Calculating the free energy difference by applying the Jarzynski equality to a virtual integrable system

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(Dated: May 28, 2018)

The Jarzynski equality (JE) provides a nonequilibrium method to measure and calculate the free energy difference (FED). Note that if two systems share the same Hamiltonian at two equilibrium states, respectively, they share the same FED between these two equilibrium states as well. Therefore the calculation of FED of a system may be facilitated by considering instead another virtual system designed to this end. Taking advantage of this flexibility and JE, we show that by introducing an integrable virtual system, the evolution problem involved in JE can be solved and as a consequence, FED is expressed in the form of an equilibrium equality. Numerically, this result allows FED to be computed by directly sampling the canonical ensemble and the computational cost can be significantly reduced. The effectiveness and efficiency of this scheme are illustrated with two one-dimensional (1D) models that represent 1D lattices and fluids, respectively.

PACS numbers: 05.70.Ln, 05.10.-a, 82.20.Wt

I. INTRODUCTION

The (Helmholz) free energy is a state variable of a thermodynamic system. When the system changes its state from one to another at the same temperature, the decrease of the free energy gives the largest work the system can output. As the free energy explains the phase behavior of a system and can be directly related to the experimentally determined properties, it plays an important role in a broad spectrum of applications [1].

Nevertheless, in general, to measure and calculate the free energy efficiently is challenging. According to the second law, the largest work can be captured only when the system changes its state reversibly, i.e., infinitely slow so that the process remains quasistatic. This makes the measurement of the free energy (the largest work) difficult, as any measurement has to be carried out in a reasonable, finite time. The numerical computation of the free energy is also difficult, because unlike ‘mechanical’ state variables, which can be computed directly by sampling the equilibrium ensemble, the free energy involves the evaluation of the whole phase space by definition [2,3]. A conventional method for computing the free energy difference (FED) between two given states is the thermodynamic integration method [4], by which one has to first compute some related state variables (e.g., the pressure, in an isothermal process) as a function of the medium equilibrium states of the quasistatic process that connects the two given states, then obtain FED by integrating this function. Obviously, this is computationally more expensive and inefficient.

In 1997, Jarzynski found a significant equality that relates FED between two equilibrium states (at the same temperature) to the work done to the system in a nonequilibrium process [5]. Precisely, suppose the Hamiltonian of the system is $H(z; \lambda)$, where $z$ is the system state and $\lambda$ is an external system parameter. When the parameter is changed in time following a given prescribed protocol $\lambda(t)$ from $\lambda_A$ at time $t_A$ to $\lambda_B$ at time $t_B$, Jarzynski’s equality (JE) states that

$$e^{-\beta \Delta F} = \langle e^{\beta w} \rangle_A. \quad (1)$$

Here $\beta \equiv 1/(k_B T)$ is the inverse temperature, $\Delta F \equiv F_B - F_A$ is FED between equilibrium state A and B parameterized by $\lambda_A$ and $\lambda_B$, respectively, and $w$ is work done to the system when it is evolved from an initial state sampled from the canonical ensemble of state A at time $t_A$ up to time $t_B$. The work depends on the initial condition; By repeating sampling the initial condition, the work distribution can be established, over which the exponential work average can be evaluated and in turn FED is obtained. The angular brackets and the subscript $A$ at the r.h.s. of Eq. (1) represent the average over the canonical ensemble of A. Note that the system does not necessarily relax to equilibrium state B at time $t_B$, which is a profound property of JE. Also note that when the system evolves, it can be isolated or coupled to the environment of temperature $T$ [3,6].

