Thermodynamics of slow solutions to the gas-piston equations

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Despite its historical importance, a perfect gas enclosed by a pistons and in contact with a thermal reservoirs is a system still largely under study. Its thermodynamic properties are not yet well understood when driven under nonequilibrium conditions, and analytic formulas that describe the heat exchanged with the reservoir are rare. In this paper we prove a power series expansions for the heat when both the external force and the reservoir temperature are slowly varying over time but the overall process is not quasistatic. To do so, we use the dynamical equations from [Cerino *et al.*, Phys. Rev. E **91**, 032128 (2015)] and an uncommon application of the regular perturbation technique.

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I. INTRODUCTION

One of the main goals of nonequilibrium thermodynamics is to understand how a thermodynamic system evolves over time [1–3]. The problem is difficult even in the simplest physical instances. For example, the nonequilibrium behavior of the adiabatic piston [4] is still a live research topic (see Refs. [4–6] ad references therein). Another problem which is conceptually simple, but difficult to treat, is the nonequilibrium thermodynamics of a perfect gas enclosed by a cylindrical canister with a movable piston and in contact with a heat reservoir (see Fig. 1). For this system there are multiple valid approaches: for example, the one-particle gas approach [7] and its legacy [8–11], the explicit-friction formulæ approach [12–14], and the average-model approach [15–18]. Among those references Ref. [15] is particularly interesting: there the authors assumed that (1) the gas is perfect and one-dimensional; (2) the piston and each gas particle undergoes elastic collisions, so work is the energy exchanged in this way; (3) the velocity of a gas particle is randomly changed according to the Maxwell-Boltzmann distribution of the reservoir when reservoir-gas particle collisions occur [19] and heat is the change in energy of the gas; and (4) the gas distribution is always Maxwellian although gas-reservoir and gas-piston collisions change the temperature of the gas over time. By combining these assumptions in a laborious averaging process, the authors were able to derive a set of dynamical equations for the time evolution of the gas temperature $\overline{T}$ and piston position $\overline{x}$ according to any externally prescribed change of the external force $\overline{\Theta}$ and reservoir temperature $\overline{\Omega}$. In Ref. [20] we showed with the multiple scales method [21–24] and some technical assumptions (discussed in Sec. II) that the equations derived in Ref. [15] allow us to find an approximated expression for the heat exchanged with the reservoir in two physically relevant cases: the *relaxation to equilibrium* and the *slow isothermal compression*. In the same paper [20] we pointed out the existence of particular solutions, which we called *dynamical equilibrium solutions*, which describe the asymptotic behavior of the system when externally driven.

Stimulated by our previous understanding, we show in this paper how to *iteratively construct* the dynamical equilibrium solution at *any desired precision order* through an uncommon application of the regular perturbation theory [22–24]. Our only assumptions will be that *both* the external force and the reservoir temperature are slow, smooth, and nonvanishing. Such a solution immediately yields a general formula for the heat exchanged with the reservoir as a formal power series in which *all the coefficients* are determined. Such kinds of results are important due to their rarity in the literature, and we believe that the method we used can be safely applied to other relevant problems in nonequilibrium thermodynamics. Moreover, we suggest that similar power series approaches can play a key role in the characterization of thermal cycles where drivings are slow but not necessarily quasistatic.

This paper is structured as follows: in Sec. II we introduce the model from Ref. [15] together with the notations and the formalism we will use throughout the paper; in Sec. III we derived our main results, namely, the full recursive relation from which we can derive the coefficients of dynamical equilibrium solution and the exchanged heat; in Sec. IV we comment on the thermodynamical relevance of our result, pointing also out similarities with the virial expansion, and make some conjectures for possible future developments.

