Work fluctuation theorems and free energy from kinetic theory

J Javier Brey, M J Ruiz-Montero and Álvaro Domínguez

Física Teórica, Universidad de Sevilla, Apartado de Correos 1065, E-41080, Sevilla, Spain
E-mail: brey@us.es

Received 11 September 2017
Accepted for publication 1 December 2017
Published 22 January 2018

Abstract. The formulation of the first and second principles of thermodynamics for a particle in contact with a heat bath and submitted to an external force is analyzed, by means of the Boltzmann–Lorentz kinetic equation. The possible definitions of the thermodynamic quantities are discussed in the light of the H theorem verified by the distribution of the particle. The work fluctuation relations formulated by Bochkov and Kuzovlev, and by Jarzynski, respectively, are derived from the kinetic equation. In addition, particle simulations using both the direct simulation Monte Carlo method and molecular dynamics, are used to investigate the practical accuracy of the results. Work distributions are also measured, and they turn out to be rather complex. On the other hand, they seem to depend very little, if any, on the interaction potential between the intruder and the bath.

Keywords: fluctuation phenomena, kinetic theory of gases and liquids, Boltzmann equation, numerical simulations

1 Author to whom any correspondence should be addressed.
1. Introduction

There are in the literature several identities related with the work distribution associated to a process starting in a thermal equilibrium state [1–4]. In particular, the so-called Jarzynski fluctuation theorem or Jarzynski relation (JR) has been rederived in a variety of model systems [4–6] and employed to discuss a series of experiments [7–9]. On the other hand, some criticisms have been also raised about the correctness of the relation, concerning mainly the separation of the system from equilibrium along the process [10] and the definition of thermodynamic work used in the derivation [11]. Although both criticisms were answered by Jarzynski and collaborators [12, 13], it is worth to consider them as well as the relevance of work fluctuation theorems starting from a different level of description of the system. The analysis includes a work fluctuation relation by Bochkov and Kuzovlev (BK) [1, 2], which will be shown to be closely related with the Jarzynski one. The aim of this paper is to address the above issues as well as others related with the meaning and usefulness of the work relations, starting from a well-established kinetic equation for a particle in contact with a heat bath.

In thermodynamics, the free energy $F$ of an homogeneous and isotropic system at equilibrium is defined as

$$F = U - TS,$$

where $U$ is the internal energy, $T$ the absolute temperature, and $S$ the entropy. According with the second principle, the change of the free energy of a closed system in an infinitesimal quasistatic process is related to the work $dW$ performed by the system in the process by

$$dF = -SdT - dW.$$
It follows that, for a finite quasistatic process carried out at constant temperature, the difference $\Delta F$ between the final and initial equilibrium free energies is given by minus the total work $W_T$,

$$\Delta F = -W_T.$$  \hfill (3)

In equilibrium statistical mechanics, the connection with thermodynamics for homogeneous and isotropic systems is made through the relationship

$$F = -k_B T \ln Z.$$  \hfill (4)

Here $k_B$ is the Boltzmann constant and $Z$ the partition function of the system defined in the classical limit as an integral over the phase space $\Gamma$ of the system,

$$Z \equiv \int d\Gamma e^{-H(\Gamma)/k_B T},$$  \hfill (5)

with $H$ being the Hamiltonian of the system. A constant needed to render $Z$ dimensionless is omitted. If the Hamiltonian depends on a parameter, the free energy difference between two equilibrium states corresponding to two different values of the parameter can be obtained from the quasistatic work needed to go from one value to the other at constant temperature. Of course, the same difference can be formally computed by means of equation (4).

Suppose a system initially at equilibrium with a temperature $T$, being $H_0(\Gamma)$ its Hamiltonian. Then, at $t = 0$ the system is submitted to a time dependent perturbation, $\phi(\Gamma, t)$ so that the Hamiltonian becomes $H(\Gamma, t) = H_0(\Gamma) + \phi(\Gamma, t)$, with $\phi(\Gamma, 0) = 0$. Along the process, the system remains isolated, i.e. there is no heat exchange with another system. Assume that the same process of variation of the Hamiltonian can be repeated many times, starting always from the same macroscopic equilibrium state, and that the work $w(t)$ required in each individual process up to time $t$ is measured.

Using the properties of the Liouville equation, Bochkov and Kuzovlev [1, 2] obtained the relation

$$\langle e^{-w(t)/k_B T} \rangle = 1,$$  \hfill (6)

for arbitrary $t > 0$. The angular brackets denote an average over the ensemble of realizations of the process, i.e. over trajectories in phase space, and

$$w(t) \equiv - \int_0^t d\tau \sum_i \mathbf{v}_i(\tau) \cdot \frac{\partial \phi[\Gamma(\tau), \tau]}{\partial \mathbf{r}_i(\tau)},$$  \hfill (7)

where the sum extends over all the particles in the system, $\Gamma(\tau)$ is the phase point obtained from $\Gamma$ due to the evolution of the system between 0 and $\tau$. Similarly, $\mathbf{r}_i(\tau)$ and $\mathbf{v}_i(\tau)$ are the position and velocity of particle $i$ at time $\tau$, respectively. Notice that only the force associated with the perturbation, which vanishes up to $t = 0$, is considered when evaluating this work. Also, let us emphasize that the work is defined with its usual sign in mechanics and not as in the thermodynamic relation given in equation (2).