Jarzynski’s equality provides an alternative method for measuring and computing FED. As the time interval $t_B - t_A$ to drive the system can be finite and short, it seems particularly favorable for experimental measurements [7–10]. However, as pointed out by Jarzynski [5,11] and other authors, in practice, to apply JE directly may be inconvenient, because small work with rare probability weights heavily for the exponential average $\langle e^{-\beta w} \rangle_A$, a hefty sample could be needed to evaluate it accurately, and thus the cost could be demanding. Therefore, a key consideration in using JE directly is how to allocate the cost for sampling and driving the system. In general, for
a given accuracy, the shorter is the time interval \( t_B - t_A \), the larger is the work fluctuation and the sampling size needed. An empirical rule is to keep the work fluctuation to be less than \( k_B T \).\(^12\)

Since JE was revealed, many efforts have been made to develop improved algorithms for computing FED. A thorough survey can be found in Ref.\(^12\). Roughly, these efforts can be classified into two categories, one is to shorten the time needed to evolve the system by molecular dynamics simulations and another is to reduce the statistical uncertainty for evaluating \( \langle e^{-\beta w} \rangle_A \). In the former, the main progress is the targeted free energy perturbation method developed by Jarzynski based on a generalized JE\(^13\). This method is a variant of the free energy perturbation theory\(^14\), which allows FED to be computed with crude trajectories simulated with large time steps\(^15\),\(^16\). To reduce the statistical uncertainty, the most ‘straightforward’ way is to take the work biased sampling schemes to generate more trajectories whose work values dominate in calculating \( \langle e^{-\beta w} \rangle_A \). In this end, one way is to introduce an explicit bias function in calculating \( \langle e^{-\beta w} \rangle_A \) to enhance the sampling of important trajectories\(^17\),\(^18\) and another is to introduce a parameter that biases the contribution of different trajectories to make sure that all their contributions are fully taken into account\(^19\),\(^20\). The latter can be viewed as a thermodynamic integration procedure in trajectory space\(^12\). In order to reduce the statistical uncertainty, another important direction to explore is to optimize the protocol. Note that JE does not depend on the details of the protocol; all paths from \( \lambda_A \) to \( \lambda_B \) give the same result of FED. But the work distribution depends on the protocol, implying the existence of an optimal protocol that can minimize the work fluctuation. If the changing rate of \( \lambda \) is small, example studies suggest that a protocol with small mean work also leads to small statistical uncertainty\(^21\),\(^22\). Considering this, Schmiedl and Seifert found that an optimal protocol may consist of two jumps at \( t_A \) and \( t_B \).\(^22\)

In fact, the flexibility implied by JE lies not only in the protocol; the dynamics of the system can be manipulated as well. For example, JE can be generalized to incorporate an artificial flow field to escort a trajectory such that in the best situations, it may give FED exactly by sampling the initial condition and evolving the system for only once\(^21\). The drawback of this scheme, however, is that it is hard to solve the appropriate flow field except in some special cases\(^21\).

Recently, Gong’s group studied the general methods to suppress the work fluctuation for a given protocol by applying a control field to the system\(^23\),\(^24\). The applied control field is expressed as an additional term to the Hamiltonian, which is turned off at time \( t_A \) and \( t_B \) but turned on for \( t_A < t < t_B \). For an integrable system, based on the shortcuts to adiabatic process, the authors worked out the control field that makes the work distribution to be identical to that of quasistatic processes from A to B\(^23\). Hence the work fluctuation is suppressed to be the minimum allowed in principle. Later this scheme was generalized to non-integrable systems where the control field is determined by the optimal control technique\(^24\). In this general scheme, minimizing the fluctuation of \( e^{-\beta \tilde{w}} \) from \( e^{-\beta F} \) has been taken as the explicit control target, hence it can be adopted as a boosting JE method for evaluating FED for both experimental and numerical studies.

Here we explore a different strategy for calculating FED based on JE. We also take advantage that the dynamics of the system can be manipulated, but unlike in Refs.\(^23\),\(^24\), we get rid of the original Hamiltonian of the system during the time interval \( t_A < t < t_B \) but replace it with an integrable dynamics such that the evolution of the system can be solved analytically. As a result, an equilibrium equality of FED, in contrast with the underlying nonequilibrium JE, is derived. Numerically, this equilibrium equality allows FED to be computed like a mechanical state variable\(^2\),\(^3\) by sampling the canonical ensemble directly, which is a significant simplification. Compared with the direct JE algorithm, the computational cost can be saved for orders in the studied examples. In the following, we will first outline the general scheme of our strategy, then apply it to protocols where the system changes its volume from state A to B. The results will be checked with two numerical examples and extended to more general protocols. Finally, some related issues will be discussed with a brief summary.

