
SHORT COMMUNICATIONS

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THE Langevin approach to nonequilibrium statistical systems has been used to derive results in Brownian motion theory for a variety of problems, and by taking ensemble averages of various molecular motions while supposing that the macroscopic kinetic laws (such as Ohm's) hold at any instant¹, dissipative constants such as the resistance and viscosity may be computed². The Langevin method focuses on the individual particle, and partitions the force acting on it into a slowly varying force and a rapidly fluctuating (random) force. This idea, together perhaps with the influence of Wiener's statements with regard to the idea that the total impulse f received by a particle has no derivative^{3,4}, has led to equations being constructed where the correlation functions $K(s)$ with respect to the random forces $F(t)$ provide information on the damping constant α for a Brownian particle via the fluctuation-dissipation theorem⁵, that is

$$\alpha = \frac{1}{2kT} \int_{-\infty}^{\infty} ds K(s), \quad (1)$$

where T is the equilibrium temperature, k the Boltzmann constant, and

$$K(s) = \langle F(t')F(t'+s) \rangle_0.$$

In thermodynamics, the concept of work pertains to the co-operative effect of all the particles within the system, which causes an average force to be exerted across some boundary (spatially extensive) so that work may be categorized; this applies to the definition of heat, where a boundary must be created to determine the extent of energy transfer (by virtue of a temperature difference usually). The Langevin approach, on the other hand, does not at first hand concern itself with such boundaries. The system (the Brownian particle and the supporting fluid environment) constitutes an isolated system so that, by Newton's third law, all the internal forces for the system as a whole must cancel, including those 'slowly varying' ones due to viscous effects etc. We shall not in this treatment consider such forces, for

that would simply replicate the well-known results of Langevin theory; we concentrate instead on the forces introduced from the environment; this leads to the irreversible effects within the system, which must be correlated to the work done by the system. The rudimentary ideas here may be extrapolated to any degree of complexity involving various force fields and heat sources. Suppose our system consists of a fluid (consisting of structureless, non-interacting particles) enclosed in a cylinder with moving boundaries and subject to heat exchange because of reservoirs placed on these boundaries. We define the directional velocity correlation function

$$\Gamma_i(\tau) = \langle v(0)v(\tau) \rangle_i$$

for such a system of particles, where $v(\tau)$ is the velocity after time τ with respect to a reference state at time $\tau=0$ in the direction i . We may also define the total velocity correlation function $\langle \bar{v}(0)\bar{v}(\tau) \rangle$, where $\bar{v}(\tau)$ is the absolute magnitude of velocity. Depending on the system, the absolute or directional velocity correlation function may be utilized. In what follows, we shall consider the velocity correlation function in one dimension only for simplicity; the total velocity correlation function may be used for three-dimensional problems following the same line of reasoning as for the one-dimensional case.

For each particle, we may write

$$m dv/dt = F, \quad (2)$$

where F is the force acting on the particle and m its mass. We suppose that the masses are constant (this may be strictly generalized). To first order, for any particle

$$v(\tau) = v(0) + \partial v / \partial \tau \tau. \quad (3)$$

The correlation functions are the average over the particles in the system. They could also represent an ensemble average, but this definition will not be considered here. Suppose that an external force F' is introduced into the system; then the impulse of that force must always equal the total change of momentum of the entire system, even after a certain time τ where $\tau \gg \tau_c$, where τ_c is the mean time between collisions. From (2),

$$m \delta v = F' \tau, \quad (4)$$

where

$$\delta v = v(\tau) - v(0).$$

We emphasize that (4) is an average over the entire system since the total change of momentum is effected by the entire number of molecular collisions. As such F' is the force per particle.

