Comment on "Failure of the Work-Hamiltonian Connection for Free-Energy Calculations"

If the arguments put forward by Vilar and Rubi in their recent work [1] were valid, quite a few accepted results in standard statistical mechanics would have to be revised. Let us consider a system with the Hamiltonian $H(x, \lambda) = H_0(x) - Q(x, \lambda)$, in which λ is a parameter, initially at equilibrium at the inverse temperature β. Its free-energy, according to the usual understanding of statistical mechanics ([[2], (484)], [[3], (133.1–2)]) is given by

$$G_\lambda = -\frac{1}{\beta}\ln Z_\lambda, \qquad (1)$$

where $Z_\lambda = \int dx e^{-\beta H(x,\lambda)}$, and the integral runs over all the microscopic states of the system. Thus, if the parameter λ changes from λ_0 to λ_1 and the system is in equilibrium both at the beginning and at the end at the inverse temperature β, its free-energy change should be given by $\Delta G = -\beta^{-1}\ln[Z_{\lambda_1}/Z_{\lambda_0}]$. According to Vilar and Rubi [1], this expression for ΔG "is not thermodynamically valid when changes of the Hamiltonian cannot be associated with the work performed on the system." If they are right, since the expression for ΔG follows from (1) by subtraction, the connection (1) between the free-energy and the partition function, which is a cornerstone of the statistical mechanics interpretation of thermodynamics, is not valid either. Let us point out that the above expression of the free-energy change is a direct consequence of the thermodynamical relation $\Delta G = \Delta(E - TS) = W^{\rm th}$, valid for reversible isothermal transformations, and of the standard expression ([[2], p. 42–44], [[3], p. 527–535]) of the thermodynamical work, $W^{\rm th} = \int_{\lambda_0}^{\lambda_1} d\lambda \langle \partial H/\partial\lambda\rangle_\lambda$, where $\langle A\rangle_\lambda = \int dx A(x) e^{-\beta H(x,\lambda)}/Z_\lambda$ is the canonical average with the Hamiltonian $H(x, \lambda)$. (See, in particular [[3], (121.8), p. 535; (124.1), p. 542].) Note, moreover, that if an ergodic system undergoes an infinitely slow parameter change, the time integral $W = \int dt \partial H(x(t), \lambda(t))/\partial\lambda \dot{\lambda}(t)$ is equal to $W^{\rm th}$ in any realization of the process, independently of the size of the system. Thus it is natural to define W as the fluctuating work, which is equal to $W^{\rm th}$ in an infinitely slow process. This quantity satisfies a number of important fluctuation relations, in particular, the Jarzynski equality (JE), $\langle e^{-\beta W}\rangle = Z_{\lambda 1}/Z_{\lambda_0} = e^{-\beta\Delta G}$, where the angular brackets denote the average with respect to all realizations of the process [4]. Vilar and Rubi contend that the time-honored statistical mechanics expression of the thermodynamical work reported above is incorrect. They maintain that W is a recently introduced *ad hoc* redefinition of work, which "does not solve the physical inconsistencies, such as the dependence of ΔG_Z on arbitrary parameters." (The fact that these "physical inconsistencies" are illusory has been discussed elsewhere [5].) Vilar and Rubi prescribe that one should consider, instead of W, the work performed on the system during a manipulation, given by $W_0 = \int dt \dot{x}(t) \partial Q(x(t), \lambda(t))/\partial x$, and that W_0 does not satisfy the Jarzynski equality, but, e.g., satisfies $\langle e^{-\beta W_0}\rangle = 1$ for the case of a sudden change of the Hamiltonian. This last identity is indeed correct, and is a special case of an identity noticed long ago by Bochkov and Kuzovlev [6]. However, it does not affect the JE, which holds for W. Indeed, W does not represent the work done on the system, but rather the work done by the system on the external bodies which produce the change of the Hamiltonian (as emphasized by Gibbs [[2], p. 42] and Tolman [[3], p. 530, 2nd paragraph]). The two works are in general different, and it is W that is related to the thermodynamical work. The connection between the two works and their fluctuation relations has been recently discussed in detail by Jarzynski [7]. When the system evolves over a finite time interval, we have in general $W_0 - W = Q(x(t), \lambda(t)) - Q(x(0), \lambda(0))$. It turns out that W is more useful than W_0 for the reconstruction of free-energy landscapes, because one has not yet identified identities satisfied by W_0 which could be applied in this context. In any case, renouncing the use of W would entail giving up the connection (1) between the free-energy and the partition function, and would therefore require an extensive rewriting of the basic principles of statistical mechanics.

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