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A hard disc analysis of momentum deficit due to dissipation

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Received 29 April 2012

Accepted for publication 6 September 2012

Published 19 October 2012

Online at stacks.iop.org/PhysScr/86/058508

Abstract

When a Brownian object is in a non-equilibrium steady state, the actual force exerted on it is different from the one in thermal equilibrium. In our previous paper (Fruleux *et al* 2012 *Phys. Rev. Lett.* **108** 160601), we discovered a general principle that relates the missing force to dissipation rates through the concept of momentum deficiency due to dissipation (MDD). In this paper, we examine the principle using various models based on hard disc gases and Brownian pistons. Explicit expressions of the forces are obtained analytically and the results are compared with molecular dynamics simulations. The good agreement demonstrates the validity of MDD.

PACS numbers: 05.40.-a, 05.70.Ln, 05.20.Dd

(Some figures may appear in colour only in the online journal)

1. Introduction

Since its inception, investigating the effect of the environments on a closed system has been a key subject of thermodynamics. In particular, when the system size is reduced to a mesoscopic scale, fluctuations in the system caused by those of the environments play a dominant role in many physical phenomena, such as Brownian motion. The state of Brownian objects is typically investigated with the Langevin theory in which the environments exert forces on the Brownian objects through deterministic linear friction and fluctuating Langevin forces [1]. This approach has been proven to be very effective for many applications. Furthermore, the recent development of stochastic energetics [2] allows one to investigate the exchange of energy between Brownian objects and the environments within the Langevin theory.

When the system is in contact with more than one environment that are not in equilibrium with each other, we expect that the energy and momentum flows between the system and the environments change in such a way that the detailed balance is broken. Strictly speaking, this loss of the detailed balance brings the environments out of equilibrium at least in the vicinity of the system–environment interfaces.

This aspect is not reflected in the Langevin description. Consider, for example, the cases when a Brownian object is simultaneously in contact with two different heat baths at different temperatures. What force will be exerted on the Brownian object by the baths? A natural extension to the standard Langevin theory is to use the frictions and the stochastic forces from each bath assuming that the fluctuation–dissipation relation of the second kind (i.e. the Einstein relation) holds independently of each bath, a condition that is sometimes called the local detailed balance. While such a simple linear model works well in many cases, there are phenomena that refuse to be understood by using the linear Langevin approach.

The most striking example is the *adiabatic piston* placed between two gases with different temperatures [3, 4]. The piston has no internal degree of freedom so that no heat flows between the baths through it. An interesting question is whether the piston moves when the two baths have the same pressure. Naively, one may think that the piston does not move because the pressure on the both the sides of the piston is the same. It turns out that the laws of thermodynamics alone cannot tell whether the piston moves or not [5]. Feynman *et al* [6] have pointed out that fluctuations of the piston's velocity should be taken into account. However, the Langevin

approach with linear frictions falsely predicts zero mean velocity.

A similar difficulty also appears in some models of Brownian motors working between two baths [7]. In these models, the body of Brownian objects, e.g. a triangular body, is not symmetric with respect to space inversion. This kind of asymmetry is not fully realized in the linear Langevin equation since the linear friction constant or tensor is non-polar. In the case of the adiabatic piston, the Brownian object itself is symmetric but the environments are not. In either case, the linear Langevin theory cannot take into account asymmetric interactions between Brownian objects and the environments.

A common solution to these problems has been to resort to full and general microscopic descriptions, such as molecular dynamics (MD) simulation or master-Boltzmann equations under pertinent perturbative approximations. These methods are effective in predicting the outcome. For the adiabatic piston, MD simulation [4] and the perturbative master-Boltzmann equation [3, 4] give quite consistent results showing that the piston moves towards the *hotter* reservoir. A more recent investigation based on the nonlinear Langevin equation confirms this [8]. Although we now know that the piston moves, we still do not fully understand the physics behind it.

Recently, we investigated the force exerted by gas particles on a Brownian object in a non-equilibrium steady state (NESS) and discovered a rather general principle [9]. When there is energy dissipation, the net momentum flux at the surface of a Brownian object is reduced from the flux without dissipation, which we shall call *momentum deficiency due to dissipation* (MDD). As a consequence, the force on the Brownian object decreases from the equilibrium force by

$$F_{\text{MDD}} = -c \frac{J_{\text{diss}}^{(e)}}{v_{\text{th}}}, \quad (1)$$

where $J_{\text{diss}}^{(e)}$ is the energy dissipation per unit time, and the thermal velocity of the gas particles of mass m at a temperature T is defined by $v_{\text{th}} \equiv \sqrt{k_B T/m}$. The Boltzmann constant is denoted by k_B . The positive prefactor c depends on the details of the system but is usually of the order of 1.

