Work-Hamiltonian connection for anisoparametric processes in manipulated microsystems

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Abstract

In this article, we show that the two expressions $W = H_{\lambda=\lambda_2} - H_{\lambda=\lambda_1}$ and $\Delta G = -T \ln(Z_{\lambda=\lambda_2}/Z_{\lambda=\lambda_1})$, which relate the work W with the Hamiltonian H and the free energy G with the partition function Z for different values of the parameter λ, are not physically valid in general, not because they are fundamentally flawed *per se* but because they can be applied in ways that violate basic physical principles. One of these unphysical ways is now widespread in the study of non-equilibrium manipulated microsystems: it consists in the straightforward application of the above-mentioned relations for changes of an external parameter that is not a coordinate. We show that the estimates of the free energy differences so obtained are in fact the result of a contradictory use of isoparametric statistical ensembles to analyze anisoparametric processes. We indicate a potential avenue to avoid this contradiction, which brings the study of manipulated microsystems to a conventional non-equilibrium thermodynamics description.

1 Introduction

It is generally accepted that microscopic theories are valid only to the extent that they are consistent with thermodynamics. The most startling example was the demise of classical mechanics as a fundamental microscopic theory when Max Planck showed that it could not reproduce the thermodynamic properties of black body radiation [1].

Recently, there has been significant interest in the possibility of obtaining thermodynamic equilibrium properties from non-equilibrium perturbations in manipulated microsystems [2, 3]. These manipulations are usually carried out by changing a parameter rather than a coordinate. As appealing as this approach might be, it relies on the extrapolation by analogy of concepts from equilibrium statistical mechanics of autonomous systems to the non-equilibrium regime of non-autonomous systems.

We address here the domain of validity of two of these extrapolations:

First, conventional wisdom associates H with the energy of the system and therefore its change would have to be the work performed on the system. This is certainly true for an autonomous system. Strictly speaking, though, classical mechanics does not show that it is valid for parametric changes that do not follow equations of motion [4]. To what extent is the association $W = \Delta H$ valid for parametric changes?

Second, statistical mechanics has shown that $-T \ln Z$ can be identified with the free energy of the system [5]. An apparently minor quirk used in the derivation is that the partition function depends on the reference zero of the energy [6]. Is this quirk actually important for the interpretation of $-T \ln(Z_{\lambda=\lambda 2}/Z_{\lambda=\lambda 1})$ as physically meaningful free energy changes?

It is important to answer these two questions explicitly because the well-established stochastic framework of non-equilibrium thermodynamics does not require the underlying extrapolations [7–10]. To this end, we use as a benchmark an elastic system that follows Hooke's law and we investigate to what extent Hamiltonian and statistical mechanics extrapolations can recover this elementary textbook result.

2   Results

The elastic system is characterized by a linear force-extension relationship of the type

$$f_{\text{sys}} = -kx,$$

where f_{sys} is the force exerted by the system, x is the extension, and k is the proportionality constant. An external force f_{ext}, which increases quasi-statically from $f_{\text{ext}} = 0$ to $f_{\text{ext}} = f_0$, is applied to reach an extension $\tilde{x} = f_0/k$. For a quasi-static process, the external applied force f_{ext} balances with the system force so that $f_{\text{ext}} + f_{\text{sys}} \approx 0$. Consequently, the (reversible) work performed by the external force on the system during this process is

$$W = \int_0^{\tilde{x}} kx\,dx = \tfrac{1}{2}k\tilde{x}^2, \tag{1}$$

which leads to a free energy change

$$\Delta G = W = \tfrac{1}{2}k\tilde{x}^2 = f_0^2/2k. \tag{2}$$

Because the process takes place without heat exchange, both free energy and internal energy changes coincide; namely, $\Delta E = \Delta G$.

The expressions we have obtained are elementary textbook results, which typically appear in introductory courses for a wide variety of disciplines, including molecular physical chemistry [11], basic engineering [12], and freshman undergraduate physics [13], and to some extent also in advanced high school physics [14].

Therefore, measurable quantities, such as force and displacement, provide all the elements needed to obtain the equilibrium thermodynamic properties of this system without relying on mathematical tools such as partition functions and Hamiltonians.

What is the result obtained for this quasi-static non-equilibrium process from straightforward application of the equilibrium Hamiltonian approach to statistical mechanics?