II. BACKGROUND

With the list of assumptions declared in Sec. I, Cerino *et al.* were able to derive a set of equations to describe the dynamics of a gas inside a piston under the action of a variable external force when the reservoir temperature also changes over time. Such equations are

$$\ddot{\overline{x}} + \frac{\overline{\Theta}}{M} - \frac{\nu N}{\nu+1}\frac{1}{\overline{x}}\operatorname{erfc}\left(\sqrt{\frac{m}{2\overline{T}}}\dot{\overline{x}}\right)\left(\dot{\overline{x}}^2 + \frac{\overline{T}}{m}\right) + \frac{\nu N}{\nu+1}\exp\left(-\frac{m\dot{\overline{x}}^2}{2\overline{T}}\right)\frac{\dot{\overline{x}}}{\overline{x}}\sqrt{\frac{2\overline{T}}{\pi m}} = 0, \tag{1a}$$

$$\dot{\overline{T}} + \frac{2\dot{\overline{x}}[m\dot{\overline{x}}^2 + \overline{T}(1-2\nu)]}{\overline{x}(\nu+1)^2}\operatorname{erfc}\left(\sqrt{\frac{m}{2\overline{T}}}\dot{\overline{x}}\right) + \sqrt{\frac{2\overline{T}}{\pi m}}\frac{\overline{T}-\overline{\Omega}}{\overline{x}} + \frac{2}{\overline{x}(\nu+1)^2}\sqrt{\frac{2m\overline{T}}{\pi}}\left(\frac{2\nu\overline{T}}{m} - \dot{\overline{x}}^2\right)\exp\left(-\frac{m\dot{\overline{x}}^2}{2\overline{T}}\right) = 0, \tag{1b}$$

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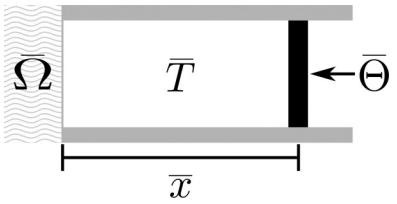

FIG. 1. A schematic representation of the gas closed by a piston and in contact with a thermal reservoir. The quantities shown are the piston position $\overline{x}$, the gas temperature $\overline{T}$, the external force $\overline{\Omega}$, and the reservoir temperature $\overline{\Theta}$.

where the upper dots denote time derivatives, M is the mass of the piston, m is the mass of a single gas molecule, N is the total number of gas molecules, $\nu = m/M$, erfc$(\cdot)$ is the complementary error function, $\overline{\Omega}$ is the externally controlled reservoir temperature, $\overline{\Theta}$ is the externally controlled force exerted on the piston, $\overline{x}$ is the piston position, and $\overline{T}$ is the gas temperature. Equation (1) gives a fairly good description of both the dynamics and the thermodynamics of the system [15], the latter being expressed through

$$\overline{E} = M\frac{\dot{\overline{x}}^2}{2} + \overline{\Theta}\,\overline{x} + \frac{N\overline{T}}{2}, \tag{2a}$$

$$\overline{Q}(\bar{t}_i,\bar{t}_f) = -\int_{\bar{t}_i}^{\bar{t}_f}\left[\overline{\Theta}\dot{\overline{x}} + M\dot{\overline{x}}\,\ddot{\overline{x}} + \frac{N}{2}\dot{\overline{T}}\right]d\bar{t}, \tag{2b}$$

where $\overline{E}$ is the total energy of the system [25] (composed by the kinetic energy of the piston, by the linear potential energy related to $\overline{\Theta}$ and by the thermal energy of the one-dimensional gas respectively), and $\overline{Q}$ is the heat [2] that the system exchanges with the reservoir.[1] In Ref. [20] we showed that the thermodynamic limit

$$\frac{m}{M} = \nu \to 0, \quad N \to \infty, \quad \varepsilon = \sqrt{\frac{Nm}{M}} = \text{const} \tag{3}$$

can be taken in Eq. (1) if we first adimension them with the following transformation:

$$\overline{x} = x\frac{\Omega_r N}{(1+\nu)g(\nu)\Theta_r}, \tag{4a}$$

$$\overline{T} = T\frac{\Omega_r}{g(\nu)}, \tag{4b}$$

$$\overline{\Theta} = \Theta\,\Theta_r, \tag{4c}$$

$$\overline{\Omega} = \Omega\,\Omega_r, \tag{4d}$$

$$\bar{t} = \frac{t}{\Theta_r}\sqrt{\frac{mN\Omega_r}{(1+\nu)g(\nu)\nu}}, \tag{4e}$$

where

$$g(\nu) = \frac{1+6\nu+\nu^2}{(1+\nu)^2} \tag{5}$$

and Θ_r (Ω_r) is an arbitrary force (temperature) reference value. Using these substitutions and then taking the thermodynamic limit Eq. (3) in Eqs. (1) and (2), we obtain the following dimensionless dynamical equations:

$$\ddot{x} + \Theta - \text{erfc}\left(\frac{\varepsilon\dot{x}}{\sqrt{2T}}\right)\frac{\varepsilon^2\dot{x}^2 + T}{x} + \exp\left(-\frac{\varepsilon^2\dot{x}^2}{2T}\right)\frac{\dot{x}}{x}\sqrt{\frac{2T}{\pi}}\varepsilon = 0, \tag{6a}$$

$$\dot{T} - 2\,\text{erfc}\left(\frac{\varepsilon\dot{x}}{\sqrt{2T}}\right)\frac{\dot{x}}{x}(\varepsilon^2\dot{x}^2 + T) + \sqrt{\frac{2T}{\pi}}\frac{T-\Omega}{\varepsilon x} - 2\sqrt{\frac{2T}{\pi}}\varepsilon\frac{\dot{x}^2}{x}\exp\left(-\frac{\varepsilon^2\dot{x}^2}{2T}\right) = 0 \tag{6b}$$

with the dimensionless E and Q densities:

$$E = \frac{\overline{E}}{N\Omega_r} = \Theta x + \frac{\dot{x}^2}{2} + \frac{T}{2}, \tag{7a}$$

$$Q(t_i,t_f) = \frac{\overline{Q}}{N\Omega_r} = -\int_{t_i}^{t_f}\left[\Theta\dot{x} + \dot{x}\ddot{x} + \frac{1}{2}\dot{T}\right]dt. \tag{7b}$$

The most important feature of Eq. (6) is that they involve only the ratio ε of the total mass of the gas and the mass of the piston as a physical parameter, a feature that this system shares with the adiabatic piston problem [4]. Since the gas we consider is perfect, ε will reasonably be small. As a consequence, if a perturbation parameter is required for some approximated approach, ε is the most natural one to choose [4]. An additional advantage of Eq. (6) is that it is easy to check that their equilibrium condition is

$$x_{\text{eq}} = \frac{\Omega}{\Theta}, \quad \dot{x}_{\text{eq}} = 0, \quad T_{\text{eq}} = \Omega, \tag{8}$$

which is exactly what the perfect gas law and standard thermodynamics require. If one is interested in situations where the system remains in the proximity of the equilibrium condition for Θ and Ω, even if Θ and Ω changes over time, then Eq. (6) can be linearized around Eq. (8). This process yields the following linear dimensionless equations:

$$\ddot{x} + \frac{\Theta^2}{\Omega}\left(x - \frac{\Omega}{\Theta}\right) + 2\sqrt{\frac{2}{\pi\Omega}}\varepsilon\Theta\dot{x} - \Theta\frac{T-\Omega}{\Omega} = 0, \tag{9a}$$

$$\dot{T} + 2\Theta\dot{x} + \sqrt{\frac{2}{\pi\Omega}}\frac{\Theta}{\varepsilon}(T-\Omega) = 0. \tag{9b}$$

In Ref. [20] we assumed ε to be a "small" perturbative parameter, the reservoir temperature to be constant (without loss of generality, $\Omega = 1$), and the external forcing Θ to be slowly varying over time [any function B can be considered "slow" if $B = B(\varepsilon t)$, which we assume from now on]. With such assumptions we were able to find *analytic approximated solutions* to (9) with the multiple scales method. In particular we showed that the relevant behavior of the system is described by the following three scales:

$$t_0 = \frac{1}{\varepsilon}\int_0^t \Theta(\varepsilon\chi)d\chi, \quad t_1 = \int_0^t \Theta(\varepsilon\chi)d\chi, \quad t_2 = \varepsilon t, \tag{10}$$

where an explicit form of Θ is not required to give them an intuitive meaning. The t_0 scale is the fastest one and characterizes a transient suppression of the temperature of

[1] Sign convention is such that $\overline{Q} > 0$ for heat given to the reservoir.

the gas. From a physical point of view, it describes the indirect coupling of the piston with the reservoir. The t_1 scale is the one at which transient oscillations of the system are established. This reflects the direct coupling of the gas with the piston position and velocity. In the t_2 scale the exponential suppression of the transient oscillatory terms appears and is the proper scale of the external forcing too.

