Second order structural phase transitions leave a clear mark in all thermodynamical, mechanical, equilibrium and non-equilibrium properties of bulk crystals. It was proposed some time ago that the critical fluctuations should also leave a footprint in the frictional dissipation of external mechanical probes such as an atomic force microscope (AFM) when temperature crosses the phase transition in the underlying bulk.\textsuperscript{1} The recent successful detection of a superconducting transition in the linear response mechanical dissipation of a noncontact, pendulum-type AFM tip hovering more than one nm above the sample surface\textsuperscript{2} suggests that continuous structural transitions might also be detectable in this manner. Here we present a first realization of this idea, with direct application to a most classic example, the antiferrodistortive transition of SrTiO\textsubscript{3} just above 100 K. At this phase transition the high temperature ideal cubic perovskite crystal structure becomes unstable against a zone-boundary phonon-like displacement of the ions, leading to a cell doubling and a tetragonal I4/mcm symmetry at lower temperatures. This exquisitely second order “displacive” transition historically provided a clean realization of nonclassical critical exponents\textsuperscript{3}. A very intriguing feature of this system, originally uncovered by neutron scattering, and later confirmed by other techniques, is the so-called “central peak”\textsuperscript{4-7}. Very close to the critical transition temperature $T_c$, inelastic neutron spectra showed, besides ordinary critical fluctuations – which proliferate and soften but never reach zero frequencies – a strikingly narrow peak (less than the 6 MHz width resolution) centered at zero frequency, whence the name. The central peak (CP) intensity appeared to obey the static critical exponents of the transition, but despite considerable efforts the actual nature and width of the central peak were not uncontroversially established\textsuperscript{8}.

Here we show that noncontact pendulum AFM dissipation, measured far from actual contact with the surface, reveals for the first time a structural phase transition, and it does so by revealing the CP of SrTiO\textsubscript{3}. A linear response analysis shows that the CP-related mechanical loss peak is as narrow as 80 kHz, a frequency orders of magnitude below the neutron established upper bound. Moreover, even if it cannot strictly determine the intimate nature of the CP, the mechanical coupling suggests a connection with critical fluctuations of strain, which are known to be associated with those of the main antiferrodistortive order parameter\textsuperscript{9}.

The probe consisted of a very soft, highly doped silicon cantilever (ATEC-Cont from Nanosensors) with spring constant $k = 0.1$ N/m, suspended perpendicularly to the surface with an accuracy of $1^\circ$ and operated in the so-called pendulum geometry where the tip vibration describes an arc parallel to the sample surface. The peculiarity of this technique is to detect phenomena, in this case phase transitions, which happen in bulk, by means of a non-invasive, ultra sensitive and local surface probe, as opposed to traditional probes such as neutrons and X-rays which invade the bulk in a much more global fashion. Moreover, the pendulum AFM is a kilohertz probe, sensitive to phenomena and to fluctuations that may take place on a much slower time scale than that accessible with neutrons or X-rays. The oscillation amplitude $A$ of the tip was kept constant to approximately 5nm using a phase-locked loop feedback circuit. The cantilever was annealed in UHV up to 700°C for 12 h, which results in removal of water layers and other contaminants from both the cantilever and the tip. After annealing the cantilever quality factor, frequency and internal damping were equal to $Q = 7\cdot10^5$, $f_0 = 11$ kHz and $W_0 = 2\cdot10^{-12}$.
kg/s, respectively. The annealing is also known to reduce all localized charges on the probing silicon tip [2], which is neutral, since the tip-sample contact potential difference was compensated (V=V_{CPD}) during the experiment.

Fig. 1 (a) shows the power W(T) dissipated by the pendulum AFM as a function of temperature at different spots on the SrTiO$_3$ surface and at different tip-sample distances, as measured by the shift of the resonance frequency $\Delta f$. The dissipation is inferred from the standard expression $W = W_0 (A_{exc}(z)/A_{exc,0} - f(z)/f_0)$ in terms of the measured distance-dependent excitation amplitude $A_{exc}(z)$ and resonance frequency $f(z)$ (where $f(z) = f_0 + \Delta f$) of the cantilever, the suffix 0 referring to the free cantilever. Since the Young modulus of the silicon cantilever is temperature dependent also the frequency of the free cantilever changes as a function of temperature - $\Delta f_0(T)$ (11). In a temperature-dependent experiment the total change of the frequency is $\Delta f(T,z) = \Delta f_0(T) + \Delta f(z)$ where $\Delta f(z)$ is the (negative) frequency shift due to the tip-sample interaction.