The Hamiltonian describing the extension x,

$$H = \tfrac{1}{2}kx^2 - f_{\text{ext}}x, \tag{3}$$

incorporates contributions from the system itself, $H_{\text{sys}} = \tfrac{1}{2}kx^2$, and the interaction with the external force, $H_{\text{int}} = -f_{\text{ext}}x$. The partition function, computed as $Z = \int e^{-H/T} dx$ leads to a free energy change

$$\Delta G_Z = -T \ln \frac{Z_{f_{\text{ext}}=f_0}}{Z_{f_{\text{ext}}=0}} = -f_0^2/2k, \tag{4}$$

which is always negative.

Conventional wisdom might assume, as in some areas in the field of manipulated systems [3, 15], that the statistical mechanics approach is completely general and that the results obtained should be applicable for non-autonomous systems. But they are not, as we have shown: in the macroscopic limit, when fluctuations are not relevant, the partition function estimate (eq. (4)) is always negative, which disagrees with the actual free energy change (eq. (2)), which is always positive [16].

What went wrong and where?

We can get insights by looking at the parametric changes of the Hamiltonian in the macroscopic limit,

$$dW_{\text{IP}} = \frac{\partial H}{\partial f_{\text{ext}}} df_{\text{ext}} = -x df_{\text{ext}},$$

which has been interpreted as work in the field of manipulated systems [15]. Here, the subscript IP emphasizes that W_{IP} is an improper redefinition of work. For a quasi-static process that changes the external force from $f_{ext} = 0$ to $f_{ext} = f_0$, one obtains $W_{IP} = -f_0^2/2k$, which has the same value as ΔG_Z. In this case, dW_{IP} is neither the work done on the system ($dW = f_{ext}dx$) nor minus the work done by the system ($-dW_{ext} = kxdx$) [17]. Therefore, parametric changes of the Hamiltonian cannot be associated in these types of cases with the energy change of the system ($dW_{IP} \neq dE$), in the same way that ΔG_Z cannot be associated with actual free energy changes. The reason is that a parameter such as the strength of a force f_{ext} cannot be identified with a generalized coordinate that follows Hamilton equations, and therefore the work-Hamiltonian connection does not apply. Other parameters that can be identified with generalized coordinates, such as the position of the prototypical piston of an ideal gas, lead to parametric changes that can indeed be identified with work done by the system.

The presence of the term $H_{int} = -f_{ext}x$ in the Hamiltonian of the system can be viewed as a Legendre transformation of a thermodynamic potential. Indeed, such a transformation provides a thermodynamic potential for constant f_{ext}. In this case, it would be the isotensional potential and, in general, it would correspond to an isoparametric potential. Therefore, ΔG_Z is not the free energy change of the system, as one might assume from naive extrapolation: it is rather the difference of isotensional enthalpies for two values of the tension set by f_{ext}.

How is it possible to reconcile the facts that Hamiltonians and partition functions can be identified with the energy and the exponential of the free energy, respectively, but they do not recover the well-established macroscopic thermodynamic results?

There is an important distinction between (free) energies and (free) energy changes. Free energies are defined up to an arbitrary additive term and consequently only free energy differences are physical measurable quantities. The reason for this, as explained in elementary physics textbooks, is that by subtracting two energies, the arbitrary additive term is removed.

This arbitrary additive term is usually omitted because it does not affect any physical property of the system, such as its motion or free energy changes [4]. Yet, it sets the reference zero of the energy. In general, it does not depend on the generalized coordinates or momenta but can depend on parameters. Therefore, the problem with subtracting two free energies computed from Hamiltonians with different parameters is that typically the

arbitrary additive term depends on the parameter and consequently the result obtained remains arbitrary [16].

Specifically, the general expression for the potential energy in constant force field f_{ext} is

$$U(x; f_{\text{ext}}) = -f_{\text{ext}}x + f_{\text{ext}}x_0,$$

which assumes that x_0 is the reference point of the energy. Elementary physics textbooks (see for instance the discussion on gravitational potential energy in [13, p. 171]) emphasize the well-established fact that only potential energy differences are physically meaningful because by subtraction, the arbitrary reference point x_0 is removed: $U(x_2; f_{\text{ext}}) - U(x_1; f_{\text{ext}}) = -f_{\text{ext}}(x_2 - x_1)$. This arbitrary reference point, however, is not removed for non-coordinate parametric changes: $U(x; f_2) - U(x; f_1) = -(f_2 - f_1)x + (f_2 - f_1)x_0$. This basic general physics argument also applies directly to partition functions because of their functional dependence on the potential energy.

