Temperature Fluctuations in the Canonical Ensemble

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We report the first quantitative measurements of spontaneous temperature fluctuations in a physical system well modeled by a canonical ensemble. Using superconducting magnetometers and a carefully controlled thermal environment, we have measured the noise spectra of paramagnetic salt thermometers that were coupled to thermal reservoirs at 2 K. The noise spectra were found to be in very good agreement with the predictions of the fluctuation-dissipation theorem. Our observations are at variance with some interpretations of fluctuations in the canonical ensemble.

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In equilibrium thermodynamics, fluctuation is treated as the width of the distribution of a variable around its mean. Because the widths of thermodynamic variables are very small in a macroscopic system, experimental tests of the relationships between them are difficult. Therefore even the fluctuation of the two fundamental quantities in thermodynamics—energy U and temperature T—is the subject of controversial debates. The controversy centers on the applicability of the relation

$$\Delta U = C\Delta T \tag{1}$$

to the fluctuations of a subsystem with heat capacity C, thermally connected to a reservoir. Energy exchanges freely between the subsystem and the reservoir and standard analysis gives the energy fluctuations as

$$\langle \Delta U^2 \rangle = kT^2 C , \tag{2}$$

where k is Boltzmann's constant. Strictly speaking, Eq. (1) is derived from the first and second laws of thermodynamics. It relates the change in the mean internal energy to the change in the mean temperature. It is not clear that ΔU and ΔT can be applied as the widths of the distributions. Nonetheless, a significant body of literature exists where Eq. (1) was used to calculate the temperature fluctuations of the subsystem as

$$\langle \Delta T^2 \rangle = kT^2/C . \tag{3}$$

The analysis of Landau and Lifshitz [1] is typical in this regard, but the roots of the idea can be traced further back [2].

Another school of thought exists where Eq. (1) was rejected. Instead, statistical analysis was used to derive a relation between ΔU and ΔT. This school conforms to the initial assertion by Gibbs that the temperature of a canonical ensemble is constant and therefore does not fluctuate. Further extension of this idea leads to the possibility of temperature fluctuation in a microcanonical ensemble where the energy of the subsystem is not allowed to change. Recent articles by Kittel [3] and later by Mandelbrot [4] are consistent with the derivation of Linhardt [5], which gave

$$\langle \Delta T^2 \rangle = kT^2/C(1+\xi) \tag{4}$$

for a subsystem connected to a reservoir of heat capacity ξC.

If temperature measurement can be made to the thermodynamic limit, the studies of the noise characteristics would examine the relation between ΔT and ΔU. Over the last few years it has become possible [6] to achieve temperature resolutions of the order 10^{-9} to 10^{-10} $K/\sqrt{Hz}$ using paramagnetic salt thermometers with SQUID readout systems. Recently we have been able to combine the advances in thermometry with an improved level of thermal control to reach the point where the noise could be meaningfully studied. We obtain very good agreement with the predictions of the fluctuation-dissipation theorem (FDT) developed by Callen and Welton [7], which is consistent with equilibrium thermodynamics with the assumption that $\Delta U = C\Delta T$.

The basic design of the first type of high-resolution thermometer (HRT) studied is the same as that reported previously [6] and is shown in Fig. 1(a). The principle of operation is the dc measurement of the temperature-dependent magnetization of a paramagnetic salt, copper ammonium bromide $[Cu(NH_4)_2Br_4 \cdot 2H_2O]$ in a fixed magnetic field. The changes of the magnetization are detected with an rf SQUID coupled to a superconducting pickup coil wound around the salt pill. Magnetic fields, H, of up to 0.02 T are trapped inside a superconducting tube surrounding a sample of the salt. The salt pill [6] is a single cylindrical crystal of 0.53 cm o.d. and 1 cm long with 76 wires of 0.0076 cm diameter uniformly embedded in it. Thermal contact to the salt material was made by soldering the wires to a copper rod which forms the link to the reservoir.

