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Thermopower in scanning-tunneling-microscope experiments

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We present a theory for the thermopower observed in scanning tunneling microscopy. The lateral variation of the thermopower is found to depend on the logarithmic derivative of the local sample density of states at the Fermi level. We also derive a relation between the thermopower and the nonlinear conductance. The heat transfer due to the tunneling electrons obeys the Wiedemann-Franz law.

Recently Williams and Wickramasinghe have measured thermopower on the atomic scale by using different tip and sample temperatures in a scanning tunneling microscope (STM).[1] We derive an expression for the thermopower[2] starting from Bardeen's formula for the tunneling current[3] and using the approximations proposed by Tersoff and Hamann.[4] We find that the magnitude of the thermopower depends on the logarithmic derivative of the local sample density of states at the Fermi level and does not decrease exponentially with sample-tip distance, in contrast to the conductance. Furthermore, we derive a relation between the thermopower and the nonlinear conductance. With respect to the heat flow due to the tunneling electrons, we find that the Wiedemann-Franz law is obeyed in STM experiments. Finally, we give quantitative estimates of the lateral variation of the thermopower for different adatoms on a metal surface.

According to Bardeen,[3] and the arguments given by Tersoff and Hamann,[4] the current is given by

$$J = a\int d\omega\, \rho_T(\omega + eV/2)\rho_S(\mathbf{r}_T;\omega - eV/2)\left[f\left(\frac{\omega - eV/2}{k_B T_S}\right) - f\left(\frac{\omega + eV/2}{k_B T_T}\right)\right]. \tag{1}$$

Here ω refers to the energy relative to the Fermi level. The transmission probability is approximated by the product $\rho_T\rho_S(\mathbf{r}_T)$, where ρ_T is the density of states associated with the tip atom, $\rho_S(\mathbf{r}_T)$ is the local density of states due to the sample, and $\mathbf{r}_T$ is the position of the tip. The measured voltage is V, T_T and T_S are the tip and sample temperatures, respectively, and $f(x) = 1/[\exp(x)+1]$ is the Fermi-Dirac distribution function. The constant prefactor a includes the electron charge and normalization of the densities of states. Note that the local sample density of states depends on the distance from the sample. This dependence includes an appropriate barrier penetration factor for tunneling across the gap between tip and sample.

The experiment is performed with an open circuit, giving zero net current across the tunneling junction. Thus (1) is an implicit equation for the thermopower V as a function of the two temperatures T_T and T_S. Since the thermopower is small ($V \sim 10^{-5}$-10^{-4} V), we may linearize (1), writing $J = J_T + \sigma V$. Here

$$J_T = a\int d\omega\, \rho_T(\omega)\rho_S(\mathbf{r}_T;\omega)\left[f\left(\frac{\omega}{k_B T_S}\right) - f\left(\frac{\omega}{k_B T_T}\right)\right] \tag{2}$$

is the thermally driven current. The conductance is

$$\sigma = ea\int d\omega\, \rho_T(\omega)\rho_S(\mathbf{r}_T;\omega)(-\tfrac{1}{2}) \times\left[f'\left(\frac{\omega}{k_B T_S}\right) + f'\left(\frac{\omega}{k_B T_T}\right)\right], \tag{3}$$

where the prime denotes derivative with respect to the energy ω. Convenient simplifications result if the local densities of states vary slowly on the scale of $k_B T_{S,T}$ (~ 25 meV) around the Fermi level. This is certainly the case for metals, and also for adatoms on a metal surface, as shown by Lang.[5] This justifies a linear expansion in the vicinity of the Fermi level:

$$\rho_T(\omega)\rho_S(\mathbf{r}_T;\omega) \approx \rho_T(0)\rho_S(\mathbf{r}_T;0) + [\rho_T(0)\rho_S(\mathbf{r}_T;0)]'\omega\,.$$

Then

$$J_T = a\frac{\pi^2 k_B^2}{6}[\rho_T(0)\rho_S(\mathbf{r}_T;0)]'(T_S^2 - T_T^2)\,, \tag{4}$$

where we used $\int_0^\infty dx\, x/[\exp(x)+1] = \pi^2/12$. Furthermore,

$$\sigma = ea\rho_T(0)\rho_S(\mathbf{r}_T;0)\,. \tag{5}$$

Zero net current yields

$$V=-\frac{J_T}{\sigma}=\frac{\pi^2k_B^2}{6e}(T_T^2-T_S^2)\frac{[\rho_T(0)\rho_S(\mathbf{r}_T;0)]'}{\rho_T(0)\rho_S(\mathbf{r}_T;0)}$$

$$=\frac{\pi^2k_B^2}{6e}(T_T^2-T_S^2)[\ln\sigma(0)]'. \qquad (6)$$

This is our result for the thermopower. It does not depend on which expression one uses for the transmission probability in Eq. (1). The approximation by the joint density of states can be replaced by whatever more accurate expression one has at hand. It is also interesting to note that (6) is identical to the old result for the thermopower in a normal metal, usually derived from the Boltzmann equation.[6]