II. A GENERAL SCHEME: APPLYING JE TO AN INTEGRABLE VIRTUAL SYSTEM

Our task is to calculate FED of the system \( \bar{H}(\bar{z}; \lambda) \) between states A and B. Consider a different Hamiltonian system \( \bar{H}(\bar{z}; \Lambda) \) that shares the same phase space, where \( \Lambda \) represents its parameter set. If, for a certain value of \( \Lambda \), denoted as \( \Lambda_A \), this Hamiltonian is identical to \( \bar{H}(\bar{z}; \Lambda_A) \), i.e., \( \bar{H}(\bar{z}; \Lambda_A) = \bar{H}(\bar{z}; \lambda_A) \), then the two systems share the same equilibrium distribution \( P_A(\bar{z}) = \exp[-\beta \bar{H}(\bar{z}; \Lambda_A)]/Z_A \) and therefore can be calculated by JE with \( \bar{H} \) and the same free energy \( \bar{F}_A = F_A = -\ln Z_A/\beta \). Here \( Z_A \) is the partition function of their common state A.

Similarly, if for \( \Lambda_B \) we have \( \bar{H}(\bar{z}; \Lambda_B) = \bar{H}(\bar{z}; \lambda_B) \), then the two systems have the same free energy \( \bar{F}_B = F_B = -\ln Z_B/\beta \). Given these, FED of the original system \( \Delta F = F_B - F_A \) is equal to that of \( \bar{H} \), \( \Delta \bar{F} = \bar{F}_B - \bar{F}_A \), and therefore can be calculated by JE with \( \bar{H} \) instead:

\[
e^{-\beta \Delta F} = e^{-\beta \Delta \bar{F}} = \langle e^{-\beta \bar{w}} \rangle_A.\tag{2}
\]

Here \( \bar{w} \) is the work performed on the ‘virtual’ system \( \bar{H} \) when it is driven by the control parameters \( \Lambda \) from \( \Lambda_A \) to \( \Lambda_B \) with a given protocol \( \Lambda(t) \). This relation has been pointed out and utilized in Refs.\(^23\),\(^24\), which is very flexible that gives us the freedom to manipulate not only the protocol, but also the Hamiltonian. We emphasize
tions (see Fig. 1(b)). For $z$ introduce the virtual system as $t \leq t_A$ and activate a virtual interaction for $t_A < t < t_B$ (and vice versa for $t < t_A$ and $t \geq t_B$). Protocol $\lambda(t)$ in our scheme (not shown) is arbitrary given that $\tilde{\lambda}(t) = \lambda_B$ for $t \leq t_A$ and $\lambda(t) = \lambda_B$ for $t \geq t_B$.

that the only requirements are

$$\tilde{H}(z; \lambda, \alpha) = H(z; \lambda), \quad \alpha = \Lambda, B. \quad (3)$$

At other system parameters, the two Hamiltonians can be different and arbitrary.

In the following we will show that indeed, this scenario can lead to significant simplification in calculating $\Delta F$. For the sake of simplicity, we consider a one-dimensional system consists of $N$ particles, but the extension to two and three dimension is straightforwardly. Suppose

$$H(z; \lambda) = \sum \frac{p_i^2}{2m_i} + U(x; \lambda), \quad (4)$$

where $z = (p, x)$ with $p \equiv (p_1, \ldots, p_N)$ and $x \equiv (x_1, \ldots, x_N)$, and the protocol follows that $\lambda(t) = \lambda_A$ for $t \leq t_A$ and $\lambda(t) = \lambda_B$ for $t \geq t_B$ [see Fig. 1(a)]. We introduce the virtual system as

$$\tilde{H}(z; \Lambda) = \sum \frac{\tilde{p}_i^2}{2\tilde{m}_i} + \theta U(x; \tilde{\lambda}) + \tilde{\theta} V(x; \tilde{\lambda}) \quad (5)$$