Two HRTs of the above design, No. 1 and No. 2, were attached to the base of a reservoir [Fig. 1(b)] consisting of a high-purity copper container [8] filled with 22 cm^3 of helium. Superfluid helium has a large heat capacity near the lambda point and a high thermal conductivity, making it an ideal material for the construction of a large thermal reservoir with a fast internal thermal response time. A pressure-operated valve was attached to the container to allow evacuation of the fill line after the reservoir was filled. A four-stage thermal isolation system [8] separated the reservoir from the helium bath of the

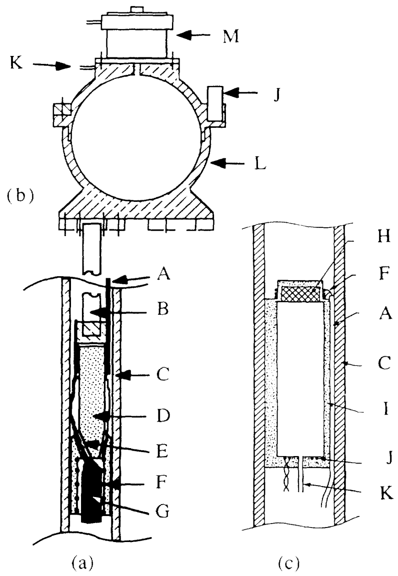

FIG. 1. Schematic view of (a) HRT with a single-crystal salt pill and copper wires thermal link; (b) reservoir with a pressure-operated valve; (c) HRT with powdered salt pill immersed in superfluid. The various elements are A, superconducting pickup coil shield; B, copper thermal link; C, niobium flux tube; D, sapphire holder; E, insulated copper wires; F, superconducting pickup coil; G, paramagnetic salt single crystal; H, powdered salt pill; I, epoxy resin; J, bifilar heater wire; K, fill line; L, superfluid thermal reservoir; M, pressure-actuated valve.

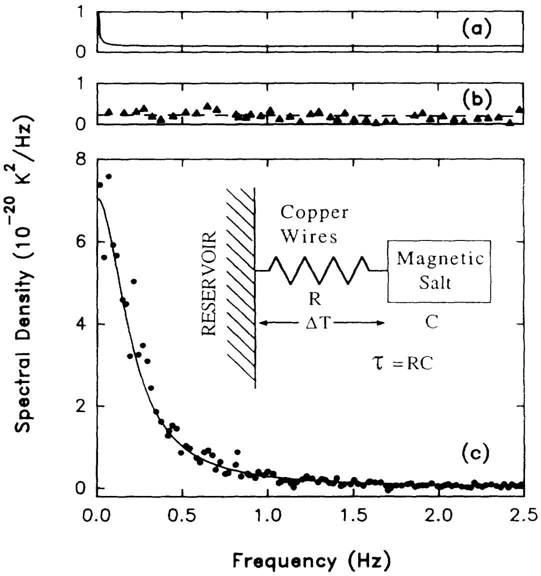

FIG. 2. (a) The background SQUID noise including $1/f$ noise, which has been subtracted from (b) and (c). (b) Spectral density of powdered salt in superfluid (HRT No. 3). Dashed line: qualitative prediction of FDT for these data. (c) Spectral density of single-crystal salt pill (HRT No. 1). Solid line: prediction of FDT.

Dewar. The innermost isolation stage formed a shield completely surrounding the reservoir. Its temperature was stabilized to within 10^{-8} K by a servo system using a third HRT. The outer three stages were controlled to within 10^{-5} K using germanium resistance thermometers.

The second type of HRT studied consisted of a smaller powdered salt pill immersed directly in a helium reservoir of volume 1.3 cm^3. The helium was contained in an epoxy chamber located inside a niobium flux tube. This assembly was set up primarily to study second sound propagation and has been described in some detail elsewhere [9]. We designate the thermometer in this setup HRT No. 3. A cross section of the assembly is shown in Fig. 1(c). It was isolated from the surroundings by a thermal control system similar to that described above.