In our discussion of Eq. (6) we rely on the following approximation of the local density of states due to the sample:[7]

$$\rho_S(\mathbf{r}_T;\omega)\approx\rho_S(x,y;\omega)e^{-2z[2m(\Phi-\omega)]^{1/2}/\hbar}. \qquad (7)$$

Here $\mathbf{r}_T=(x,y,z)$ with z perpendicular to the surface, $\rho_S(x,y;\omega)$ is the local density of states in a plane $\mathbf{r}=(x,y,0)$ close to the sample surface, and Φ is the work function that gives the barrier height for tunneling through vacuum. This approximation has the advantage of separating the dependence on the sample-tip distance from the density of states dependence. The choice of z dependence in (7) is the natural one when one thinks of STM in terms of a one-dimensional tunneling process. However, one should keep in mind that the simple exponential decay may not be suitable for strongly localized d states in transition metals. Within approximation (7) the thermopower consists of three terms,

$$V=\frac{\pi^2k_B^2}{6e}(T_T^2-T_S^2)\left[\frac{\rho_T'(0)}{\rho_T(0)}+\frac{\rho_S'(x,y;0)}{\rho_S(x,y;0)}+\frac{z}{\hbar}\left(\frac{2m}{\Phi}\right)^{1/2}\right]. \qquad (8)$$

The main concern of the experiments is the lateral dependence of V. The decomposition (8) shows that the (x,y) dependence is not affected by the choice of tip material and tip-sample distance. As expected, the lateral variation only reflects properties of the sample. Important also is the fact that the thermopower depends on the logarithmic derivative which can be appreciable even in (x,y) positions with a small density of states.

We now derive a relation between the lateral variation of the thermopower and the nonlinear conductance. We keep the sample and tip temperatures equal and expand Eq. (1) to second order in V, writing $J=\sigma V+\Sigma V^2$. Within approximation (7) we obtain

$$\frac{\Sigma}{\sigma}=\frac{e}{2}\left[\frac{\rho_T'(0)}{\rho_T(0)}-\frac{\rho_S'(x,y;0)}{\rho_S(x,y;0)}\right]. \qquad (9)$$

The (x,y) dependence of V and Σ/σ are both given in terms of ρ_S'/ρ_S. Thus,

$$V(x,y)=\frac{\pi^2k_B^2}{3e^2}(T_S^2-T_T^2)\frac{\Sigma(x,y)}{\sigma(x,y)}+\text{const}. \qquad (10)$$

This relation may be checked experimentally by measuring the lateral variation of the J-V curve (for small voltages) and the thermopower on the same sample. An experimental verification of Eq. (10) would lend support to the approximations inherent in our derivation: (i) The neglect of other proposed contributions to the lateral dependence of the thermopower.[1] (ii) The expansion in the vicinity of the Fermi level. (iii) The approximation of the tunneling probability by the joint density of states. (iv) The decoupling of the dependence on the sample-tip distance and the density-of-states dependence.

Up to now we have assumed that the tip temperature is independent of position in the (x,y) plane. This assumption will only be satisfied if the heat transfer due to the tunneling electrons is negligible compared to other heat transfer mechanisms, for example the dipole coupling proposed by Dransfeld and Xu.[8] An estimate of the heat flow due to the tunneling electrons, based on the Wiedemann-Franz law, shows that this contribution is indeed negligible. Next we verify that the Wiedemann-Franz law *is* obeyed with respect to the tunneling process in STM experiments. The heat flow associated with the tunneling electrons is given by

$$Q=\frac{a}{e}\int d\omega(\omega+eV/2)\rho_T(\omega+eV/2)\rho_S(\mathbf{r}_T;\omega-eV/2)$$

$$\times\left[f\left(\frac{\omega-eV/2}{k_BT_S}\right)-f\left(\frac{\omega+eV/2}{k_BT_T}\right)\right]. \qquad (11)$$

