PHYSICAL REVIEW E VOLUME 48, NUMBER 4 OCTOBER 1993

Comment I on "Possible experiment to check the reality of a nonequilibrium temperature"

W. G. Hoover
University of California at Davis/Livermore and Lawrence Livermore National Laboratory, Livermore, California 94550

Brad Lee Holian
Los Alamos National Laboratory, Los Alamos, New Mexico 87545

Harald A. Posch
University of Vienna, Vienna A-1090, Austria

(Received 27 July 1992; revised manuscript received 18 December 1992)

We comment on a recent paper by Jou and Casas-Vázquez [Phys. Rev. A **45**, 8371 (1992)] from our perspective of classical computer simulation. We emphasize and discuss the utility of the ideal-gas temperature scale of kinetic theory in describing systems far from equilibrium.

PACS number(s): 05.70.Ln, 44.10.+i

Jou and Casas-Vázquez, culminating an extensive investigation of nonequilibrium systems [1], describe the measurement of nonequilibrium temperature in a stationary nonequilibrium system with a constant vertical heat flux Q_y. Their suggestion cuts through the formal mysteries of irreversible thermodynamics by means of a clear-cut example. Their idea, illustrated in their figure, is to couple, horizontally, a nonequilibrium system with Q_Y to an equilibrium system at temperature T. The equilibrium system acts as a thermometer: if a heat flux Q_X develops, then the nonequilibrium coupling point is *a fortiori* at a different temperature than the equilibrium temperature T.

Jou and Casas-Vázquez favor a generalized temperature, $T_{\mathrm{JC}} \equiv (\partial E/\partial S_{\mathrm{JC}})_V$. The entropy S_{JC} in their generalized definition differs from the local equilibrium one, $S_{\mathrm{LE}}(E,V)$, by a term of order Q_Y^2. Likewise the local-equilibrium temperature, $T_{\mathrm{LE}} \equiv (\partial E/\partial S_{\mathrm{LE}})_V$, differs from T_{JC}. For copper, their generalized theory additionally predicts a heat flux $Q_X \propto Q_Y^2$ with $Q_X \approx Q_Y/10^4$ under favorable, but reasonable, assumptions.

It might be possible to test such temperature definitions with molecular-dynamics simulations. In our own simulations we have favored yet a third definition of local temperature, the ideal-gas thermometer definition, familiar from kinetic theory: $\frac{3}{2}kT_{\mathrm{IG}} \equiv \frac{1}{2}\langle mv^2\rangle$. We prefer this choice for two reasons.

(1) The definition is the *simplest* consistent with thermostatics.

(2) Nonequilibrium entropy definitions are a precarious base. Our own experience [2] with multifractal phase-space distributions calls into question the utility of Gibbs's entropy far from equilibrium.

There is a third argument, based on an elementary thought experiment, in favor of the ideal-gas-thermometer definition. The thought experiment is the conventional treatment of Brownian motion, though here we have in mind a nonequilibrium many-body system.

In Gibbs' statistical mechanics the definition $\frac{3}{2}kT_{\mathrm{IG}} \equiv \frac{1}{2}\langle mv^2\rangle$ follows from the canonical-ensemble maximum-probability distribution over phase-space states. The same definition can be usefully extended and applied to *any* stable classical $[H(q,p) \equiv \Phi(q)+K(p)]$ system, not just ideal gases, even far from equilibrium. We wish to show that with this kinetic definition of T_{IG}, thermometry behaves correctly, with a nonequilibrium system absorbing heat from any hotter ideal-gas thermometer and giving off heat to a colder one.

We analyze the interaction of an individual, but typical, nonequilibrium-system particle (mass M) with an ideal-gas thermometer. The ideal-gas thermometer is a collection of light particles (mass m) with the equilibrium Maxwell-Boltzmann velocity distribution characteristic of the temperature T_{IG}. These light particles are enclosed by a semipermeable membrane open to nonequilibrium particles. The thermometer measures the temperature of any nonequilibrium degree of freedom by making frequent impulsive elastic collisions.