Twenty years later, Jarzynski [3, 4] derived for the same process the relation

$$\langle e^{-w(t)/k_B T} \rangle = e^{-\Delta F(t)/k_B T}.$$  \hfill (8)
In this expression, the angular brackets have the same meaning as in equation (6), and 
\[ \Delta F \equiv F[T; H(t)] - F[T; H_0] \] is the free energy difference between the two equilibrium 
states corresponding to \( H(\Gamma, t) \) and \( H_0(\Gamma) \). It is important to realize that the system is 
at equilibrium only at the initial time. As a consequence, the Jarzynski relation pro-
vides a method to get the difference between equilibrium values of the free energy \( F \) 
from measurements of the fluctuations of the work \( w' \) along trajectories extending well 
inside non-equilibrium regions. The quantity \( w' \) is identified as the work performed 
during each repetition of the process. In spite of the difference between equations (6) 
and (8), both results are mathematical identities, following directly from the Hamilton 
equations of motion and the form of the equilibrium canonical distribution. The apparent 
contradiction lies in the different definitions of work along a trajectory being used 
[14]. Jarzynski’s expression is 
\[ w'(t) \equiv \int_0^t d\tau \phi_\tau [\Gamma(\tau), \tau], \] 
\[ \phi_\tau (\Gamma, \tau) = \left( \frac{\partial \phi(\Gamma, \tau)}{\partial \tau} \right)_\Gamma. \] 
Again, the mechanical criterium for the sign of work has been used. Both work 
fluctuation relations were originally derived by means of (reversible and deterministic) 
Hamiltonian dynamics, although later on they were proven to remain valid for Markov 
stochastic dynamics [4]. A first question is whether the relations also remain valid for 
irreversible non-equilibrium dynamics as provided by kinetic theory, not necessarily 
with an underlying Markov process. Another significant issue is which are the right 
definitions of work and free energy to be used in the formulation of the second principle 
for these, in general, inhomogeneous systems, if one wants to keep the formulation 
given by equation (2). A particularly relevant context in which to study the above 
points seems to be a small system in contact with a heat bath, which corresponds to an 
idealization of most of the reported experiments related with work fluctuation relations. 
It is fair to mention that some of the above issues, concerning stationary properties of 
inhomogeneous systems, have been extensively studied by means of density functional 
theory [15].

The remaining part of the paper is organized as follows. In section 2, the Boltzmann– 
Lorentz (BL) kinetic equation for a particle in an external potential and in contact with 
a heat bath is introduced and used to derive energy balance equations, pointing out the 
several options that appear when defining the thermodynamic energy and the work in 
a process. Also, a modification of the celebrated \( H \) Boltzmann theorem is derived, lead-
ning to the identification of a thermodynamic potential that is associated with the free 
energy \( F \) of the inhomogeneous system. Details of the proof are given in appendix. The 
BK relation and the JR are derived from the kinetic equation in section 3. Both rela-
tions are explicitly checked by solving numerically the BL kinetic equation by means of 
the direct simulation Monte Carlo method in section 4. Equivalent results follow from 
molecular dynamics simulations in sufficiently dilute systems. In addition, the form of 
the work distributions along trajectories is investigated. The last section of the paper 
contains a short summary and some final comments.
2. Boltzmann–Lorentz kinetic equation in the presence of an external field

To address the questions raised in the previous section, consider a particle (intruder) of mass \( m \) immersed in a low density gas of particles of mass \( m_b \) and number of particles density \( n_b \). The gas is at equilibrium at temperature \( T_b \), and it is assumed that the state of the gas is not affected by the state of the intruder, i.e. it acts as a thermal bath. There is an external force acting on the particle of the form

\[
F = -\frac{\partial \phi(r, t)}{\partial r},
\]

where \( \phi_1(r, t) \) vanishes for \( t \leq 0 \). The probability density \( f(r, v, t) \) of finding the particle at position \( r \) with velocity \( v \) at time \( t \) obeys the Boltzmann–Lorentz (BL) equation \([16]\]

\[
\frac{\partial f}{\partial t} + v \cdot \frac{\partial f}{\partial r} + \frac{F}{m} \cdot \frac{\partial f}{\partial v} = J_{BL}[r, v, t| f, f_b],
\]

with the BL collision term given by

\[
J_{BL}[r, v, t| f, f_b] = \int dv_1 \int d\Omega \sigma(\Omega, g) g \left[ f(r, v', t) f_b(v'_1) - f(r, v, t) f_b(v_1) \right].
\]

Here \( v' \) and \( v'_1 \) denote the postcollisional velocities, \( g \equiv v - v_1 \) is the relative velocity of the intruder with respect to the gas particle before the collision, \( \sigma \) is the differential cross section, \( d\Omega \) is the solid angle element, and the primes indicate post-collisional velocities. Moreover, \( f_b(v_1) \) is the (equilibrium) one-particle distribution function of the gas,

\[
f_b(v_1) \equiv n_b \varphi_b(v_1),
\]

\[
\varphi_b(v_1) = \left( \frac{m_b}{2\pi k_B T_b} \right)^{3/2} e^{-m_b v_1^2 / 2 k_B T_b}.
\]