The approximated solution derived in Ref. [20] falls, as $t \to \infty$, into a peculiar solution:

$$x_{\text{d.eq.}}(t) = \frac{1}{\Theta(\varepsilon t)} + \varepsilon^2\left[\frac{\Theta'(\varepsilon t)}{\Theta^4(\varepsilon t)} - 2\frac{(\Theta')^2(\varepsilon t)}{\Theta^5(\varepsilon t)} + \left(2\sqrt{\frac{2}{\pi}} + \sqrt{2\pi}\right)\frac{\Theta'(\varepsilon t)}{\Theta^3(\varepsilon t)}\right] + O(\varepsilon^4) \quad (11)$$

with prime notation

$$B'(s) = \left.\frac{\partial B(\mu)}{\partial \mu}\right|_{\mu=s}. \quad (12)$$

We called this solution a *dynamical equilibrium solution* as, from a physical point of view, it describes the system when it asymptotically follows the slow external driving. Mathematically this solution arises as the particular solution of the inhomogeneous ordinary differential equations coming from the multiple scales expansion and can be computed in practice by taking all the integration constants in the multiple scale expansion equal to zero. In Ref. [20], we also indicated that the dynamical equilibrium solution (11) could have been obtained with the "slow" regular perturbation

$$x_{\text{d.eq.}}(t) = x_0(\varepsilon t) + \varepsilon x_1(\varepsilon t) + \varepsilon^2 x_2(\varepsilon t) + \varepsilon^3 x_3(\varepsilon t) + O(\varepsilon^4). \quad (13)$$

In the next section we expand this point to show the generalization of the ansatz Eq. (13) allows us to *iteratively construct the dynamical equilibrium solution at any order* when *both* the external force Θ and the reservoir temperature Ω are slow.

III. DERIVATION OF THE DYNAMICAL EQUILIBRIUM SOLUTION AND OF THE HEAT

Differently from Ref. [20], where $\Omega \equiv 1$, we assume that the external force and the reservoir temperatures are slow, i.e., $\Theta = \Theta(\epsilon t)$, $\Omega = \omega(\epsilon t)$. Following the same procedure we used in Ref. [20] we transform the system (9) into a single third order equation: we solve (9a) for T:

$$T = \frac{\Omega(\varepsilon t)}{\Theta(\varepsilon t)}\ddot{x} + 2\sqrt{\frac{2}{\pi}}\sqrt{\Omega(\varepsilon t)}\varepsilon\dot{x} + \Theta(\varepsilon t)x \quad (14)$$

and substitute in Eq. (9b) to obtain

$$\frac{\Omega(\varepsilon t)}{\Theta(\varepsilon t)}\dddot{x} + \left[2\frac{\sqrt{\Omega(\varepsilon t)}\sqrt{2}\varepsilon}{\sqrt{\pi}} - \frac{\Omega(\varepsilon t)\Theta'(\varepsilon t)\varepsilon}{\Theta^2(\varepsilon t)} + \frac{\Omega'(\varepsilon t)\varepsilon}{\Theta(\varepsilon t)} + \frac{\sqrt{\Omega(\varepsilon t)}\sqrt{2}}{\sqrt{\pi}\varepsilon}\right]\ddot{x} + \left[3\Theta(\varepsilon t) + \frac{\sqrt{2}\varepsilon^2\Omega'(\varepsilon t)}{\sqrt{\pi}\sqrt{\Omega(\varepsilon t)}} + 4\frac{\Theta(\varepsilon t)}{\pi}\right]\dot{x} + \left[\Theta'(\varepsilon t)\varepsilon + \frac{\sqrt{2}(\Theta(\varepsilon t))^2}{\sqrt{\pi}\varepsilon\sqrt{\Omega(\varepsilon t)}}\right]x - \frac{\sqrt{2}\Theta(\varepsilon t)\sqrt{\Omega(\varepsilon t)}}{\sqrt{\pi}\varepsilon} = 0. \quad (15)$$