To obtain noise data, each system was first cooled to a fixed temperature below the superfluid transition temperature. The temperature of the innermost isolation stage was then adjusted to reduce the cooling rate of the reservoir below 10^{-13} K/sec. The output of the HRT was connected to a spectrum analyzer [10] and the noise density determined. The small background noise from the SQUID sensors—including $1/f$ noise—is shown in Fig. 2(a), and was removed from the data using the sum rule for incoherent signals. The constants relating the SQUID output voltage to temperature were obtained by calibration against germanium thermometers. The results for HRT No. 1 at 2.172 K with 0.01 T of trapped field are shown by the solid circles in Fig. 2(c). It can be seen that substantial excess noise exists in the region below 1 Hz.

The FDT states [1,7] that the spectral density of the fluctuations of a generalized displacement X is approximated by

$$(X^2)_{f+} = 4\tau kT[dX/dF]_{f=0}/(1+4\pi^2\tau^2 f^2)\,, \qquad (5)$$

where F is the corresponding generalized force, which gives the free energy as $U-FX$, and τ is the response time of the variable X to a sudden application of F. When Eq. (5) is applied to the case of temperature fluctuations we obtain [2] the expression

$$(T^2)_{f+} = 4\tau kT^2/C(1+4\pi^2\tau^2 f^2)\,, \qquad (6)$$

where τ is the thermal relaxation time and $(T^2)_{f+}$ is the temperature noise density defined for positive frequencies f. The mean square fluctuation, $\langle\Delta T^2\rangle = kT^2/C$, can be obtained from the definition $\langle\Delta T^2\rangle = \int_0^\infty (T^2)_{f+}\,df$. To apply Eq. (6), we must first determine the appropriate thermal relaxation time and heat capacity. In the assemblies discussed here, four relaxation times are of potential interest: τ_1 describing the spin-lattice relaxation in the salt; τ_2 describing the relaxation of the salt material to the temperature of the embedded copper wires assumed to be held at the reservoir temperature; τ_3 characterizing heat transfer between the salt pill and the reservoir with the copper wires acting as thermal "bottle necks"; and τ_4 characterizing the internal relaxation of the reservoir. In the temperature range of our measurements, τ_1 has been shown [11] to be $\sim 10^{-6}$ sec. For HRT No. 1 we estimate [12] $\tau_2 \approx 2\times 10^{-3}$ sec, $\tau_3 \approx 1.3$ sec, and $\tau_4 \approx 10^{-4}$ sec. These values imply that for frequencies below a few Hz, the salt and the reservoir can be treated as lumped systems, each with a high degree of internal equilibrium. The inset in Fig. 2(c) shows the lumped system model with $\tau_3 = RC$, where R is the thermal resistance of all the copper wires in parallel. By observing the response of the HRT to a pulse of heat applied to the reservoir we can measure the longest time constant in the system. We obtained $\tau \sim 0.8$ sec, which is consistent with the above value of τ_3 to within the uncertainty of the estimate. Using the heat-capacity data of Miedema *et al.* [13], Eq. (6) is plotted as the solid line in Fig. 2(c).

It can be seen from Eq. (6) that for small τ, the low-frequency noise density is proportional to τ. The effect of reducing τ is to spread a fixed amount of noise energy over a wider frequency band. For HRT No. 3, τ is greatly reduced by using a powdered salt pill immersed directly in the superfluid. In a previous experiment [9], we used this thermometer to detect second sound at frequencies greater than 800 Hz, verifying the reduction. The solid triangles in Fig. 2(b) show the measured noise density of this thermometer at 2.172 K with a trapped field of 0.02 T. As expected, the low-frequency peak seen with HRT No. 1 is absent. For a qualitative comparison, the dashed line in Fig. 2(b) is a plot of Eq. (6) with $\tau_3 = 0.03$ sec. A quantitative analysis for this thermometer is not yet possible because the observations are dominated by SQUID noise. Strictly speaking, it is not clear that the lumped model is applicable to this situation, but it would appear to represent a worse case.