The tip-sample distance z was accurately controlled by means of feedback loop regulating the z position in such a way that $\Delta f$ was kept constant. (see Supplementary Material).

Data at the large distance $z = 12$ nm, corresponding to $\Delta f = -10$ Hz, show a dissipation peak which is barely visible, corresponding to an exceedingly weak van der Waals tip-surface interaction. All other spectra, taken at closer distances, exhibit a narrow dissipation peak at a temperature between 114 and 118 K depending upon the surface spot investigated, reflecting local changes of $T_c$ determined by inhomogeneous heavy Nb doping, surface oxygen vacancies, and/or stress irregularities. The 105K transition temperature of stress free pristine SrTiO$_3$ is notoriously shifted by Nb doping and formation of oxygen vacancies [12]. At surfaces, moreover, $T_c$ may under suitable conditions show differences of tens of degrees with respect to the bulk, as seen on SrTiO$_3$(110) [13]. The dissipation peak in this raw data provides a first qualitative confirmation of the suggested connection between critical structural fluctuations and AFM dissipation [11].

Fig. 1 (b) shows a scanning tunneling microscope (STM) atomically resolved surface topography of the 1%-Nb doped SrTiO$_3$(001) surface taken at low temperature $T = 5$ K. The flat terraces are obtained after a 2h annealing to 1000$^\circ$ C under ultra high vacuum (UHV) [14] [15].Detailed STM images (see also Supplementary Material) show dark spots (surface defects, perhaps O vacancies [13]) and bright features, decorating what could be edge dislocations [16] or other domain walls.

We now consider the origin of the pendulum AFM loss process. For a start, the tip is sufficiently far from the surface to guarantee that only van der Waals (vdW) (or electrostatic if charges were present) tip-substrate interactions are relevant. Pure SrTiO$_3$ is an insulator and the coupling of a neutral tip must be phononic [17]. Resistivity measurements of 1%-Nb doped crystals exhibit conducting behaviour, however with a carrier density of about 10$^{20}$cm$^{-3}$ [18], orders of magnitude below that of a good metal.

Moreover, Auger electron spectroscopy on SrTiO$_3$ (2x2) surface has suggested that the Nb presence is negligible in the near-surface region [19], so that the low level metallicity due to Nb doping can be considered irrelevant in our experiment. Fig. 1 (c) shows the maximum dissipation value against tip-sample separation. For a spherical tip oscillating above a solid surface the dissipation is proportional to $F^2(z)$, where $F(z)$ is the static force resulting from tip-sample interaction. The vdW interaction yields a static force $F(z) \propto z^{-2}$, so that the
dissipation due to creation of phonons in the solid (acoustic phonons in this case, corresponding to the oscillating strain wave under the tip sketched in the inset in Fig. 2) should vary as $z^{-4}$ \cite{2} \cite{17}. The experimental distance dependence, is indeed best fit by $z^{-p}$ with $p \approx 4.2$ is in excellent agreement with that expectation.

\begin{equation}
W(\omega, T) = W_0 + \alpha k_B T \Im \chi(\omega, T),
\end{equation}

where $W_0$ is the dissipation of the free cantilever ($T$-independent in the considered temperature range), $\chi$ is an appropriate momentum average of the lattice susceptibility $\chi(q, \omega, T)$, $\alpha$ is a positive, distance-dependent constant and the temperature factor originates from the term $\hbar \omega n_B(\omega, T)$, with $n_B$ the Bose function, in the experimentally relevant regime $\hbar \omega \ll k_B T$. Using the form by Shapiro et al. \cite{5} which accurately describes neutron scattering, the order parameter (zone boundary) susceptibility can be written as

\begin{equation}
\chi(q, \omega, T) = \left[\Omega^2(q) - \omega^2 + i \Omega(q, \omega, T)\right]^{-1},
\end{equation}