Now, instead of looking for a general approximation of $x(t)$ with the multiple scale method, we limit ourselves to the search for dynamical equilibrium solution $x_{\text{d.eq.}}(t)$. To this end we must get rid of transient-like behaviors, i.e., those governed by the t_0 and t_1 scales in (10). The observation in Ref. [20] that the dynamical equilibrium solution (11) is obtainable from the ansatz (13) suggests that we consider the following expansion:

$$x_{\text{d.eq.}}(t) = \sum_{n=0}^{\infty} x_n(\varepsilon t)\varepsilon^n. \quad (16)$$

The series (16) is a *regular perturbation expansion* with an uncommon feature: its coefficients are functions of the slowest time scale t_2 in (10). With this choice all transient-like behaviors are automatically ruled out, exactly as desired.[2] We then substitute (16) in Eq. (15) and, upon defining

$$s = \varepsilon t, \quad (17)$$

isolating the ε coefficient, and then equating them to zero, we obtain a system of *linear algebraic equations for* $x_n(s)$. Solving it, we find

$$x_0(s) = \frac{\Omega(s)}{\Theta(s)}, \quad (18a)$$

$$x_1(s) = 0, \quad (18b)$$

$$x_2(s) = \sqrt{\frac{2}{\pi}}(\pi+2)\frac{\Theta'(s)\Omega^{3/2}(s)}{\Theta^3(s)} - \frac{\Omega''(s)\Omega(s)}{\Theta^3(s)} + \frac{\Omega^2(s)\Theta''(s)}{\Theta^4(s)} - \frac{1}{2}\sqrt{\frac{2}{\pi}}(3\pi+4)\frac{\sqrt{\Omega(s)}\Omega'(s)}{\Theta^2(s)} + 2\frac{\Omega(s)\Theta'(s)\Omega'(s)}{\Theta^4(s)} - 2\frac{\Omega^2(s)\left(\Theta'\right)^2(s)}{\Theta^5(s)}, \quad (18c)$$

$$x_3(s) = 0, \quad (18d)$$

$$x_n(s) = L_2 x_{n-2} + L_4 x_{n-4}, \quad n \geqslant 4, \quad (18e)$$

[2]This choice is justified because it is a special case of the multiple scales method. Therefore expansion validity and errors are ensured *a priori*.

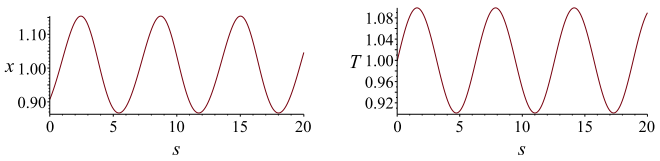

FIG. 2. Sample trajectories for $\varepsilon = 1/16$ with the first three nonzero terms of x and T expansions for $\Omega(s) = 1 + 0.1\sin(s)$ and $\Theta(s) = 1 + 0.1\cos(s)$.

where L_2 and L_4 are the linear differential operators:

$$L_2 = -\frac{\Omega(s)}{\Theta^2(s)}\frac{d^2}{ds^2} - \sqrt{\frac{1}{2\pi}}\frac{\sqrt{\Omega(s)}(3\pi+4)}{\Theta(s)}\frac{d}{ds} - \sqrt{\frac{\pi}{2}}\frac{\Theta'(s)\sqrt{\Omega(s)}}{\Theta^2(s)}, \tag{19a}$$

$$L_4 = -\sqrt{\frac{\pi}{2}}\frac{\Omega^{3/2}(s)}{\Theta^3(s)}\frac{d^3}{ds^3} - \frac{\Omega'(s)}{\Theta^2(s)}\frac{d}{ds} - \left[\frac{2\Omega(s)}{\Theta^2(s)} + \sqrt{\frac{\pi}{2}}\frac{\sqrt{\Omega(s)}}{\Theta^2(s)}\left(\frac{\Omega}{\Theta}\right)'(s)\right]. \tag{19b}$$

Equation (18e) defines a recurrence relation where $x_0(s), x_1(s), x_2(s)$, and $x_3(s)$ act as initial conditions. We can therefore use Eq. (18) and Eq. (19) to obtain every term in the series (16) simply by differentiation and multiplication. Furthermore, Eq. (18e) is homogeneous and $x_1 = x_3 = 0$, then $x_{2n+1} = 0$ for every $n \in \mathbb{N}$. A sample plot of $x_{\text{d.eq.}}(t)$ and the corresponding $T_{\text{d.eq.}}(t)$ with

$$\Omega(s) = 1 + \tfrac{1}{10}\sin(s), \quad \Theta(s) = 1 + \tfrac{1}{10}\cos(s) \tag{20}$$

is shown in Fig. 2.