Additional measurements were made at a different trapped field (0.02 T) and temperature (2.076 K), and with HRT No. 2. In all cases, we obtained good agreement with Eq. (6). Table I summarizes the results. The sensitivity of an HRT is roughly proportional to the magnetic field at fixed temperature and varies rapidly with temperature because the Curie temperature of the salt is close to 1.8 K. Since the heat capacity of the salt and the thermal conductivity of the wire depend only weakly on magnetic field [13] and temperature over the range of interest here, the temperature noise should be roughly independent of sensitivity, as observed. On the other hand, if the noise is from stray pickup, it should be inversely proportional to the sensitivity. The data in Table I confirm the thermal source of the noise.

Since the surroundings of the reservoirs were controlled to a stability of only 10^{-8} K, the observed fluctuations may be caused by a lack of thermal stability. We estimate the noise coupled into the reservoir using a one-pole *RC* filter model. Using a heat capacity of 38 J/K for the reservoir and 2.2×10^4 K/W for the thermal resistance to the surroundings, we obtain an attenuation factor of more than 5×10^4 for $f > 0.01$ Hz. This reduces the coupled temperature disturbances to 2×10^{-13} K, well below our resolution. Second, the temperature of the reservoir could also undergo spontaneous fluctuations. Equation (6) predicts that the reservoir temperature should fluctuate with a low-frequency noise of 5.7×10^{-18} K^2/Hz with a roll-off frequency of 2×10^{-7} Hz. For $f > 0.01$ Hz, $(T^2)_{f+} < 1.1\times 10^{-22}$ K^2/Hz. This source of temperature fluctuation is also negligible. To check these points, we measured the correlation between the noise of HRTs No. 1 and No. 2. Over the frequency range of Fig. 2 we found no significant correlation [6], completely ruling out the reservoir as the source of the noise.

Since the fundamental quantity we measure is the magnetization of the salt, it is also possible to argue that the signal we observe is due to a magnetic moment fluctuation, ΔM, rather than a temperature fluctuation. In this case we can again make use of Eq. (5) by identifying X with M and F with H. We obtain $(M^2)_{f+} = 4\tau_M \times kT\chi V/(1+4\pi^2\tau_M^2 f^2)$, where τ_M is the response time of the spin system to a sudden application of field, V is the volume of the fluctuating element, and χ is the susceptibility. An upper limit on the noise can be obtained by assuming that the fluctuations are spatially correlated throughout the salt and demagnetization effects are negligible. We then obtain [11,14] an effective noise of 2×10^{-23} K^2/Hz, which is well below the SQUID noise.

TABLE I. The sensitivity and noise of the three HRTs described in the text at different temperatures and trapped fields. $(T^2)_{f+}(0)$ is the spectral density near zero frequency. The "white" SQUID noise subtracted is given. Data indicated by * are obtained by scaling to the heat capacity data in Ref. [13].

HRT	H (T)	T (K)	Sensitivity (10^6 V/K)	C (10^{-3} J/K) $\pm 15\%$	τ (sec) $\pm 3\%$	SQUID noise (10^{-20} K^2/Hz)	$(T^2)_{f+}(0)$ Eq. (4) (10^{-20} K^2/Hz)	$(T^2)_{f+}(0)$ observed (10^{-20} K^2/Hz)
1	0.02	2.172	13.6	2.9*	0.75*	0.02	6.8 ± 1.0	6.7 ± 1.0
	0.01	2.172	6.89	3.0*	0.77	0.16	6.8 ± 1.0	7.5 ± 0.5
	0.01	2.076	11.4	3.5*	0.90*	0.03	6.2 ± 1.0	4.0 ± 2.0
2	0.02	2.172	9.09	2.0*	0.81	0.05	10 ± 1.6	11 ± 1.0
	0.01	2.172	4.78	2.1*	0.84	0.34	10 ± 1.6	11 ± 0.5
	0.01	2.076	8.03	2.5*	0.98*	0.12	9.5 ± 1.5	11 ± 1.0
3	0.02	2.172	2.42	1.0*	< 0.03	0.68	0.0	0.2 ± 0.1

The roll-off frequency of $\sim 2.4\times 10^7$ Hz also does not match our results.