with $\Lambda = (\tilde{\lambda}, \tilde{\theta}, \tilde{\theta})$, where $\theta$ and $\tilde{\theta}$ are two switch functions [see Fig. 1(b)]. For $t \leq t_A < t_A$ and $t \geq t_B$, the interaction of the original system, $U$, acts. We assume $\tilde{\lambda}(t) = \lambda(t)$ for $t \leq t_A$ and $t \geq t_B$ to ensured that at $t_A$ and $t_B$ the two Hamiltonians are the same. For $t_A < t < t_B$, the original interaction $U$ is suppressed while an introduced virtual interaction, $V$, takes over. In principle, any $V$ is acceptable, and our main motivation in this work is to take this advantage. As to the control parameter $\tilde{\lambda}(t)$, it is arbitrary for $t_A < t < t_B$, given that it changes from $\lambda_A$ at $t = t_A$ to $\lambda_B$ at $t = t_B$.

Before proceeding, we notice that taking the limits $t_A \to t_A$ and $t_B \to t_B$ can facilitate the calculation of work. As the Hamiltonian changes abruptly at $t_A$ and $t_B$, the work done to the system is $	ilde{w}_A \equiv \Delta \tilde{H}|_{t_A} = V(x; \lambda_A) - U(x; \lambda_A)$ and $	ilde{w}_B \equiv \Delta \tilde{H}|_{t_B} = U(x; \lambda_B) - V(x; \lambda_B)$, respectively [5]. Following Eq. (2), we then have

$$e^{-\beta \Delta F} = (e^{-\beta (\tilde{w}_A + \tilde{w}_B + \tilde{w}_V)})_A, \quad (6)$$

where $\tilde{w}_V$ is the work done to the system with the introduced interaction $V(x; \tilde{\lambda})$ when being driven by $\lambda$ from $\lambda_A$ to $\lambda_B$.

One advantage of this scheme is now apparent: In principle, for an integrable interaction $V$, $\tilde{w}_V$ can be solved; then the calculation of FED reduces to an equilibrium average without any explicit nonequilibrium quantities. Numerically, as evolving the system is avoided, the simulation cost can be greatly reduced.

### III. FREE ENERGY DIFFERENCE BETWEEN TWO VOLUMES

Let us first discuss FED of a system at two different volumes (lengths) $L_A$ and $L_B$. The derivation of FED between two volumes of any other parameter(s) is similar (see Sect. V). By JE [Eq. (1)], we can take the protocol, identifying $\lambda$ with $L$, as follows: At $t_A$, the system volume is $L_A$; then we press or pull one end of the system at a fixed velocity $u$ to make its volume to be $L_B$ at $t_B = t_A + $
During this process the system keeps its interaction $U(x, \lambda(t))$. By our scheme, the key difference is that at $t_B$, we replace $U$ by the virtual potential $V$. A convenient option of $V$ is that consists of $n_c$ cells of hard walls (see Fig. 2). We set $n_c$ large enough to ensure that in each cell there is at most one particle, so that the particles become noninteractive. We then press or pull one boundary of each cell with velocity $u$ as well to time $t_B$, during which when a particle collides with any boundary of its cell, it is reflected back elastically. The work $\tilde{w}_V$ done to the system can thus be obtained by summing up the work done to each particle by the moving boundary of its cell, denoted as $\tilde{w}_V,i$, that can be solved analytically (Eq. (A8) in Appendix A; also see Ref. [25]). The advantage of the adopted $V$ is that it keeps the order of particles. This is particularly crucial for a lattice, otherwise the original interaction $U$ may not be retrieved at time $t_B$.

It is rewarding to take the limits $n_c \to \infty$ and $u \to 0$ further, following which we have immediately $x_i(t_B) = rx_i(t_A) \ [r \equiv L_B/L_A; \ see \ Fig. \ 2(a) \ and \ (g)]$ and $\tilde{w}_V = (1/r^2 - 1)\rho r^2/(2m_i)$ (Eq. (A9) in Appendix A), allowing Eq. (6) to be rewritten as

$$ e^{-\beta \Delta F} = r^N \langle e^{\beta [U(x;L_A) - U(x;L_B)]} \rangle_{A,x} \tag{7} $$