The BL equation can be considered as an exact equation in the low density limit, if it is assumed that the gas acts as an equilibrium bath with respect to the intruder, although the collisions between the intruder and the gas particles are left arbitrary, as long as they correspond to the qualitative picture of a repulsive part at short distances and a possible attractive part at larger distances, vanishing sufficiently fast in the limit of an infinite separation of the involved particles. In particular, let us emphasize that it does not presuppose anything about the macroscopic or thermodynamic description of the state of the particle. On the other side, it is assumed that the range of the interaction potential between the intruder and the bath particles is much shorter that the mean free path of the latter. As already mentioned, a particle inside an equilibrium fluid is the prototype of situations to which the work theorems have been applied, both in theoretical studies \([14, 17, 18]\), and in experiments \([7–9, 19]\). The average kinetic energy of the intruder at time \( t \) is

\[
e(t) \equiv \int dr \int dv \frac{m v^2}{2} f(r, v, t),
\]

\[
https://doi.org/10.1088/1742-5468/aa9f48
\]
and from equation (13) it is obtained
\[ \Delta e(t_1, t_2) \equiv e(t_2) - e(t_1) = Q(t_1, t_2) - W(t_1, t_2) \] (18)
with
\[ W(t_1, t_2) = -\int_{t_1}^{t_2} dt \int dr \int dv \ v \cdot F(r, v, t) \] (19)
and
\[ Q(t_1, t_2) = \int_{t_1}^{t_2} dt \int dr \int dv \ \frac{mv^2}{2} J_{BL}[r, v, t] \{ f, f_b \}. \] (20)

The physical meaning of the term denoted by \( Q \), as representing the energy exchange with the gas bath through collisions, strongly suggests identifying it with the heat dissipated in the process. Consistently, it seems appropriate to define \( e \) as the internal energy of the intruder, and the term \( W \) as the work, with the usual sign convention in thermodynamics. Alternatively, the total energy average
\[ e_0(t) \equiv \int dr \int dv \left[ \frac{mv^2}{2} + \phi(r, t) \right] f(r, v, t) \] (21)
can be considered. Then, again from the BL equation one gets
\[ \Delta e_0(t_1, t_2) \equiv e_0(t_2) - e_0(t_1) = Q(t_1, t_2) - W'(t_1, t_2), \] (22)
where \( Q(t_1, t_2) \) is the same as in equation (20) and
\[ W'(t_1, t_2) = -\int_{t_1}^{t_2} dt \int dr \int dv \ \frac{\partial \phi}{\partial t} f(r, v, t) \]
\[ = -\int_{t_1}^{t_2} dt \int dr \int dv \ \frac{\partial \phi_1}{\partial t} f(r, v, t). \] (23)

Therefore, there is an apparent ambiguity in the definition of internal energy (and work), raising the issue of which of the two above definitions is consistent with the classical formulation of thermodynamics. Let us point out that in kinetic theory [16, 20], and also in usual hydrodynamics [21], the local internal energy does not include the potential energy associated to an external field. In order to avoid misunderstandings, it is worth insisting on that the work expression considered by BK and given in equation (7) does not correspond exactly to the work expression defined by equation (19), since the force appearing in the former does not include the contribution from the external potential acting already before \( t = 0 \), i.e. the potential \( \phi_0(r) \). On the other hand, in the formulation of the JR, the difference between \( \phi \) and \( \phi_1 \) disappears, since the difference, \( \phi_0 \), does not depend on time.

Suppose for a while that the external field \( \phi \) does not depend on time (e.g. \( \phi_1 = 0 \)). Define the functional of the distribution function
\[ \mathcal{H}(t) \equiv \int dr \int dv f(r, v, t) \left[ \ln f(r, v, t) + \frac{mv^2}{2k_B T_b} + \frac{\phi}{k_B T_b} \right]. \] (24)
To avoid misunderstandings, it is worth emphasizing that no physical meaning is given to this quantity \textit{a priori}, but this issue will be considered once its dynamical behaviour is established. It can be proven (see appendix) that for any solution of the BL equation it is

\[
\frac{\partial H(t)}{\partial t} \leq 0,
\]

for all times. The equality only holds if

\[
f(r, v, t) = n(r, t) \varphi(v),
\]

where

\[
\varphi(v) = \left( \frac{m}{2\pi k_B T_b} \right)^{d/2} e^{-mv^2/2k_B T_b}
\]

and \( n(r, t) \) is an arbitrary intruder density field. Moreover, if the two physical conditions

\[
\int dv f(r, v, t) < \infty,
\]

\[
\int dv v^2 f(r, v, t) < \infty
\]

are verified, and \( \phi(r, t) \) is bounded from below, \( H(t) \) is also bounded from below \cite{16}, implying that for any solution of the BL equation \( H(t) \) tends to a steady value \( H_{st} \). As a consequence, the probability density also tends to a stationary form \( f_{st} \). Requiring stationarity to the solution of the BL equation implies that the number density of the intruder be stationary and it has the form

\[
n(r) = ce^{-\phi(r)/k_B T_b},
\]

with

\[
c^{-1} = \int dr e^{-\phi(r)/k_B T_b}.
\]