Knowing the terms of the expansion (16), we can find an analogous series expansion for the heat:

$$Q(0,s) = \sum_{n=0}^{\infty} Q_{2n}(0,s)\varepsilon^{2n}. \tag{21}$$

Indeed, substituting Eq. (17) into (7b) we first find

$$Q(0,s) = -\int_0^s \Theta(\sigma)x'(\sigma)\,d\sigma - \frac{\varepsilon^2}{2}[x'(s) - x'(0)] - \frac{T(s) - T(0)}{2}, \tag{22}$$

which, upon the substitution of (16) and (14), yields the following values for the coefficients in (21):

$$Q_0(0,s) = \Theta(s)[x_0(0) - x_0(s)] - \int_0^s \Theta(\sigma)x_0'(\sigma)d\sigma, \tag{23a}$$

$$Q_{2n}(0,s) = -\int_0^s \Theta(\sigma)x_{2n}'(\sigma)d\sigma - \frac{1}{2}\sum_{l=0}^{n-1}[x_{2l}'(s)x_{2n-2l-2}'(s) - x_{2l}'(0)x_{2n-2l-2}'(0)] - [\Theta(s)x_{2n}(s) - \Theta(0)x_{2n}(0)] - 2\sqrt{\frac{2}{\pi}}[\sqrt{\Omega(s)}x_{2n-2}'(s) - \sqrt{\Omega(0)}x_{2n-2}'(0)] - \left[\frac{\Omega}{\Theta}(s)x_{2n-2}''(s) - \frac{\Omega}{\Theta}(0)x_{2n-2}''(0)\right]. \tag{23b}$$

It is worth noting that all the coefficients (23) can, in principle, be determined from the recurrence relation for x_n (18). An integration is involved, which may be nontrivial, but, from a formal point of view, the series is well defined for sufficiently small values of ε.

IV. DISCUSSION

In this concluding section, we comment on the relevance of Eq. (18) and of Eq. (23) and point out interesting features. Speaking specifically about the dynamical equilibrium solution, Eq. (18) possesses remarkable properties. The first one is that it allows us to calculate the dynamical equilibrium solution $x_{\text{d.eq.}}$ and hence T via (14) with an arbitrary precision. Only multiplications and differentiations are required in such formula, thus making the evaluation of x and T a trivial task. For practical purposes, the evaluation of the series (16) must be truncated at some point. Being absent the odd terms, if we stop at the Nth iteration we will have an error of order $O(\varepsilon^{2N+2})$, which gives us a pretty high precision with few iterations. Obviously this is valid only within the convergence radius; this can be in principle determined from the recurrence relation (18e), but its determination is a complex task far beyond the scope of this paper.

The second remarkable property is that (18e) is valid for general instances of Θ and Ω provided that they (1) depend on time only through εt, (2) are smooth, and (3) never vanish. This last condition must necessary hold for Θ, while it can be slightly relaxed for Ω. *A priori* the vanishing of both Θ and Ω introduces singularities in Eq. (15). As Eqs. (18) and (19) show, we cannot get rid of the singularities introduced by Θ. Conversely, we see from the same equations that the singularities in Ω do not explicitly appear in the solution, so they are in a certain sense *removable*. However, the price to pay is that the solution is compelled to live in a compact subset of the real line: if there exists a $s_0 > 0$ such that $\Omega(s_0) = 0$, then our solution is defined only on the subset $0 \leqslant s < s_0$ due to the presence of square roots in Eqs. (18) and (19). Physically $\Omega(s_0) = 0$ means that we allow the reservoir temperature to reach absolute zero in a finite time, which is forbidden by thermodynamics. As a consequence a vanishing $\Omega(s)$ is mathematically acceptable (even if with some limitations), but non physically.