Multiplying (3) by $v(0)$ and averaging over the entire system, and using (2), we get

$$\begin{aligned} \langle v(\tau) v(0) \rangle &= \langle v(0) v(0) \rangle + \langle v(0) \partial v / \partial \tau \tau \rangle \\ &= \langle v^2(0) \rangle + \langle v(0) F' / m \rangle \tau. \end{aligned} \quad (5)$$

If there exists an average force \bar{F}' , then we may write (5) as

$$\langle v(\tau) v(0) \rangle = \langle v^2(0) \rangle + \tau \langle v(0) \rangle \bar{F}' / m. \quad (6)$$

We justify the partitioning by supposing that the velocities of the particles at the beginning of the time of introducing the force are not related to the magnitude of the force introduced.

Therefore the average force which the system impresses on the environment \bar{F} in a short enough time τ is (per particle)

$$-(\langle v(\tau) v(0) \rangle - \langle v^2(0) \rangle) / m \tau \langle v(0) \rangle = -\bar{F}' = \bar{F}. \quad (7)$$

We can make one further approximation. Suppose that the direction of force is along the mean velocity of the particles at time $\tau=0$. Then the increment of work done δW on the system is $\bar{F}' \cdot \delta r$, where

$$\delta r / \delta t = \langle v(0) \rangle = \delta r / \tau. \quad (8)$$

Thus, for a short enough period of time τ , we have from (6)

$$m \{ \langle v(\tau) v(0) \rangle - \langle v^2(0) \rangle \} = \bar{F}' \cdot \delta r = \delta W, \quad (9)$$

where δW is simply the increment of the work done on the system per particle (negative of the work done on the environment) for a macroscopically small enough time τ . The problem may be generalized to quantal systems with the use of the correspondence principle and operator algebra⁶. This is a first-order result. A different ensemble averaging method is required for higher order terms to be explicitly incorporated into the work term. Equation (9) is important because it gives the coarse-grained differential for work in a system not at equilibrium, where the definition of 'temperature' is either non-applicable and non-characterizable or, at best, ambiguous. In spite of this, most theories admit the temperature parameter as a valid parameter in

nonequilibrium systems, for instance in the determination of the damping constants. Equation (9) gives an explicit relationship for the work or the work potential in terms of the actual particle phase-space configuration with no reference to 'heat' or thermal energy. Hitherto, most forms of macroscopic equations describing irreversible processes have been extrapolations of Gibbsian thermostatic equations where the partitioning of heat and work have assumed classical definitions (i.e. boundaries and 'temperature gradients' for the case of heat flow) and where various principles of 'local equilibrium' are assumed to hold⁷. The elegant Caratheodory statement⁸ of the second law was based on the existence of exactly adiabatic and non-adiabatic processes, thus presupposing the classical definitions of heat and work, which at present are independent of any kinetic or statistical model; it follows that more general statements from a kinetic or statistical point of view may be attempted if the work increment of a system can be determined from a distribution function, as above. The fluctuation-dissipation theorems derived from ensemble averages of systems that obey linear laws (such as Ohm's) supposes that spontaneous fluctuations of such quantities as current are possible in a system at equilibrium while the damping constants remain invariant; there is no immediate reason *a priori* why the fluctuations could not be caused by fluctuations in the damping constants in a constant energy system. It should prove interesting to consider the 'reciprocal space' of fluctuating damping parameters subject to fixed currents or field gradients in the linear constitutive equations to determine whether a further set of relationships are obtainable. A related problem to be addressed involves the theoretical efficiency of non-cyclic heat engines not in the steady state.

The author thanks C. J. Mundy for helpful discussions and Prof. Eric Hood for a fellowship.