with the distribution function for averaging $P_{A,x} \equiv e^{-\beta U(x;L_A)}/Z_{A,x} \text{ and } Z_{A,x} \equiv \int e^{-\beta U(x;L_A)} dx$. Here the prefactor $r^N$ on the r.h.s. is the result for $\langle e^{-\beta \tilde{w}_V} \rangle_A$, which can be integrated independently from $\langle e^{-\beta \tilde{w}_A + \tilde{w}_B} \rangle_A$ as $\tilde{w}_V$ depends only on variable $p$ while $\tilde{w}_A$ and $\tilde{w}_B$ depend only on $x$. The exponential average on the r.h.s. is for $\langle e^{-\beta \tilde{w}_A + \tilde{w}_B} \rangle_A$.

Theoretically, this result reveals a new equilibrium relation between the free energy of a system has at two different volumes. Numerically, the standard Monte Carlo algorithm involving variable $x$ only can be applied directly. In doing so, as here only the exponential average of $\tilde{w}_A + \tilde{w}_B$, rather than $\tilde{w} = \tilde{w}_A + \tilde{w}_B + \tilde{w}_V$, is evaluated, the ensemble size can be reduced, as the distribution of the former is narrower.

IV. FREE ENERGY DIFFERENCE OF TWO ONE-DIMENSIONAL MODELS

In order to test the effectiveness and efficiency of our main results Eq. (6) and (7), here we study two illustrating examples. The first one is the one-dimensional (1D) diatomic Toda lattice [26] with

$$ U = \sum [e^{-\beta (x_{i+1}-x_i)} + (x_{i+1} - x_i - 1)]. \tag{8} $$

The two kinds of particles have mass 1 and 2 and align alternatively. The fixed boundary conditions are taken by fixing the zeroth and the $(N+1)$th particle at the left and right boundary. For our aim here we also calculate FED with the conventional thermodynamic integration method [4] and use the result as a benchmark. To this

end, the pressure of the system as a function of the system size, or equivalently, the particle density $\rho \equiv N/L$, is calculated with high accuracy (the error is smaller than $2 \times 10^{-5}$) and the results are presented in Fig. 3. The free energy difference is then obtained by integrating the pressure based on the relation $\langle \int \frac{\partial F}{\partial x} \rangle_{N,T} = -p$ with high accuracy as well: The error of FED per particle $\Delta \epsilon \equiv \Delta F/N$ is less than $10^{-5}$ (see the dashed and the solid line in Fig. 4).

The results of FED computed in various ways are compared in Fig. 4. For the direct JE method with $u = 0.1$ and sample size $10^5$, the relative deviation from the
benchmark is less than 0.9% for system size $N = 20$. For the same setting, our method based on Eq. (6) gives the same accurate result. But as $\tilde{w}_V$ has been solved analytically, the simulation time is greatly saved. The best one is our method based on Eq. (7); for the same accuracy, the results by the direct JE method ($u = 0.1$) have been confirmed by changing the ensemble size.

The second example is a gas model with repulsive interaction given by potential

$$U = \sum (x_{i+1} - x_i)^{-6}. \quad (9)$$

All particles have a unity mass and the fixed boundary conditions are assumed as well. In Fig. 6, FED between two system volumes is shown, where we can see that our scheme based on Eq. (7) outperforms again. Note that the systematically biased deviation of other two methods at larger particle density is due to insufficient sampling, which has been confirmed by changing the ensemble size.

For the gas of identical particles where their position order is irrelevant, $\Delta F$ between two system volumes can be calculated in a different way. First, FED between the system with interaction $U$ and the ideal gas of the same mass particles and volume $L_A$ is $\Delta F_A = -\ln \langle e^{\beta U} \rangle_A / \beta$, which is the result of the free energy perturbation theory [14] and the limiting result of JE [5]. Similarly, FED between the system with interaction $U$ and the ideal gas of volume $L_B$ is $\Delta F_B = -\ln \langle e^{\beta U} \rangle_B / \beta$. Considering that FED of an ideal gas at volumes $L_A$ and $L_B$ is

$$\Delta F_{AB} = -N \ln \langle L_B/L_A \rangle / \beta = -N \ln r / \beta,$$

we then have

$$e^{-\beta \Delta F} = r^N \langle e^{\beta U(x; L_A)} \rangle_{A,x} / \langle e^{\beta U(x; L_B)} \rangle_{B,x}. \quad (10)$$