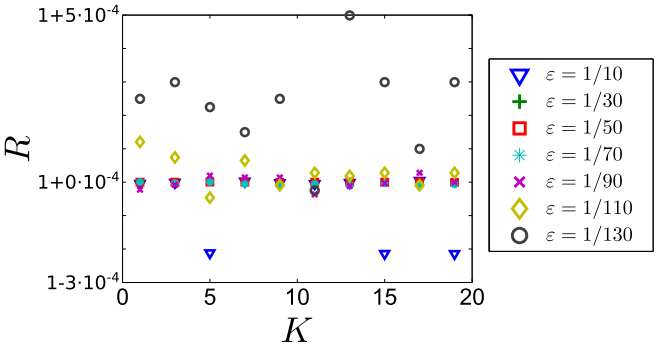

FIG. 3. Plot of R as a function of K for different values of ε.

The third interesting feature of Eq. (16) is that it extends the results of our previous paper [20] where we were limited to using $\Omega = 1$ and opens the possibility to study thermodynamic cycles. In turn, using this regular expansion technique, we lost the characterization of transient phenomena. This is not a major drawback, if, for example, one is interested in the study of the thermodynamic cycles efficiency, where transient behaviors are neglected. Moreover numerical evidence leads us to conjecture that, for ε sufficiently small, all solutions of (9) will at some time fall into our dynamical equilibrium solution. One example of such evidence is obtained as follows: using the particular form of Θ and Ω given in Eq. (20) we simulate Eq. (15) with $x(0) = x_{\text{d.eq.}}(0)$ and $x(0) = x_{\text{d.eq.}}(0) + K\varepsilon$, thus obtaining $x^{\text{num}}(t)$ and $x^{\text{num}}_{\text{d.eq.}}(t)$ respectively. We then study

$$R = \frac{\max\limits_{s\in[7\pi,9\pi]} |x^{\text{num}}(s) - x_{\text{d.eq.}}(s)|}{\max\limits_{s\in[7\pi,9\pi]} |x^{\text{num}}_{\text{d.eq.}}(s) - x_{\text{d.eq.}}(s)|} \tag{24}$$

as a function of K and ε, where $x_{\text{d.eq.}}$ is truncated at $n = 4$ and $s \in [7\pi,9\pi]$ ensures that we are way ahead of the time evolution of the system. As emerges by Fig. 3, $R \approx 1$ for various values of N and ε, so we reasonably say that $x^{\text{num}}(s)$ is attracted by Eq. (16). This means that the dynamical equilibrium solution has a quite general usefulness.

The last interesting feature of the expansion (16) is that if we limit ourselves to the 0th order term, we obtain the law of perfect gases. Higher orders terms are small corrections arising from the fact that Ω and Θ are changed in a finite time. In this sense Eq. (16) and Eq. (18) can be qualitatively considered as an analog of the virial expansion for a perfect gas where finite time effects play the role of interparticle interaction contributions. Clearly, this analogy is a formal one: in Ref. [15] the gas is assumed to be perfect and remains perfect during the whole time evolution. However, it is not unreasonable to think that the corresponding equation will have as a 0th order term the usual virial theorem for real gasses if the gas particles are allowed to interact. This suggests the existence of higher order time-dependent virial theorems.

Coming to the relevance of (21) and (23), they allow us to calculate the heat as a formal series in which all the coefficients are well determined through a purely mechanical model [15]. Equation (23) is therefore a quite uncommon result in the framework of nonequilibrium thermodynamics, as similar formal results are rare in the literature. It gives an explicit expression of heat exchanged at any intermediate time that can be evaluated *a priori* with the sole knowledge of the driving protocol. This opens interesting scenarios to analyze. For example, it reduces the evaluation of heat to the problem of finding the terms in (16) and to performing the integration in Eq. (23). Another interesting possibility is the formal evaluation of the efficiency of thermodynamic cycles when drivings are slow but not necessarily quasistatic, i.e., to characterize situations where efficiency is expected to be high while the power is close to zero. We point out that in the original model we are not allowed to consider adiabatic transformations. Therefore we are unable to describe Carnot cycles, but it is possible to study Ericsson-like cycles [15,16], with the only caveat that Ω and Θ must be smooth function. This may seems an internal contradiction as Ericsson cycle is not smooth; however, any periodic functions can be reasonably approximated by a smooth trigonometric polynomial [26]. To satisfy the "slow" driving condition such trigonometric polynomial should not contain high order harmonics, but this is usually sufficient to yield a good approximation.