1 June 1988; Revised 10 October 1988

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INFLUENCE OF HYDROGEN DIFFUSION ON THE RESISTIVITY OF COLD-WORKED NICKEL WIRES

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It is well known that the result of cold work on a metallic sample is the creation of defects and dislocations in it. The effect of slow-cycle-creep cold work (by winding-unwinding method) on the thermoemf of nickel wire was reported earlier¹. Lee and Lee² have reported that hydrogen diffused into

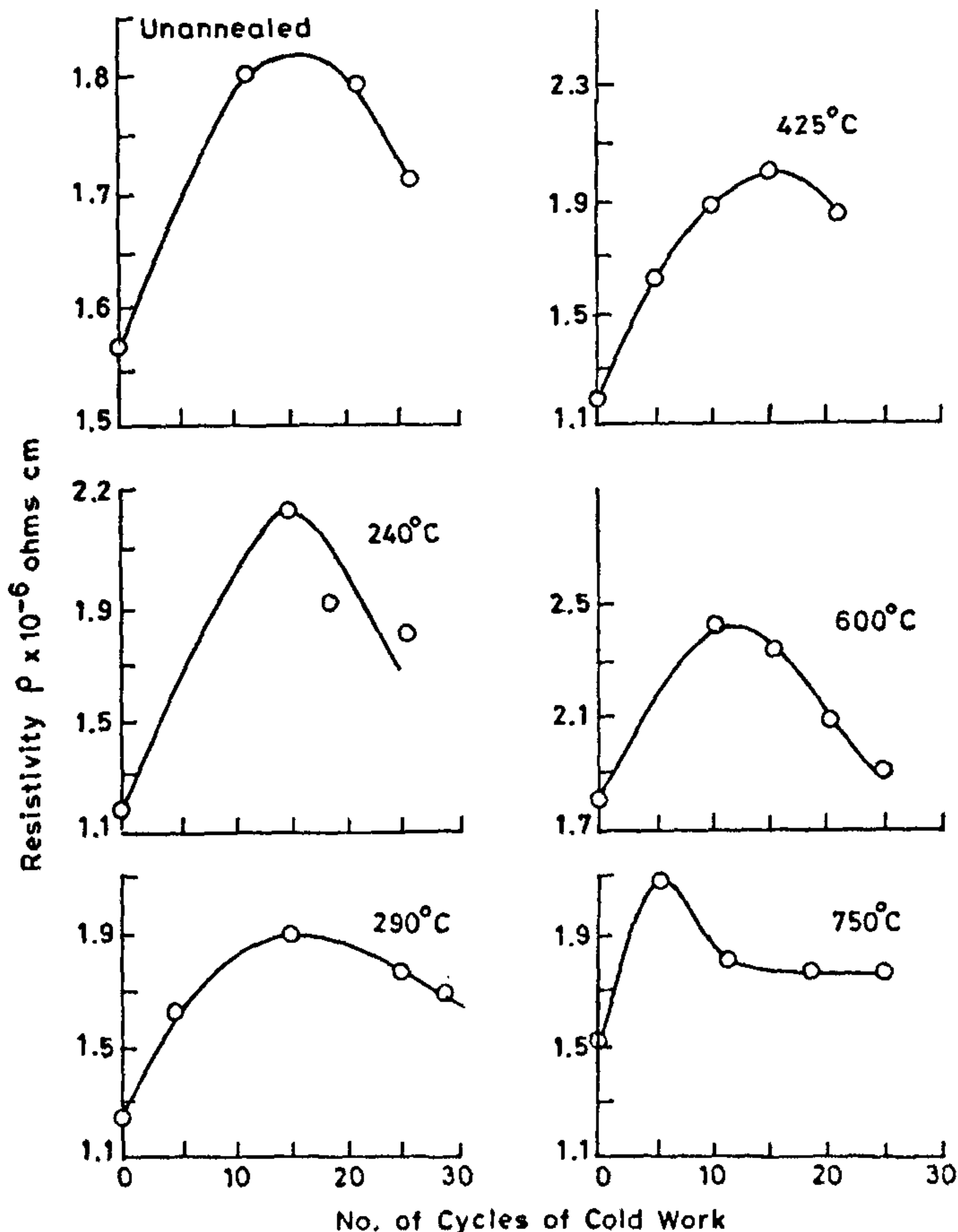


Figure 1. Variation of resistivity with cold work of nickel wires annealed at different temperatures.