Therefore, the stationary distribution, which is always reached in the long time limit, is given by the expected expression

\[
f_{st}(r, v) = n(r) \varphi(v).
\]

A short sketch of the derivation of the above property is provided in appendix. In the steady state, it seems appropriate to identify the temperature of the intruder, assumed homogeneous, with that of the gas bath \( T_b \). Moreover, the steady value of the functional \( H \) is

\[
H_{st} = \ln c + \frac{d}{2} \ln \frac{m}{2\pi k_B T_b},
\]

and it is easily seen that it accomplishes the relation

\[
H_{st} = -\ln Z,
\]
where $Z$ is the partition function of the intruder,

$$Z \equiv \int dr \int dv \ e^{-\beta \left( \frac{mv^2}{2} + \phi \right)}, \quad (35)$$

with $\beta \equiv (k_B T_b)^{-1}$. The above results strongly suggest to identify the equilibrium free energy of the intruder as

$$F_{st} \equiv -k_B T_b \ln Z. \quad (36)$$

The identification of $T_b$ as the temperature of the intruder, as well as the above definition for the free energy are not trivial extensions of equilibrium thermodynamics of homogenous systems to systems submitted to an external field, and they have been extensively analyzed in the literature from the perspective of ensemble theory, since they are crucial starting points for the development of the density functional theory for inhomogeneous fluids [15]. A simple calculation shows that the stationary average total energy of the intruder $e_{0, st}$ can be expressed as

$$e_{0, st} = -\left( \frac{\partial \ln Z}{\partial \beta} \right)_{\phi}. \quad (37)$$

From the expression of $\ln Z$ it follows that for a quasistatic process,

$$dF = -k_B (\ln Z + \beta e_{0, eq}) dT + \int dr \ n(r) \delta \phi(r), \quad (38)$$

where $\delta \phi$ is the variation of the external potential, for instance, as a consequence of the variation of an external parameter. Therefore, if one wants equation (2) to hold as the formulation of the second principle for systems submitted to a nonuniform external field, we have to identify the entropy and the work as

$$S = k_B (\ln Z + \beta e_{0, eq}) \quad (39)$$

and

$$dW = -\int dr n(r) \delta \phi(r), \quad (40)$$

respectively. Note that this definition of work is consistent with the expression used in the JR, aside from the different criteria used for the sign. Actually, not realizing the different expressions of both $dF$ and $dW$ in equations (2) and (38) is at the origin of some discussions about the validity of the JR appearing in the literature [11, 12, 22]. We believe that the above discussion provides a physical justification, and interpretation, for the definition of work used in the formulation of the Jarzynski relation.

### 3. Work fluctuation relations from the Boltzmann–Lorentz equation

It is convenient to express the BL equation in the compact form

$$\frac{\partial f(r, v, t)}{\partial t} = \Lambda(r, v, t) f(r, v, t), \quad (41)$$