We have shown that $\Delta U = C\Delta T$ is applicable to the fluctuation in U and T to an accuracy of 20%. More subtle deviations at a lower model may still be possible. But since the heat capacity ratio $\xi > 1700$ in our case, Eq. (4) is 1700 times too small.

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[1] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, London, 1980), 3rd ed., Pt. 1, Chap. 7.

[2] J. M. W. Milatz and H. A. Van Der Velden, Physica (Utrecht) **10**, 369 (1943); G. L. de Haas-Lorentz, *Die Wissenschaft* (Vieweg, Braunschweig, 1913); also L. S. Ornstein and J. M. W. Milatz, Physica (Utrecht) **6**, 1139 (1939).

[3] C. Kittel, Phys. Today, **41**, No. 5, 93 (1988).

[4] B. B. Mandelbrot, Phys. Today **42**, No. 1, 71 (1989).

[5] J. Linhardt, in *The Lesson of Quantum Theory*, edited by J. de Boer, E. Dal, and O. Ulfbeck (North-Holland, New York, 1986), p. 99.

[6] J. A. Lipa, B. C. Leslie, and T. C. Wallstrom, Physica (Amsterdam) **107B**, 331 (1981); T. C. P. Chui and J. A. Lipa, in *Proceedings of the Seventeenth International Conference on Low Temperature Physics, Karlsruhe, 1984* (North-Holland, Amsterdam, 1984), p. 931; M. J. Adriaans, T. C. P. Chui, M. Ndesandjo, D. R. Swanson, and J. A. Lipa, Physica (Amsterdam) **169B**, 455 (1991); T. C. P. Chui, D. R. Swanson, M. J. Adriaans, J. A. Nissen, and J. A. Lipa, in Proceedings of the Seventh International Symposium on Temperature, Toronto, 1992 (to be published).

[7] H. B. Callen and T. A. Welton, Phys. Rev. **83**, 34 (1951); also Ref. [3], Eq. 124.18.

[8] J. A. Lipa, T. C. P. Chui, J. A. Nissen, and D. R. Swanson, in Proceedings of the Seventh International Symposium on Temperature (Ref. [6]).

[9] T. C. P. Chui and D. Marek, J. Low Temp. Phys. **73**, 161 (1988); D. Marek, J. A. Lipa, and D. Philips, Phys. Rev. B **38**, 4465 (1988).

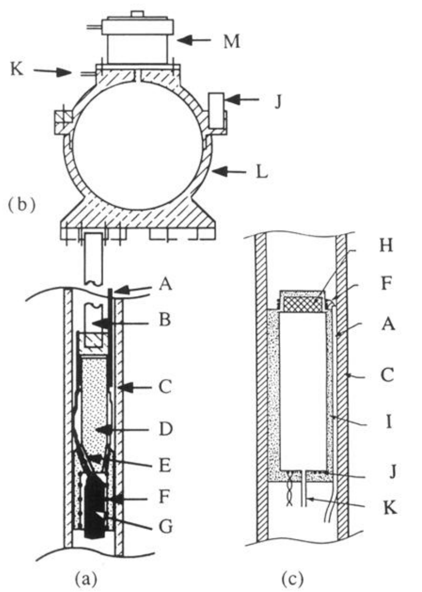
[10] Hewlett Packard model 3582A spectrum analyzer.

[11] See R. V. Duncan, Ph.D. dissertation, University of California, Santa Barbara, 1988 (unpublished), p. 89 for magnetic relaxation data.

[12] The thermal conductivity value of J. N. Haasbroek and A. S. M. Gieske, Phys. Lett. **31A**, 351 (1970), and the heat capacity value in Ref. [13] were used to compute τ_2 and τ_3.

[13] A. R. Miedema, H. Van Kempen, and W. J. Huiskamp, Physica (Utrecht) **29**, 1266 (1963); A. R. Miedema, R. F. Weilinga, and W. J. Huiskamp, Physica (Utrecht) **31**, 1585 (1965).

[14] See E. Velu, J. P. Renard, and B. Lecuyer, Phys. Rev. B **14**, 5088 (1976), for susceptibility data.



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