To illustrate first in one dimension, consider the impulsive (instantaneous) head-on collision of a relatively heavy nonequilibrium particle, having mass M and x velocity component $\dot{X}$, with a light ideal-gas-thermometer particle, having mass $m \ll M$ and x velocity component $\dot{x}$. The resulting x velocity components which satisfy conservation of momentum and (kinetic) energy are

$$\dot{X}' = [(M-m)/(M+m)]\dot{X} + 2[m/(M+m)]\dot{x} \ ,$$

$$\dot{x}' = [(m-M)/(M+m)]\dot{x} + 2[M/(M+m)]\dot{X} \ .$$

In a general three-dimensional collision, occurring parallel to the x axis, these same relations hold for the three-dimensional (3D) particles' x velocity components, with the y and z velocity components unchanged. The *averaged* velocity change $\langle(\dot{X}'-\dot{X})\rangle$, averaged over a light-particle Maxwell-Boltzmann distribution, can be expressed as the collision-averaged value of a power series in the mass ratio m/M. The various terms in this expansion all lead to simple Gaussian integrals. For $m \ll M$ the first nonvanishing term comes from the Taylor's-series expansion of two integrals:

$$\ddot{X} \propto \int |\dot{X}-\dot{x}|(\dot{X}'-\dot{X})\exp(-m\dot{x}^2/2kT)d\dot{x} \Big/ \int |\dot{X}-\dot{x}|\exp(-m\dot{x}^2/2kT)d\dot{x} \rightarrow \ddot{X} \propto -4(m/M)\dot{X} \ ,$$

where the probability normalization integral in the denominator is proportional to the collision rate. The arrow indicates the limit $m \ll M$. Thus the ideal-gas thermometer furnishes a frictional force proportional to the massive particle's speed. The effective frictional acceleration could alternatively be written $-(m/M)\dot{X}/\tau$, where τ is an effective collision time.

In thermostatics, where temperature corresponds to kinetic energy, the averaged (kinetic) *energy* change is relevant. The same correspondence holds for nonequilibrium systems, as we now show in detail. The kinetic-energy change depends only upon the massive particle's (nonequilibrium) speed *relative to the (equilibrium) thermal speed.* For a collision taking place along the x axis the averaged energy change for the massive particle, $\langle \dot{E} \rangle_{1D}$, is proportional to a ratio of integrals:

$$\int |\dot{X}-\dot{x}|(M/2)(\dot{X}'^2-\dot{X}^2)\exp(-m\dot{x}^2/2kT)d\dot{x} \Big/ \int |\dot{X}-\dot{x}|\exp(-m\dot{x}^2/2kT)d\dot{x} \rightarrow \langle \dot{E} \rangle_{1D} \propto 4(m/M)[kT-M\dot{X}^2] \ .$$

Again the arrow indicates the limit $m \ll M$. An average over all three space directions gives the result

$$\langle \dot{E} \rangle_{3D} \propto (m/M)[3kT-M\dot{X}^2-M\dot{Y}^2-M\dot{Z}^2] \ .$$

This same result follows, but with a little more labor, from a kinetic-theory calculation using cylindrical coordinates coaxial with the velocity V of the heavy particle. These kinetic-theory approaches can be regarded as derivations for the Langevin and Fokker-Planck equations, from which the same result, $\langle \dot{E} \rangle_{3D} \propto (3km/M)[T_{1G}-T_M]$, also follows directly. The details of the fluctuations around the limiting $[m/M \rightarrow 0]$ averages could be analyzed from the Fokker-Planck standpoint.

A simpler, but approximate, derivation can be based on writing the *averaged* collisional energy change:

$$\langle \Delta E_M \rangle \approx 2(m/M)[m\langle v^2 \rangle + M\langle v \cdot V \rangle - M\langle V^2 \rangle] \ .$$

If the dot product on the right-hand side is ignored, then the averaged energy change again depends only on the kinetic temperature difference, $T_{IG}-T_M$.

We conclude that our classical ideal-gas thermometer (an enclosed collection of many light particles with a Maxwell-Boltzmann velocity distribution) provides a unique and consistent definition of temperature, T_{IG}, even for a *single* particle *arbitrarily far from equilibrium.* With a thermometric bath at temperature T the (averaged) effect of collisions is to heat any cooler particle and to cool any hotter particle. For an atom in a classical system the (averaged) direction of thermometric heat flow is invariably from hot to cold.

From the logical standpoint the Jou–Casas-Vázquez experiment leaves an unanswered question. Within the nonequilibrium system their temperature scale T_{JC} is translated, away from T_{LE} or T_{IG}, so that the thermal treatment of the system-reservoir boundary, or equivalently the reservoir temperature, is puzzling. Nevertheless it is certainly possible to set up a laboratory or computer experiment containing a steady heat flux Q_Y. Unfortunately, second-order effects are difficult to measure precisely. For insulating materials typical of computer simulations, such as CO_2, conductivities are several orders of magnitude smaller than those for metals so that very large gradients would be required for measurable nonlinear effects [3].