https://doi.org/10.1088/1742-5468/aa9f48
with
\[ \Lambda(r, v, t)g(r, v) \equiv -v \cdot \frac{\partial g}{\partial r} - \frac{F}{m} \cdot \frac{\partial g}{\partial v} + J_{BL}[g, f_b], \tag{42} \]
for arbitrary \( g(r, v) \). The BL equation is an evolution equation for the distribution function of the intruder. To go a little deeper into the meaning of the kinetic theory description, let us consider the mechanical Hamiltonian analysis of both the bath particles and the intruder, assuming that the system as a whole is isolated, so all the particles obey deterministic evolution equations. Consistently with the hypothesis that the surrounding gas acts on the intruder as a thermal bath, let us assume that the initial joint probability distribution for the bath particles and the intruder factorizes in the form
\[ \rho(\Gamma, 0) = \rho_b(\Gamma_b) f(x_0, 0), \tag{43} \]
where \( x \equiv \{r, v\} \) denotes the phase space coordinates of the particle and \( \Gamma_b \) is a point in the phase space associated to all the bath particles. The probability function \( f(x, t) \) is defined as
\[ f(x, t) \equiv \int d\Gamma_b \int dx_0 \delta[x - x(t)] \rho_b(\Gamma_b) f(x_0, 0). \tag{44} \]
In this expression, \( x(t) \) is the phase space point describing the dynamical state of the intruder at time \( t \), assuming that at \( t = 0 \) the point was \( x_0 \). Of course, \( x(t) \) is determined by the deterministic equations of motion of all the particles composing the system. The form of the BL kinetic equation can be formally expressed by saying that inside phase space integrals averaging over the initial conditions, for times large enough it is
\[ \frac{\partial}{\partial t} \delta[x - x(t)] = \Lambda(x, t) \delta[x - x(t)]. \tag{45} \]
Of course, this implies in particular that \( f(x, t) \), as defined in equation (44), is accurately described by the BL equation. Next, define the function [8]
\[ I(x, t) \equiv \int d\Gamma_b \int dx_0 \rho_b(\Gamma_b) f_{st}(x_0, 0) \delta[x - x(t)] e^{-\beta w'(t)}, \tag{46} \]
with the work \( w'(t) \) being given by equation (9), and therefore it is a function of both the coordinates of the bath particles \( \Gamma_b \) and of the intruder \( x_0 \). It is
\[ I(x, 0) = f_{st}(x, 0). \tag{47} \]
Here and in the following we use the notation
\[ f_{st}(x, t) = Z(t)^{-1} e^{-\beta \left[ \frac{m v^2}{2} + \phi(r, t) \right]}, \tag{48} \]
\[ Z(t) = c(t) \left( \frac{m}{2 \pi k_B T_b} \right)^{-3/2}, \tag{49} \]
\[ c(t) = \int dr e^{-\beta \phi(r, t)}. \tag{50} \]
Time derivative of the expression of $I$ yields
\[
\frac{\partial I}{\partial t} = -\beta \phi_t(x, t) I + \Lambda(x, t) I,
\] (51)
where equation (45) has been employed. Taking into account that $f_{st}(x, t)$ verifies $\Lambda(x, t) f_{st}(x, t) = 0$, it is easily verified that the solution of the differential equation (51) with the initial condition (47) is
\[
I(x, t) = Z(0)^{-1} e^{-\frac{\beta}{2} \left[ \frac{mv^2}{2} + \phi_0(x) \right]}.
\] (52)
Integration of this expression over $x$, taking into account the definition of $I$ given in equation (46), gives
\[
\int d\Gamma_b \int dx_0 \rho_b(\Gamma_b) f_{st}(x_0, 0) e^{-\beta w(t)} = \frac{Z(t)}{Z(0)}.
\] (53)
Finally, by employing the definition of the free energy, equation (36), the Jarzynski relation (8) follows directly.

Next, the BK relation, equation (6), will be derived. To do so, the function
\[
L(x, t) \equiv \int d\Gamma_b \int dx_0 \rho_b(\Gamma_b) f_{st}(x_0, 0) \delta [x - x(t)] e^{-\beta w(t)},
\] (54)
is introduced. The work $w(t)$ is defined by equation (7), i.e.
\[
w(t) = -\int_0^t d\tau \v (\tau) \cdot \phi_{1r} \left[ x(\tau), \tau \right],
\] (55)
with
\[
\phi_{1r} \left[ x, \tau \right] \equiv \left( \frac{\partial \phi_1 (r, \tau)}{\partial r} \right) \tau.
\] (56)
From equation (54) it follows that
\[
L(x, 0) = f_{st}(x, 0).
\] (57)
Consider
\[
\int_0^t d\tau \frac{d}{d\tau} \phi_1 \left[ x(\tau), \tau \right] = \int_0^t d\tau \left\{ \phi_r \left[ x(\tau), \tau \right] + \v (\tau) \cdot \phi_{1r} \left[ x(\tau), \tau \right] \right\},
\] (58)
and, since $\phi_1(x, 0) = 0$,
\[
\phi_1 \left[ x(t), t \right] = w'(t) - w(t).
\] (59)
Therefore, equation (46) and (54) give
\[
L(x, t) = e^{\beta \phi_1(x, t)} I(x, t) = e^{-\beta \left[ \frac{mv^2}{2} + \phi_0(x) \right]} \frac{Z(t)}{Z(0)}.
\] (60)
In the last transformation, equation (52) has been used. Integration of the above equality with respect to $x$ leads to the desired result,
\[ \int d\Gamma_b \int d\mathbf{x}_0 \rho_b(\Gamma_b) f_{\text{st}}(\mathbf{x}_0, 0)e^{-\beta w(t)} = 1. \] (61)

Let us emphasize that equation (60) shows that both work fluctuation relations, although apparently very different, are closely related. Also, it is worth stressing that the functions \( I \) and \( L \) remain Maxwellian, with the \( \beta \) parameter determined by the bath temperature, for all times and then the collision term in equation (51) vanishes.

4. Numerical simulations of the kinetic equation

In order to investigate whether the above theoretical predictions are easy to observe, in the sense of how many trajectories are needed to get reliable results, and also to study the work probability distributions for both definitions (Jarzynski and Bochkov and Kuzovlev), the kinetic equation has been solved using the direct simulation Monte Carlo (DSMC) method [23]. This is a particle simulation method, in which the actual dynamics of the particles is substituted by an effective stochastic dynamics consistent with the low density limit. It has been rigorously proven that the average over trajectories provides a solution of the Boltzmann equation. The method, originally designed for the nonlinear Boltzmann equation, can be easily adapted for the BL equation [24].