To illustrate in detail the implications of the reference zero of the energy, let us consider the Hamiltonian

$$H = \tfrac{1}{2}kx^2 - f_{\text{ext}}x + g(f_{\text{ext}}), \tag{5}$$

which includes the term $g(f_{\text{ext}})$ as an unspecified function of the external applied force. The total force acting on the system, $f_{\text{tot}} = -\partial H/\partial x = -kx + f_{\text{ext}}$, does not depend on $g(f_{\text{ext}})$. The partition function however does, which results in

$$\Delta G_Z = g(f_0) - g(0) - f_0^2/2k. \tag{6}$$

Therefore, the naive extension to non-autonomous systems of the Hamiltonian statistical mechanics approach leads to a result that is negative for $g \equiv 0$, in contradiction with the thermodynamic spontaneity criterion, and arbitrary in general, in contradiction with the fact that physical (experimentally measurable) quantities are unambiguous [16].

How is it possible to reconcile equilibrium statistical mechanics with thermodynamics for quasi-static non-equilibrium processes in non-autonomous systems?

Once the thermodynamic result $\Delta G = f_0^2/2k$ is known, it is possible to choose the arbitrary term by selecting *ad hoc* $g(f_0) = f_0^2/k + g(0)$ so that $\Delta G_Z = \Delta G = f_0^2/2k$. Following this approach, we find that the Hamiltonian that gives the actual physical energy and free energy changes of the system is

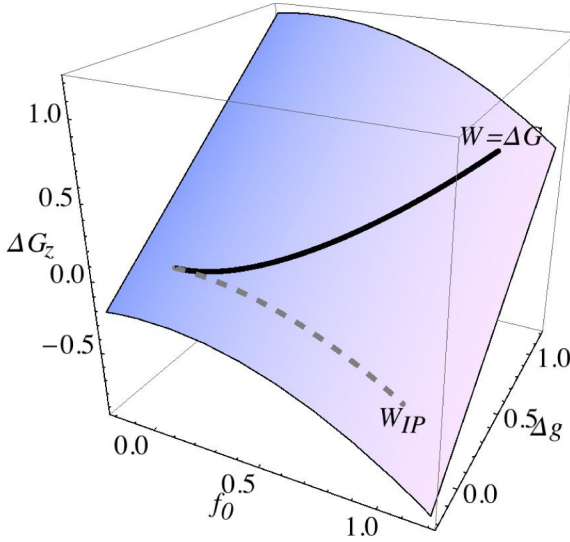$$H = \tfrac{1}{2}kx^2 - f_{\text{ext}}x + f_{\text{ext}}^2/k. \tag{7}$$

Figure 1. The quantity $\Delta G_Z = g(f_0) - g(0) - f_0^2/2k$ is shown as a function of both the final value of the external force f_0 and the arbitrary additive term change $\Delta g = g(f_0) - g(0)$ for $k = 1$ and zero initial external force. The dashed gray line for $\Delta g = 0$ indicates the nonphysical isoparametric enthalpy changes given by W_{IP} in a quasi-static anisoparametric process. The average work for a quasi-static process, $W = \Delta G = f_0^2/2k$, selects a trajectory in the $(f_0, \Delta g)$ space that provides actual thermodynamic free energy changes along the black line on the surface ΔG_Z.

In this case, for a quasi-static macroscopic process, parametric changes of the Hamiltonian agree with the actual definition of work in the macroscopic limit:

$$\frac{\partial H}{\partial f_{ext}} df_{ext} = (2 f_{ext}/k - x) df_{ext} \approx f_{ext} d\tilde{x},$$

where $\tilde{x} = f_{ext}/k$ is the equilibrium extension.

We illustrate these concepts in Figure 1, which shows the surface corresponding to ΔG_Z as a function of both the external force and the arbitrary additive term. The average work W for a quasi-static process selects a line in the surface that provides consistent thermodynamic free energy changes. Any other trajectory in this surface would provide nonphysical enthalpy changes, such as the line for $g \equiv 0$, which corresponds to the improper definition of work W_{IP}.

3   Conclusions

In summary, we have shown that non-equilibrium reinterpretation of partition functions and improper redefinitions of work, as used in some areas in the field of manipulated systems, can lead to results that do not fit into the conventional frameworks of equilibrium statistical mechanics and thermodynamics, not even in the case of the classic textbook example of a Hookean spring. In particular, the estimates of the free energy changes computed using those reinterpretations and redefinitions correspond in actuality to ambiguous changes of constant-parameter enthalpies when the parameter is changed. These enthalpy changes depend on the arbitrary choice of the reference system and by themselves are not physically meaningful.

Our results show a potential avenue to overcome these limitations through the use of the actual definition of work to choose the inherent arbitrary dependence so that the relationship between free energy changes and partition functions holds. In this way, it is possible to recover a work-Hamiltonian connection that is valid in the macroscopic limit for non-equilibrium quasi-static anisoparametric processes.

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