.

To sum up, The area of the ellipse in the T-Q-plane, and with it C'', is a measure of the dissipated energy of the driving force of the time-dependent process. This energy can be calculated from Eq. (6) on dividing A_{ell} by the average temperature of one cycle (T_0). Simultaneously, the area A_{cell} reflects the distance of the pathway of the process from the quasi-static (reversible) one. This distance becomes larger with larger time constant(s) of the respective process. In fact, energy dissipation and the distance of the pathway from equilibrium is connected with a certain entropy production in principle, but its precise value need not be known in this context. The dissipated energy is a term with much more information about the process in the sample. The pathway which the system runs at a certain frequency should, by the way, be such as to give a minimum entropy production in accordance with Prigogine's well-known principle. From this it follows, that the ellipse is the 'best' pathway in the *T*-*Q*-plane, if we assume entropy to be proportional to the dissipated energy or area *A* (which seems reasonable), because it includes the lowest area for given amplitudes. All these conclusions can be drawn without knowing the exact value of entropy production and we avoided to go on slippery ice by trying an entropy definition for time-dependent processes.

References

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