In the simulations to be reported, hard-sphere interactions of diameter \( d \) between the intruder and the gas particles have been employed. Moreover, the mass of the intruder has been taken the same as that of the bath particles, i.e. \( m = m_b \). Two different external fields have been employed. In case I, an harmonic potential is perturbed by a uniform force whose amplitude grows linearly in time. More specifically,

\[ \phi_0(x) = \frac{m\omega_0^2x^2}{2} \] (62)

and

\[ \phi_1(x, t) = -f_0 \frac{t}{t_0} x \Theta(t). \] (63)

In case II, the unperturbed potential \( \phi_0(x) \) is the same as in case I, and \( \phi_1 \) is another harmonic field,

\[ \phi_1(x, t) = \frac{m\omega_1(t)^2x^2}{2} \] (64)

with

\[ \omega_1^2(t) = \omega_1^2f_1 \frac{t}{t_0} \Theta(t). \] (65)

In the above expressions, \( \omega_0, f_0, t_0, \) and \( \omega_1f_1 \) are constants to be specified later, and \( \Theta(t) \) is the Heaviside step function. The time parameter \( t_0 \) controls how fast the perturbation is applied, the limit \( t_0 \to \infty \) defining the quasistatic process. Notice that all the forces act along the same direction, namely along the \( x \) axis.
The simplicity of the chosen external fields allows to evaluate analytically the partition function defined in equation (35) and hence to get the value of the equilibrium free energy associated to each value of $\phi(x, t)$ by means of equation (36). In the simulations, the time origin is always taken after the system has reached a stationary state with the harmonic potential $\phi_0$. The form for the external potentials was motivated by comparison purposes, since these potentials have been used previously in the literature [11, 12]. The reported results have been averaged over $10^7$ trajectories, and dimensionless quantities have been defined by taking the mean free path of the gas particles, $\lambda$, as the unit of length, the mass of the gas particles $m_e$, as the unit of mass, and $k_B T_b$ as the energy unit.

In figure 1, the average values of $e^{-\beta w(t)}$ and of $e^{-\beta w'(t)}$ are plotted as functions of time for the perturbation referred to as case I. The values of the parameters are $\omega_0 = 0.5$, $f_0 = 1$, and $t_0 = 80$. Symbols are simulation results, while the solid line is the theoretical prediction of the JR, using the values of the free energy obtained analytically from equations (35) and (36). It is observed that both work theorems are quite well fulfilled by the numerical data. A similar conclusion is reached for the perturbation corresponding to case II as it can be observed in the results shown in figure 2. In the reported results, two different values of the final frequency of the perturbation, $w_{1f}$, have been employed, as indicated in the inset of the figure.

Consider the Jarzynski definition of work, and define the probability density, $P(w', t)$, of getting a given value for it along a given protocol of variation of the external field, so that

$$\langle e^{-w'(t)/k_B T_b} \rangle = \int dw' P(w', t) e^{-w'/k_B T_b},$$

(66)

and similarly for any other function of $w'(t)$. Let us introduce the joint probability density, $P(x, w', t)$, for given values of the position and velocity of the intruder at time $t$, and the work carried out up to that time, along a given protocol of variation of the external potential. This quantity is given by

$$P(x, w', t) = \int d\Gamma_b \int dx_0 \rho_b(\Gamma_b) f_{st}(x_0, 0) \delta [x - x(t)] \delta [w' - w'(t)],$$

(67)

where once again it has been assumed that the intruder was at equilibrium at $t = 0$, when the perturbation is switched on. Trivially it is

$$\int dx P(x, w', t) = P(w', t).$$

(68)

From equations (67) and (45) it follows that

$$\frac{\partial}{\partial t} P(x, w', t) = \Lambda(x, t) P(x, w', t) + \phi_t(x, t) \frac{\partial}{\partial w'} P(x, w', t).$$

(69)

This differential equation is to be solved with the initial condition

$$P(x, w', 0) = f_{st}(x, 0) \delta(w').$$

(70)

An analogous equation can be derived for the joint distribution of $x$ and the work along a trajectory $w(t)$ considered by Bochkov and Kuzovlev. Nevertheless, both equations are
hard to solve for nontrivial external potentials, so in the following numerical results obtained by the DSMC method will be reported.

In figure 3, the time evolution of the probability distribution of the BK expression of work $w$ at different times is shown for the same system as in figure 1. It is observed that as time progresses the width of the distribution increases and its maximum moves to the right, i.e. positive values of the work become more frequent. Actually, the
distribution seems to be Gaussian at all times, as seen in figure 4, where the distributions of \((w - \langle w \rangle) / \sigma\), with \(\sigma\) being the standard deviation of each original distribution, are plotted on a logarithmic scale.

Figure 3. Bochkov and Kuzovlev work distribution for the same system as considered in figure 1. The different symbols correspond to DSMC results at five different times, as indicated in the inset. As time increases the curves move to the right.

Figure 4. The same as in figure 3 but now each of the curves is scaled with its standard deviation and displaced its mean value. Moreover a logarithmic representation is employed. The solid line is the Gaussian distribution with zero mean and unit standard deviation.

In the case of the work definition used by Jarzynski, the behaviour of the probability distribution is similar, but with two key differences, as it can be observed in figures 5 and 6. First, as time increases the curves move to the left, i.e. negative values of the work are more frequent. The second difference is that now the distributions seem to be clearly non-Gaussian since the deviation observed at both tails of the distribution in figure 6 can hardly be attributed to statistical uncertainties, given the systematic
character of the deviations. In any case, the sharp collapse of the curves when scaling must be noticed.