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[1] S. R. de Groot and P. Mazur, *Non-equilibrium Thermodynamics* (North-Holland, Amsterdam, 1962).
[2] U. Seifert, Stochastic thermodynamics, fluctuation theorems and molecular machines, Rep. Prog. Phys. **75**, 126001 (2012).
[3] K. Sekimoto, *Stochastic Energetics* (Springer-Verlag, Berlin, 2010).
[4] G. Gruber and A. Lesne, *Encyclopedia of Mathematical Physics (Lemma: Adiabatic Piston)* (Elsevier, Oxford, 2006), Vol. 1.
[5] E. A. Gislason, A close examination of the motion of an adiabatic piston, Am. J. Phys. **78**, 995 (2010).
[6] R. de Abreu and V. Guerra, Comment on a close examination of the motion of an adiabatic piston, by Eric A. Gislason [Am. J. Phys. **78**, 995 (2010)], Am. J. Phys. **79**, 684 (2011).
[7] R. C. Lua, and A. Y. Grosberg, Practical applicability of the Jarzynski relation in statistical mechanics: A pedagogical example, J. Phys. Chem. B **109**, 6805 (2005).
[8] A. Baule, R. M. L. Evans, and P. D. Olmsted, Validation of the Jarzynski relation for a system with strong thermal coupling: An isothermal ideal gas model, Phys. Rev. E **74**, 061117 (2006).
[9] J. Hoppenau, M. Niemann, and A. Engel, Carnot process with a single particle, Phys. Rev. E **87**, 062127 (2013).

[10] Z. Gong, Y. Lan, and H. T. Quan, Stochastic thermodynamics of a particle in a box, arXiv:1602.08702.
[11] K. Proesmans, C. Driesen, B. Cleuren, and C. Van den Broeck, Efficiency of single-particle engines, Phys. Rev. E **92**, 032105 (2015).
[12] J. P. S. Bizarro, Entropy production in irreversible processes with friction, Phys. Rev. E **78**, 021137 (2008).
[13] J. P. S. Bizarro, Thermodynamics with friction. I. The Clausius inequality revisited, J. Appl. Phys. **108**, 054907 (2010).
[14] J. P. S. Bizarro, The thermodynamic efficiency of heat engines with friction, Am. J. Phys. **80**, 298 (2012).
[15] L. Cerino, A. Puglisi, and A. Vulpiani, Kinetic model for the finite-time thermodynamics of small heat engines, Phys. Rev. E **91**, 032128 (2015).
[16] L. Cerino, A. Puglisi, and A. Vulpiani, Linear and non-linear thermodynamics of a kinetic heat engine with fast transformations, Phys. Rev. E **93**, 042116 (2016).
[17] Y. Izumida and K. Okuda, Onsager coefficients of a finite-time carnot cycle, Phys. Rev. E **80**, 021121 (2009).
[18] T. G. Sano and H. Hayakawa, Efficiency at maximum power output for a passive engine, arXiv:1412.4468.
[19] R. Tehver, F. Toigo, J. Koplik, and J. R. Banavar, Thermal walls in computer simulations, Phys. Rev. E **57**, R17 (1998).
[20] D. Chiuchiù and G. Gubbiotti, Multiple scales approach to the gas-piston non-equilibrium themodynamics, J. Stat. Mech. (2016) 053110.
[21] G. E. Kuzmak, Asymptotic solutions of nonlinear second order differential equations with variable coefficients, J. Appl. Math. Mech. (PMM) **23**, 730 (1959).
[22] J. Kevorkian and J. D. Cole, *Multiple Scale and Singular Perturbation Methods* (Springer-Verlag, New York, 1996).
[23] M. H. Holmes, *Introduction to Perturbation Methods* (Springer, New York, 2013).
[24] C. M. Bender and S. A. Orszag, *Advanced Mathematical Methods for Scientists and Engineers* (McGraw-Hill, New York, 1978).
[25] C. Jarzynski, Comparison of far-from-equilibrium work relations, C. R. Physique **8**, 495 (2007).
[26] T. E. Whittaker and G. N. Watson, *A Course of Modern Analysis* (Cambridge University Press, Cambridge, 1927).