Work, work fluctuations, and free energy from kinetic theory

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The Boltzman-Loretnz kinetic equation [1] describes the dynamics of a particle immerse in a low density gas at equilibrium, and there is no doubt about its validity in the appropriate limit. Since it does not contain any hypothesis about the macroscopic description of the state of the particle, it seems an appropriate starting point to investigate questions related with the thermodynamic description of a particle in contact with a heat bath and, in particular, the validity under those circumstances of the two work theorems proposed by Jarzynski [2] and by Bochkov and Kuzovlev [3], respectively. It must be realized that these theorems are derived using reversible hamiltonian dynamics. Moreover, both theorems use different definitions of work, and the question of the relevance of both definitions in the context of thermodynamic is addressed. The theoretical analysis is complemented by particle simulations of the Boltzmann-Lorentz equation using the Direct Simulation Monte Carlo (DSMC) method. The conclusion reached is that the Jarzynski definition of work seems more appropriate for inhomogeneous systems, but that this theorem is not suitable when the dynamics of the macroscopic system, i.e. the time interval in which the measurements are carried out, occurs on time scales over which relaxation to equilibrium is observed. On the other hand, the theorem by Bochkov and Kuzovlev, referring to the usual thermodynamical definition of work for homogeneous systems, seems to be obeyed also when the tendency to the steady state must be taken into account.

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