Comparing with Eq. (7), an essential difference is that another ensemble average with $P_{B,x} = e^{-\beta U(x; L_B)} / Z_{B,x}$, $Z_{B,x} = \int e^{-\beta U(x; L_B)} d\mathbf{x}$, is involved. For the gas model under study, the algorithm based on Eq. (10) is not so efficient as that based on Eq. (7), either, though it is more efficient than the direct JE algorithm where evolving the system is avoided.

V. FREE ENERGY DIFFERENCE BETWEEN TWO GENERAL STATES

As discussed in Sect. II, not only for FED between two volumes, the general scheme based on Eq. (6) is equally applicable to FED between two states determined by other parameters as well. The key task is to design the virtual potential to facilitate the calculation of $\tilde{w}_V$. This can be fulfilled by cutting interactions to make particles move independently, just as we have done by introducing the hard-wall-cell potential. In principle, as the motion of each particle is a one-body problem, it is integrable and can be solved definitely. To this end, the hard-wall-cell potential is only one option. If the considered parameter is not the volume, another feasible choice could be an on-site harmonic potential array that confines each particle to move around its equilibrium position. For numerical calculations, for a given parameter a better choice of the virtual potential should be that makes the distribution of $\tilde{w}_A + \tilde{w}_B + \tilde{w}_V$ narrower so that the sampling cost for evaluating its exponential average is less. To this end, an
appropriate protocol can help additionally. For example, assuming \( t_B - t_A \to \infty \) will not add any computational cost as \( \tilde{w}_V \) can be solved analytically, but it may suppress the fluctuations of \( \tilde{w}_V \) and \( \tilde{w}_A + \tilde{w}_B + \tilde{w}_V \).

If the state the system is parameterized by a set of parameters \( \Gamma \) to which the volume does not belong, FED protocol that \( \Gamma \) changes instantaneously from \( \Gamma_A \) to \( \Gamma_B \). As \( x \) keeps unchanged, it cannot be applied when the volume change is involved.

However, taking our scheme, Eq. (11) can be extended straightforwardly to incorporate the volume change as follows: At time \( t_A \), the potential \( U(x; \Gamma_A, L_A) \) is switched off and the hard-wall-cell potential is switched on; then the volume is changed from \( L_A \) to \( L_B \) following the same procedure as in deriving Eq. (7); finally, at time \( t_B \) the hard-wall-cell potential is switch off and \( U(x; \Gamma_B, L_B) \) is switched on. It gives that

\[
e^{-\beta \Delta F} = \langle e^{\beta [U(x; \Gamma_A, L_A) - U(x; \Gamma_B, L_B)]} \rangle_{A, x},
\]

(12)

where \( r = L_A/L_B \). For \( L_A = L_B \) it reduces to Eq. (11).

VI. DISCUSSIONS AND SUMMARY

In summary, we have explored the idea to investigate the free energy by taking advantage of a virtual system. The tremendous flexibility and possibility it implies can be envisaged, as both the Hamiltonian and the protocol can be assigned arbitrarily to some extent. Particularly, we have discussed one ‘realization’ of this idea, i.e., a scheme that consists of an integrable virtual system activated (removed) simultaneously when the protocol begins (stops). Its effectiveness and efficiency have been corroborated with the numerical studies.

We emphasize that our scheme represents only one possibility. Other options of the virtual system and the protocol are worth investigating, which may lead to different results that resemble Eq. (7). Theoretically, we believe these results may deepen our understanding to the free energy: Numerically, they may provide more optional tools for computing the free energy. In this regard, as Eq. (7) shows, its advantage (compared with JE) is that the conventional Monte Carlo algorithm and molecular dynamics algorithm can be adopted directly. In fact, as the computation has reduced to a sampling problem, various techniques developed for enhancing the sampling \[3, 6\] can be employed to increase its efficiency further. This may be another interesting issue to explore for future studies.