The ideal-gas thermometer will necessarily measure T_{IG} in *any* computer experiment. The situation is clearest for a dilute gas, for which the potential energy can be ignored. In this dilute-gas case, the thermometer measures T_{IG} which is exactly equal to T_{LE}. Both these temperatures lie above the flux-dependent definition T_{JC}. Thus the ideal-gas thermometer provides a consistent operational definition of temperature, even far from equilibrium, under the conditions of the Jou–Casas-Vázquez experiment. We feel that this is a cogent argument for the ideal-gas definition of temperature. The fact that the *direction* of the energy change, system to bath or bath to system, is the same, no matter how far from equilibrium the system atom might be, bolsters the adoption of the ideal-gas temperature scale for classical nonequilibrium systems.

There already exists a large and varied body of literature, both in kinetic theory and in irreversible thermodynamics. A wide-ranging sampling of this work is referred to by Jou and Casas-Vázquez [1] and surveys a host of difficult problems, mainly at the level of definitions, as opposed to numerical calculations. The kinetic-theory research [4,5] that they cite is closest to our own [6] interests. For instance, in 1966 Ernst, Garcia-Colin, and Green [4] pointed out, at length, that either local kinetic-energy density or local total-energy density can be used as bases for *defining* nonequilibrium temperature. These authors established that, in a nonideal gas (with nonvanishing potential energy), these *definitions* lead to *different* state-dependent bulk viscosity coefficients, but to exactly the *same* macroscopic relation between stress and strain rate. In 1988 van Beijeren, Karkheck, and Sengers [5] made this distinction clear cut. They calculated the difference between the two bulk viscosity coefficients, and the two corresponding temperature scales, for a low-density square-well fluid. In our 1980 nonequilibrium simulations of bulk viscosity [6] we pointed out our preference for the choice based on kinetic temperature.

These issues are interesting, particularly with respect to the interpretation of shock-wave profiles. But *we* do not wish to assess here the relative utility of all the possible temperature definitions in the most general case. Simply being able to define temperature in quantum systems remains a challenging problem in measurement theory.

Here we adopt explicitly a point of view appropriate to *classical molecular dynamics,* now a powerful computational tool capable of realistic simulations, but barely in its infancy in 1966. In molecular-dynamics simulations energy, stress tensor, and heat flux all have simple mechanical definitions. From that same standpoint the ideal-gas thermometer furnishes a robust, logically consistent, and computationally operational definition. We have detailed in this Comment our reasons for preferring that definition. There is a real possibility that entropy and free energy are not well defined for nonequilibrium systems, making a mechanical nonentropic definition of temperature highly desirable, just for the purpose of interpreting and correlating the simulations with experiments.

This work was performed, in part, under the auspices of the U.S. Department of Energy at the Lawrence Livermore National Laboratory and at the Los Alamos National Laboratory, and was supported by Contract No. W-7405-Eng-48, at Livermore, and Contract No. W-7405-Eng-36, at Los Alamos.

---

[1] D. Jou and J. Casas-Vázquez, Phys. Rev. A **45**, 8371 (1992); J. Casas-Vázquez and D. Jou, J. Phys. A **14**, 1221 (1981); D. Jou and J. Casas-Vázquez, *ibid.* **20**, 5371 (1988); J. Casas-Vázquez and D. Jou, Acta Phys. Acad. Sci. Hung. **66**, 99 (1989); D. Jou and J. Casas-Vázquez, Physica A **163**, 47 (1990); D. Jou, J. Casas-Vázquez, and G. Lebon, Rep. Prog. Phys. **51**, 1105 (1988); G. Lebon, D. Jou, and J. Casas-Vázquez, J. Phys. A **13**, 275 (1980).

[2] B. L. Holian, W. G. Hoover, and H. A. Posch, Phys. Rev. Lett. **59**, 10 (1987).

[3] W. G. Hoover, B. Moran, R. M. More, and A. J. C. Ladd, Phys. Rev. A **24**, 2109 (1981).

[4] L. S. Garcia-Colin, and M. S. Green, Phys. Rev. **150**, 153 (1966); M. H. Ernst, Physica **32**, 209 (1966); **32**, 252 (1966).

[5] H. van Beijeren, J. Karkheck, and J. V. Sengers, Phys. Rev. A **37**, 2247 (1988).

[6] W. G. Hoover, D. J. Evans, R. B. Hickman, A. J. C. Ladd, W. T. Ashurst, and B. Moran, Phys. Rev. A **22**, 1690 (1980).