where $\Omega$ is a bare soft phonon frequency far from the transition and $\Pi \sim \Delta(T) - \omega \Gamma_0(T)$ is a self energy renormalization from anharmonic effects (we shall from now on drop the wave-vector $q$ dependence of these quantities). This simple form of $\Pi$ would lead, in the standard textbook description of a displacive transition \cite{20} to a $T$-dependent shift of $\Omega$, resulting in a lorentzian peak in $\Im \chi(\omega)$ at $\omega_\infty(T) = \sqrt{\Omega^2 + \Delta(T)}$, of width $\Gamma_0$, such that $\omega_\infty(T) \to 0$ at $T = T_c$. However, the neutron data of SrTiO$_3$ showed that phonon softening is incomplete, $\omega_\infty(T_c) \approx 0.5$ meV, but accompanied by an extra feature centered at some very-low-energy $\omega_{\text{low}}$, the central peak, phenomenologically captured \cite{5} by an additional contribution to the self-energy $\Pi$

\begin{equation}
\Pi(\omega, T) = \Delta(T) - i\omega \Gamma_0(T) - \frac{\delta^2(T)}{1 - i\omega/\omega_{\text{low}}},
\end{equation}

For $\omega \sim \omega_\infty \gg \omega_{\text{low}}$ one recovers the usual soft-phonon lorentzian peak at $\omega_\infty$, but for $\omega \lesssim \omega_{\text{low}}$ a second peak appears, well approximated by (see upper inset of Fig. 2)

\begin{equation}
\Im \chi_{\text{CP}}(\omega) = \frac{\omega_{\text{low}} \delta^2(T)}{\omega_\infty^2(T) + [\omega_{\text{low}} \omega_\infty^2(\omega)/\omega_\infty^2(T)]^2},
\end{equation}

where $\omega_{\text{low}}^2(T) = \omega_\infty^2(T) - \delta^2(T)$ is the quantity that actually vanishes as $T \to T_c$. Indeed, the static susceptibility can be shown to be simply related to $\omega_{\text{low}}^2$

\begin{equation}
\chi(\omega) = \frac{\omega}{\pi} \frac{d\omega}{\omega} \Im \chi(\omega) = \frac{1}{\omega_\infty^2(T)} \sim \omega^{-\gamma}.
\end{equation}

The divergence of the order-parameter susceptibility $\chi$ with an exponent $\gamma$, as the reduced temperature $t = [T - T_c]/T_c$ goes to 0 is a standard result of the theory of critical phenomena. The critical behavior of SrTiO$_3$ is in the 3D-Ising universality class, for which $\gamma \sim 1.24$ \cite{21}. The low-energy susceptibility $\Im \chi_{\text{CP}}(\omega)$ of Eq. \cite{3} displays a sharp peak at a frequency $\omega_{\text{peak}}(T) = \omega_{\text{low}} \omega_\infty^2(\omega)/\omega_\infty^2(T)$, which moves towards 0 as $T \to T_c$. We can now consider the temperature dependence of the linear response AFM dissipation at the fixed and very low oscillation frequency $\omega_{\exp} = 2\pi f$. As $T \to T_c$ from above the dissipation will increase, roughly as $t^{-2\gamma}$, because $\omega_{\exp} < \omega_{\text{peak}}(T) \sim t^{-\gamma}$, to reach saturation value at $T = \bar{T}$ such that $\omega_{\text{peak}}(\bar{T}) \approx \omega_{\exp}$. Essentially $\bar{T}$ (here about 1 K above $T_c$) is the temperature below which CP fluctuations average out. Correspondingly, below $\bar{T}$ the dissipation levels off as we can essentially take $\Im \chi_{\text{CP}}(\omega_{\exp}) \approx \omega_{\text{low}} \delta^2(T)/[\omega_{\exp} \omega_\infty^2(T)]$, which depends very mildly on $T$. (Experimental values for $\delta^2(T)$ and