We have performed the same study for case II, i.e. for external potentials given by equations (62) and (64). The results reported in figures 7 and 8 are for a system with the same values of the parameters as in figure 2, but only the value $\omega_{1f} = 1$ is displayed. It follows from the figures that the scaling does not collapse the curves for this perturbation. Moreover, the curves strongly deviate from a Gaussian and exhibit exponential tails. The conclusion is that the shape of the work distributions strongly depends on the definition of work used and on the particular external perturbation applied to the system. These features were expected. Something more surprising is that the shape of the work distribution for a given external potential changes in time in a nontrivial way.

Figure 5. Jarzynski work distribution for the same system as considered in figure 1. The different symbols correspond to DSMC results at five different times, as indicated in the inset. As time increases the curves move to the left.

Figure 6. The same as in figure 5 but now each of the curves is scaled with its standard deviation and displaced its mean value. Moreover a logarithmic representation is employed. The solid line is the Gaussian distribution with zero mean and unit standard deviation.
in spite of the fact that the two work fluctuation relations we are studying, which refer to the average of exponential functions, hold for all times.

To test the actual accuracy of the theoretical predictions derived from the BL equation, we have also performed molecular dynamics (MD) simulations of a tagged particle immersed in a bath of identical particles, so that the explicit form of the kinetic equation is not assumed. The particles interact by a Lennard-Jones potential of diameter $\sigma$ and depth of the attractive well $\epsilon$. As in the previous simulations, only the tagged particle feels the external potentials, that were chosen identical to those of the DSMC study, cases I and II. In our MD simulations, a system of $N = 1000$ particles

**Figure 7.** Bochkov and Kuzovlev work distribution for the same system as considered in figure 2. The different symbols correspond to DSMC results at five different times, as indicated in the inset. Each of the curves is scaled with its standard deviation and displaced an amount equal to the work mean value. Moreover a logarithmic representation is employed.

**Figure 8.** Jarzynski work distribution for the same system as considered in figure 2. The different symbols correspond to DSMC results at five different times, as indicated in the inset. Each of the curves is scaled with its standard deviation and displaced an amount equal to the work mean value. Moreover a logarithmic representation is employed.
was considered, and the results were averaged over 4000 trajectories. Three different values of the density were investigated, namely \( n\sigma^3 = 0.1, 0.3, \) and 0.5. In figure 9 the MD results for the averages of both \( e^{-\beta w(t)} \) and of \( e^{-\beta w'(t)} \) are plotted as a function of \( t/t_{LJ} \), with \( t_{LJ} = \sigma (m/\epsilon)^{1/2} \) for the perturbation named case I. The density in this case was \( n\sigma^3 = 0.3 \), and the external potential parameters were \( f_0/(m\omega_0^2\sigma) = 4, \) \( t_0/t_{LJ} = 15 \). The solid line is the exact theoretical value for \( e^{-\beta \Delta F} \).

Figure 9. MD results for the BK function (stars) and the Jarzynski work function (circles) in a Lennard-Jones system with \( n\sigma^3 = 0.3 \). The external potential for the intruder was case 1, with \( f_0/(m\omega_0^2\sigma) = 4, \) \( t_0/t_{LJ} = 15 \). The solid line is the exact theoretical value for \( e^{-\beta \Delta F} \).

5. Summary and final comments

It has been shown that both the Bochkov and Kuzovlev relation and the Jarzynski relation, are fulfilled by a particle or intruder immersed in a much larger dilute system at equilibrium. Although the theoretical results presented here are restricted to the BL kinetic equation, we have also performed molecular dynamics (MD) simulations at low density, and obtained fully consistent results.

On the other hand, it must be emphasized that the required measurements of the fluctuations of the respective works involved in each relation seem hard tasks in practice. The order of magnitude of the number of trajectories required to obtain a result with low noise level is very high, at least several thousands in the simulations we have performed (DSMC and MD). This difficulty has already been pointed out in
the literature [25–27]. Consequently, it is hard to see any advantage of this procedure over measuring the work in the quasistatic limit of an isothermal process, in order to measure equilibrium free energy changes.

It has been shown that on the basis of kinetic theory it is possible to formulate a well founded non-equilibrium macroscopic theory for a particle in contact with a heat bath. This approach can be a complementary alternative to the so-called stochastic thermodynamics.

The analysis presented here can be directly extended to systems described by a linear kinetic theory. This extension can be seen to be trivial for all tagged particle kinetic equations with a collision term that vanishes for Mawellians with the appropriate temperature parameter. A nontrivial and interesting extension, surely requiring a more complex analysis, is to consider nonlinear kinetic equations, e.g. the Boltzmann and Enskog equations.

Acknowledgments

This research was supported by the Ministerio de Economía y Competitividad (Spain) through Grant No. FIS2014-53808-P (partially financed by FEDER funds).