Comparing with Eq. (1) for the electric current, we have replaced the electron charge e with the energy $\omega+eV/2$ relative to the Fermi level in the tip. We can write (11) as

$$Q=\tfrac{1}{2}VJ+\frac{a}{e}\int d\omega\,\omega\rho_T(\omega+eV/2)\rho_S(\mathbf{r}_T;\omega-eV/2)$$

$$\times\left[f\left(\frac{\omega-eV/2}{k_BT_S}\right)-f\left(\frac{\omega+eV/2}{k_BT_T}\right)\right]. \qquad (12)$$

Since $J=0$ in the experiment, there is no joule heating due to the tunneling process, and the only contribution comes from the second term. Again we expand in the vicinity of the Fermi level. Since there is already a factor ω in the integrand, only $\rho_T(0)\rho_S(\mathbf{r}_T;0)\omega$ survives, and one finds

$$Q=a\frac{\pi^2k_B^2}{6e}\rho_T(0)\rho_S(\mathbf{r}_T;0)(T_S^2-T_T^2)$$

$$=\frac{\pi^2k_B^2}{6e^2}\sigma(T_S^2-T_T^2). \qquad (13)$$

Now, introduce the average temperature $T=(T_S+T_T)/2$, the temperature difference $\Delta T=T_S-T_T$, and the thermal conductance $\kappa=Q/\Delta T$. Since the ratio between two conductances and two conductivities is the same, (13) is equivalent to the Wiedemann-Franz law, $\kappa/\sigma=LT$, where $L=\pi^2k_B^2/3e^2$ is the Lorenz number.

From (10) we want to give an order of magnitude estimate of the lateral variation of the thermopower. This requires knowledge of the temperature difference across the gap, $\Delta T=T_S-T_T$. The experimentally known temperatures are not T_T at the end of the tip and T_S at the sample surface, but rather T_1 and T_2 of the reservoirs to which the tip and sample are connected.[9] For an accurate calculation of T_T and T_S one needs to know the tip and sample geometries in detail as well as their thermal conductivities. In addition one has to determine the dominant process of heat transfer across the STM gap.

We have made a rough estimate of ΔT, assuming a conical tip of diameter 100 Å and a sample-tip separation of 5 Å. The reservoirs are typically kept at $T_1 = 300$ K and $T_2 = 350$ K.[1] Replacing the gap with tip material, we find $\Delta T \sim 1$ K. This is clearly an underestimate, since a metal has a much higher thermal conductivity than water or air, which typically make up the gap in the experiments. The dipole coupling proposed by Dransfeld and Xu may give a considerable heat transfer, but presumably this will be smaller than our estimate with a metal connecting the tip and the sample. Thus, for a lower bound on the thermopower we will use $T = 325$ K and $\Delta T = 1$ K. We should add that the thermocoupling in STM is not well enough understood to give a reliable estimate of ΔT. However, although there is no direct measurement of the temperature difference, our order-of-magnitude estimate of 1 K is supported by Williams and Wickramasinghe.[9]

Unfortunately, we have not found experimental values of the nonlinear conductance Σ in print. For a crude idea we will use the results derived by Lang.[5] He evaluated the tip corrugation s as a function of bias V for Na, Mo, and S adatoms on a model sample surface of jellium.[10] Using a work function $\Phi = 4$ eV, we find that $\Delta(\Sigma/\sigma) \sim 2.0\Delta(ds/dV)_{V=0}$ V^{-1}, with ds/dV given in units of Å/V and Δ denoting the variation between different adatoms. Lang's results yield $\Delta(\Sigma/\sigma) \sim 0.6$ V^{-1} for Mo and S adsorbates on jellium. Using the above values of T and ΔT, we find a spatial variation in the thermopower of about 10 μV. This is likely to be somewhat smaller than the observed variation. First, as argued above, we have probably underestimated the temperature difference across the gap. Second, since MoS_2 is a semiconductor with an energy gap, the values of ρ_S'/ρ_S, and thus Σ/σ, may be substantially larger than the estimates based on adatoms on jellium. However, whereas Lang's model may be inadequate for making quantitative predictions in the case of semiconductors, it should provide a good description for metals and adsorbed atoms on metal surfaces.

In conclusion, from Bardeen's formula for the tunneling current we have derived an expression for the thermopower observed in STM measurements. An experimental test of our theory would be to measure the lateral variation of the nonlinear conductance and the thermopower on the same sample. The lateral variation in the thermopower can be attributed to local changes in the logarithmic derivative of the sample density of states at the Fermi level, and the amplitude of the variation is not sensitive to the sample-tip distance.

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