



Thermodynamically induced particle transport: Order-by-induction and entropic trapping at the nano-scale

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HIGHLIGHTS

- Thermodynamic induction (TI) under isothermal conditions has been studied.
- Gate stationary states allow the entire system to attain equilibrium sooner.
- Example systems include electrolytes, superfluids and semiconductors.
- TI is important in the manipulation of atoms and molecules by STM.
- A detailed scheme is laid out for the construction of a tether just one atom thick.

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ABSTRACT

A theory for thermodynamic induction (TI) under isothermal conditions is presented. This includes a treatment of the Helmholtz free energy budget available for a gate variable to utilize towards aiding another variable's approach towards thermodynamic equilibrium. This energy budget could be used to help create interesting physical structures and examples of order-by-induction. I also show how to treat TI in the continuum limit which can be obtained from a variational principle.

Several important examples of isothermal TI have been discussed, including a type of electromigration that may be detectable in electrolytes, superfluids and semiconductors. As an example of a bottlenecked system exhibiting enhanced TI, manipulation of atoms and molecules by STM has been discussed in detail. My considerations provide strong support for microscopic bond-breaking mechanisms being governed by a general thermodynamic principle. In particular, I show that induced entropy trapping can explain the level of control that sliding-type manipulations demonstrate. The most reasonable choices for the parameters input into the simple formula give a threshold condition for STM manipulations that is strikingly close to what is required to match results reported in the literature. My continuum model predicts the shape of the adsorbate potential well for the STM case and from this I predict a level of force detectable by AFM. A final proposal, and example of order-by-induction, predict a long tether may be constructed between sample and tip that is just one atom thick.

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1. Introduction

Recently, the Onsager relations [1,2] have been extended from the linear to the nonlinear realm inside the class of nonequilibrium thermodynamic systems governed by variable kinetic coefficients (VKC) [3]. Though the result is not quite as simple to express as $L_{ik} = L_{ki}$ is, the extended result may be expressed concisely as $N_{ki} = -rN_{ik}$ where r is a ratio of

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two relevant time scales. That kinetic, or transport, coefficients are not always constant is well known [4–6] and the direct N_{ik} coefficients arise as 1st order corrections to kinetic coefficients. The rate of the relaxation process for state variable x_i depends on the gating variable x_k . The main result of Ref. [3] is the existence of the previously unknown N_{ki} coefficients (across the diagonal). These induction coefficients change the dynamics of gating variables. For example, such variables can be induced to move away from equilibrium by a significant amount. Thermodynamic induction (TI) may be described as the adjustment of the gate variable in order to enhance the approach towards equilibrium of variable x_i , the dynamical reservoir (DR).

In Ref. [3] it was suggested that systems that have a bottlenecking or gating property might be good candidates for displaying measurable TI effects. In addition TI predicts the enhancement of transport rates for a bottlenecked process, as a consequence of maximizing entropy production [3]. Entropy production also plays a key role in studies of bottlenecked systems exhibiting so-called entropic barriers, which are distinguished from traditional energy barriers [7–10]. An interesting result of transport process dominated by entropy is the entropy trap which can be used to trap macromolecules under nonequilibrium conditions [11,12]. The entropy trap works because the system fluctuates and attempts to sample all available microstates. In this work I explore the possibility of entropy traps being created as a consequence of TI. This will require coupling of at least two transport processes, i.e., coupling between a DR and a gate, or control variable. One area of activity that warrants careful inspection for TI and any resulting entropic trapping effects is the highly controlled manipulation of atoms and molecules by STM. Scanning tunneling microscopy is an inherently nonequilibrium technique because of the applied bias across the tunnel junction. It is well known that adsorbates underneath the tip have strong effects on the junction conductance. Thus it is reasonable to explore the possibility that adsorbates near the junction might be affected by TI effects.

The STM technique has recently been established as a powerful tool that can be widely used to consistently modify surfaces in such ways. Basic manipulation mechanisms that have been clearly established may be grouped into the following categories: (a) Near-contact type, (b) Electronic excitation of adsorbates, (c) Ladder-type multiple vibrational excitation, and (d) Single electron resonant excitation. Examples of (a) include the lateral pushing/sliding of Xe atoms on Pt(111) at low temperatures, as well as the reversible transfer of Xe between tip and sample, where in both cases the tip is placed very close to the surface [13]. An example of (b) is H desorption from Si(100) at >6 V applied bias [14]. Examples of (c) include the dissociation of O_2 molecules [15] and desorption of hydrogen from silicon surfaces [16], while examples of (d) include the reversible transfer of CO between tip and sample [17] and the desorption of organic molecules from silicon [18–21].

Subsequent work has introduced many refinements: For example, several of the basic mechanisms have been employed to carry out the full Ullmann reaction on two specific iodobenzene molecules [22]. Also, large molecules can now be rotated and translated by small amounts on a surface, TBPP for example [23]. Atomic manipulation can even be used as a characterization tool for identifying products of surface dissociation studies, for example chlorine atoms from trichloroethylene [24]. Also noteworthy are recent results showing non-local STM induced manipulations (See [25] and references within) where it appears that the spread of injected carriers over ≈ 100 Å after tunneling plays an important role.

I begin, in Section 2, by developing a theory for thermodynamic induction involving n variables, under isothermal conditions, and deriving dynamical equations for the approach to equilibrium. The isothermal approach is naturally based on the Helmholtz free energy and is well-suited for describing particle transport. In Section 3 the importance of the quasistationary states is pointed out in the form of an important inequality regarding rates of free energy production. This is followed, in Section 4, by the establishment of a variational principle governing the minimization of a free power function specifically designed for the VKC systems. Important two-variable example systems are discussed in Section 5 and Section 6. Before concluding, I demonstrate in Section 7 how TI is incorporated into the limit of continuous variables. This section is a significant step towards incorporating TI into more complex continuum systems such as diffusing systems and systems with fluid flow.

2. General theory for isothermal thermodynamic induction

I consider a system A described by n thermodynamic variables x_i with equilibrium values x_{i0} . In this work I follow closely the approach presented in Ref. [3], with the main difference being that in this treatment I assume isothermal conditions, i.e., $dT = 0$ throughout. This approach involves a coupling of system A to a large heat bath, or reservoir, always held at temperature T . This traditional sort of reservoir will play a passive role in the analysis and is not to be confused with the DR which I introduced in Ref. [3] and plays a prominent role in my analysis below. I begin by considering only discrete variables, and subsequently develop a continuum theory in Section 7.

For system A, the Helmholtz free energy, $F = U - TS$, may be written as a function of the n variables x_i . The heat bath is not included, i.e., all subsystems considered below are part of system A, not the heat bath. The positive definite change ΔF , from equilibrium, of the total free energy, may be written as a function of the n state variables $a_i = x_i - x_{i0}$.

$$\Delta F \equiv F(x_1, x_2, \dots, x_n) - F(x_{10}, x_{20}, \dots, x_{n0}) = \frac{T}{2} \sum_{pq} c_{pq}^{-1} a_p a_q. \quad (1)$$

Generalized forces (affinities) are defined by

$$Y_p = -\frac{1}{T} \frac{\partial \Delta F}{\partial a_p}. \quad (2)$$

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