Appendix. The H theorem for the Boltzmann–Lorentz equation in an external field

In this appendix a short outline of the derivation of the theorem stated in section 2 is provided. Taking time derivative in equation (24) yields

$$\frac{\partial H}{\partial t} = \int dr \int dv \frac{\partial f}{\partial t} \left( \ln f + \frac{mv^2}{2k_BT_b} + \frac{\phi}{k_BT_b} \right).$$

(A.1)

The BL kinetic equation is decomposed in the form

$$\frac{\partial f}{\partial t} = \left( \frac{\partial f}{\partial t} \right)_{\text{flux}} + J_{BL}[f, f_b],$$

(A.2)

with

$$\left( \frac{\partial f}{\partial t} \right)_{\text{flux}} \equiv -v \cdot \frac{\partial f}{\partial r} - \frac{F}{m} \cdot \frac{\partial f}{\partial v}.$$  

(A.3)

Consider first

$$\left( \frac{\partial H}{\partial t} \right)_{\text{flux}} \equiv \int dr \int dv \left( \frac{\partial f}{\partial t} \right)_{\text{flux}} \left( \ln f + \frac{mv^2}{2k_BT_b} + \frac{\phi}{k_BT_b} \right).$$

(A.4)

A simple calculation, assuming that the system is closed and isolated in the sense that there is no flux of particles or any other property through the boundaries, and that the distribution function $f$ decays fast enough for large values of the velocity, as it is usually done, leads to
\[\left(\frac{\partial \mathcal{H}}{\partial t}\right)_{\text{flux}} = 0.\] (A.5)

Therefore,
\[\frac{\partial \mathcal{H}}{\partial t} = \int dr \int dv J_{\text{BL}}[r, v, t \mid f, f_b] \left( \ln f + \frac{mv^2}{2k_B T_b} + \frac{\phi}{k_B T_b} \right).\] (A.6)

The BL collision term verifies
\[\int dv a(v) J_{\text{BL}}[r, v, t \mid f, f_b] = \int dv \int dv_1 \int d\Omega \left[ a(v') - a(v) \right] \sigma(\Omega, g)f(r, v, t) f_b(v_1),\] (A.7)

for any arbitrary function \(a(v)\). This relation follows from the properties of elastic collisions, namely the volume conservation in velocity space, the equality of the cross section for a collision and its inverse, and the conservation of the module of the relative velocity. Use of the property (A.7) leads to
\[\begin{aligned}
&\int dr \int dv J_{\text{BL}}[r, v, t \mid f, f_b] \left( \frac{mv^2}{2k_B T_b} + \frac{\phi}{k_B T_b} \right) \\
&\quad = -\int dr \int dv \int dv_1 \int d\Omega \sigma(\Omega, g)g \left[ f(r, v', t) f_b(v_1) - f(r, v, t) f_b(v_1) \right] \frac{mv_1^2}{2k_B T_b} \\
&\quad = \int dr \int dv \int dv_1 \int d\Omega \sigma(\Omega, g)g \left[ f(r, v', t) f_b(v_1) - f(r, v, t) f_b(v_1) \right] \ln f_b(v_1),
\end{aligned}\] (A.8)

and substitution of this result into equation (A.6) gives
\[\frac{\partial \mathcal{H}}{\partial t} = \int dr \int dv \int dv_1 \int d\Omega \sigma(\Omega, g)g \left[ f(r, v', t) f_b(v_1') \right. \\
\left. \quad - f(r, v, t) f_b(v_1) \right] \ln \left[ f(r, v, t) f_b(v_1) \right] \\
\quad = \frac{1}{2} \int dr \int dv \int dv_1 \int d\Omega \sigma(\Omega, g)g \left[ f(r, v', t) f_b(v_1') \right. \\
\left. \quad - f(r, v, t) f_b(v_1) \right] \ln \left( f(r, v, t) f_b(v_1) \right)f(r, v', t) f_b(v_1') \leq 0.\] (A.9)

The equality sign only holds if \(f(r, v, t) = f_i(r, v, t)\) such that
\[\frac{f_i(r, v, t) f_b(v_1)}{f_i(r, v', t) f_b(v_1')} = 1,\] (A.10)

i.e.
\[f_i(r, v, t) = n(r, t) \varphi(v),\] (A.11)

where \(\varphi(v)\) is given by equation (27) and \(n(r, t)\) is up to this point arbitrary, aside from the normalization condition. Moreover, if the two conditions (28) and (29) are verified, \(\mathcal{H}(t)\) is bounded from below [16] and

https://doi.org/10.1088/1742-5468/aa9f48
\[
\lim_{t \to \infty} f(r, v, t) = f_l(r, v, t). \quad (A.12)
\]

Now, we have to require \(f_l(r, v, t)\) to be a solution of the BL equation. This is easily seen to imply that \(n\) does not depend on time and that it obeys the equation
\[
\frac{\partial n(r)}{\partial r} = -\frac{1}{k_B T_b} \frac{\partial \phi}{\partial r}. \quad (A.13)
\]

The solution of this equation is given by equation (30), and then \(f_l\) in equation (A.11) becomes \(f_{st}\) in equation (32).

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