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig2}
\caption{Im$\chi_{\text{CP}}(\omega)$, the low-energy central peak component of Im$\chi(\omega)$ in log-log scale for various temperatures, showing a peak at $\omega_{\text{peak}}(T) \sim t^{2\gamma}$ that moves towards 0 as $T \to T_c$. (Upper inset) Sketch of the full Im$\chi(\omega)$ in linear $\omega$ scale, showing the broad soft-phonon lorentzian at $\omega_\infty$ with the sharp low-energy central peak. For clarity we used here a high value of $\omega_{\text{low}}$ to show both peaks on the same scale. (Lower inset) Cross section of 3D simulation of a tip perturbing a semi-infinite crystal through a vdW interaction. The tip (red dots) is shown as a truncated pyramid where every atom exerts a $-C/r^6$ vdW potential on crystal atoms (blue dots), that are held together by a harmonic potential. Arrows (magnified for clarity) represent on a log scale the atom displacements from the relaxed positions.}
\end{figure}
\( \omega_c(T) \) given by \([5]\). We finally obtain an overall predicted critical form for the AFM dissipation:

\[
W = W_0 + \frac{U}{1 + V \tau^{2\gamma}},
\]

(5)

where \( U \) and \( V \) are positive constants. (In the notation of Ref. \([5]\), \( V \tau^{2\gamma} = \gamma^2 \omega_0^2(T)/(\omega_0^2(T) \omega_{\text{exp}}^2) \) and at low \( t \) the relevant dependence on temperature is given by the \( \omega_0^2(T) \) term.)

Third, the unknown breadth \( \omega_{\text{low}} \) of the central peak in the dynamical structure factor \( S(\omega) = \text{Im} \chi(\omega)/\omega \) now obtained as an intrinsic property of SrTiO\(_3\) is about 80 kHz, well below the upper bound set by the neutron resolution limit of 6 MHz. This CP width is manifested in AFM dissipation as a peak at \( \omega_{\text{peak}}(T) = \omega_{\text{low}} \omega_0^2(T)/\omega_\infty^2(T) = 3.2 \tau^3 \text{ MHz} \). Fourth, the noncontact, large distance tip-surface coupling elicits a phononic dissipation attributable in turn to a slowly varying tip-induced strain, and not to the primary antiferrodistortive order parameter, to which the far away tip and its motion cannot directly couple. While this realization does not reveal by itself the intimate nature of the CP, which remains open to discussion \([8]\) it does show that the exceedingly slow critical CP fluctuations must involve a large component of strain, which is the secondary and not the primary order parameter of the structural transition.

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\[\text{FIG. 3. Experimental dissipation } W \text{ above } T_c \text{ as a function of temperature (black dots). Inset: the same data in a linear temperature scale, showing data both below and above } T_c. \text{ Red and green lines: fit above and below } T_c \text{ according to Eq. } [5]; \text{ pink dashed line: fit above } T_c \text{ excluding the high plateau data. The value of } \omega_{\text{low}} \text{ is } 156 \text{ kHz (solid curve) and } 44 \text{ kHz (dashed curve), both within a factor } 2 \text{ of } 83 \text{ KHz, the value obtained from a simple fit of the saturation temperature (see text). } \bar{t} \text{ is roughly the temperature where, upon cooling from above } T_c \text{ the dissipation levels off to a plateau. Horizontal error bars corresponding to } \delta t \sim 10^{-4} \text{ are small and omitted.} \]

Fig. 3 shows on a log-log scale the data for \( W - W_0 \) at \( \Delta \bar{t} = -40 \text{ Hz (} z \sim 3.5 \text{ nm)} \) for \( T > T_c \approx 117.58 \text{ K}. \)

Considering the experimental uncertainty mainly due to noise in the dissipation signal, a slope \( t^{-2\gamma} \) provides a good fit well above \( T_c \), followed by a saturation when \( t < \bar{t} \sim 10^{-2} \). Taking from Ref \([5]\) \( \omega_{\text{low}}^2 \approx 0.3 \text{ meV}^2 \) and \( \omega_0^2(\bar{t}) \approx 0.04 \text{ meV}^2 \), we finally observe that this saturation of AFM dissipation determines the low-energy width parameter \( \omega_{\text{low}} \) as \( \omega_{\text{low}} = \omega_{\text{exp}}^2(\bar{t})/\omega_0^2(\bar{t}) \approx 83 \text{ kHz}. \)

We draw in summary four conclusions. First, bulk structural phase transitions are indeed revealed by AFM dissipation, as was predicted. Strikingly, in the present noncontact realization, this is realized without literally touching the crystal. Second, the pendulum AFM dissipation picks up precisely the long debated central peak fluctuations, here responsible for the dissipation at the extremely low AFM pendulum frequency of 11 kHz.

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