Acknowledgements

This work is supported by the NSFC (Grants No. 11535011 and No. 11335006).

Appendix A: Motion of a particle in a cell with a moving boundary

See Fig. 7: Consider a point particle of mass \( m \) confined to move freely in a one-dimensional cell with two hard boundaries. When the particle collides with one boundary, it will be reflected back elastically. The left boundary is kept fixed and the right boundary moves at a fixed velocity, \( u \). Initially, the size of the cell is \( c_0 \), the position and the velocity of the particle is \( x \) and \( v \), respectively. After a certain time, denoted as \( \tau \), the size of the cell becomes \( c \). Apparently, \( \tau = (c - c_0)/u \). Given these, in the following we will discuss the position and the velocity of the particle, denoted as \( x' \) and \( v' \), at time \( \tau \). Note that in Ref. \[25\] this problem has been studied for confirming Jarzynski’s equality with one-dimensional, noninteracting gas.

Let us consider the case \( u < 0 \), i.e., the right boundary moves to the left. The results can be extended to \( u \geq 0 \) straightforwardly. In this case, (a) if \( 0 < x + v \tau < c \), then the particle does not collide with any boundary during time \( \tau \) and \( v' = v \), \( x' = x + v \tau \); Otherwise, (b) if \( -c < x + v \tau \leq 0 \), then the particle only collides with the left boundary for once, so that \( v' = -v \) and \( x' = -(x + v \tau) \).

Other than these two simple cases, particle will collide with the right boundary for at least one time. (c) For \( x + v \tau \geq c \), right before the first collision (with the right boundary), the particle’s position and velocity is, respectively, \( v_1 = v \) and \( x_1 = c_0 + u \tau_1 \), where \( \tau_1 = (c_0 - x)/(v - u) \) is the time when the first collision occurs. Similarly, (d) for \( x + v \tau \leq -c \), we have \( v_1 = -v \), \( x_1 = c_0 + u \tau_1 \), and \( \tau_1 = -(c_0 + x)/(v + u) \), instead.

For cases (c) and (d), it is easy to establish the map from \( x_1 \) and \( v_1 \) to the particle’s state right before the \( \delta \)-th collision with the right moving boundary that occurs at

\[ \text{FIG. 7: Schematic plot for the to-and-fro motion of a point particle in a cell with the right boundary moving at a fixed velocity } u. \text{ The initial position of the right boundary is at } c_0; \text{ the initial position and velocity of the particle is } x \text{ and } v. \text{ When the right boundary moves to } c, \text{ the position and velocity of the particle becomes } x' \text{ and } v'. \]
The total number, $n$, of collisions with the right moving boundary during time $\tau$ satisfies $t_n < \tau < t_{n+1}$, which gives that

$$n = 1 + \left\lceil \frac{(v_1 - u)(\tau - t_1)}{2c} \right\rceil, \quad (A3)$$

where the brackets represent the integer part of the variable inside. Right after the last collision, the particle’s velocity becomes

$$v_n^+ = 2nu - v_1. \quad (A4)$$

Finally, for cases (c) and (d), if

$$0 < x_n + (\tau - t_n)v_n^+, \quad (A5)$$

then we have

$$v' = v_n^+, \quad x' = x_n + (\tau - t_n)v_n^+, \quad (A6)$$

otherwise,

$$v' = -v_n^+, \quad x' = -[x_n + (\tau - t_n)v_n^+]. \quad (A7)$$

It follows that the total work the right boundary does to the particle during the whole process is

$$w = \frac{1}{2} m[(v')^2 - v^2]. \quad (A8)$$

In the limit $u \to 0$, i.e., the right boundary moves infinitely slow, from Eq. (A3) and (A4) we have $nu \to v_1(c - c_0)/(2c)$ and $v_n^+ \to v_1c_0/c$, suggesting that the kinetic energy of the particle becomes $(c_0/c)^2$ times of its initial value; Therefore, the total work performed on the particle is

$$w = \frac{1}{2} mu^2 \left[ \frac{c^2}{c_0^2} - 1 \right]. \quad (A9)$$

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