With this new principle, we are able to explain all of the above-mentioned phenomena without the lengthy calculation [9]. It is this MDD that is missing in the linear Langevin theory. The stochastic energetics [2] tells us that the linear Langevin theory is sufficient for obtaining the dissipation rate. Therefore, one can evaluate the missing force (1) within the Langevin description. Furthermore, we note that this fundamental principle is applicable to systems beyond the regular Brownian objects, such as inelastic pistons and granular Brownian ratchets [10, 11].

In this paper, we will demonstrate the validity of the new principle (1) using hard disc systems, including MD simulation. In the next section, we heuristically explain the idea of MDD. Then, we derive explicit expressions of F_{MDD} for hard disc systems. The results are compared with MD simulation of shared Brownian pistons. We also derive the non-equilibrium forces on an inelastic Brownian piston. Despite the fact that the origin of dissipation is quite different from the previous model, we arrive at the same expression, (1), and MD simulation confirms this.

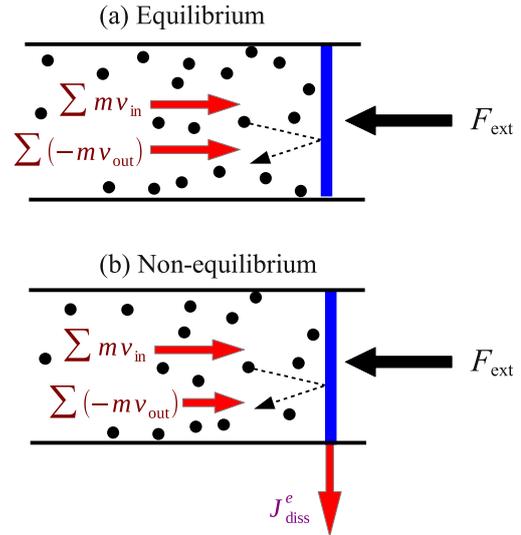


Figure 1. Simple models illustrating the key point of MDD. The upper panel (a) shows an equilibrium case where a gas is confined by a piston pressed with a constant force F_{ext} . In this case, the momentum flow of the outgoing particles, $\sum(-mv_{\text{out}})$, equals the momentum flow of the incoming particles, $\sum mv_{\text{in}}$. The sum of the two flows is the pressure of the gas, which balances with the external force. The lower panel (b) illustrates a non-equilibrium case where the gas loses energy through the piston to external environments. In this case, the momentum flow of the outgoing particles is smaller than that of the incoming particles, resulting in a reduction of the force exerted on the piston by the gas.

2. Momentum deficit due to dissipation: a heuristic argument

In this section, we briefly summarize the key concept developed in [9]. First, we consider a simple equilibrium system illustrated in figure 1(a). The system consists of a two-dimensional cylinder filled with a gas and a piston of mass M with surface size L , pressed with a constant external force F_{ext} . The piston is a Brownian object and its velocity fluctuates owing to the collision with gas particles. However, when the piston is in thermal equilibrium, its mean velocity is zero. Hence, the sum of the pre-collisional and post-collisional momentum flows, $\sum mv_{\text{in}} + \sum(-mv_{\text{out}})$, is balanced by the external force. Here the summation is taken over all collisions during unit time. The detailed balance tells us that at equilibrium the two momentum flows must be equal and therefore, on average, $2 \sum mv_{\text{in}} = |F_{\text{ext}}| = pL$, where p is the pressure of the gas. Note that unlike a simple kinetic theory used in elementary textbooks the individual collisions can transfer energy and momentum between the gas and the piston at the microscopic time scale, since the piston is a Brownian object. It is the detailed balance that makes the two momentum flows identical on average.

Now we turn to a non-equilibrium case shown in figure 1(b), where energy flows from the gas through the piston into another environment. We assume that the piston is in a NESS so that its mean velocity is zero. The magnitude of the external force is the same as that in the equilibrium case, i.e. $F_{\text{ext}} = pL$. In non-equilibrium cases, this relation does not necessarily indicate mechanical equilibrium. Even for a non-fluctuating macroscopic object, the actual force exerted

by the gas deviates from pL as observed in a radiometer⁴. Our question is: what is the actual force on the piston when it is a Brownian object? We expect that the post-collisional speed is smaller than that in the equilibrium case. Hence, the net momentum flow must be reduced. This is the MDD and the force induced by MDD, F_{MDD} , is defined by

$$F_{\text{MDD}} = \sum m v_{\text{in}} + \sum (-m v_{\text{out}}) - pL, \quad (2)$$

which vanishes in the absence of dissipation.

The magnitude of F_{MDD} can be estimated from the energy balance

$$\sum \frac{m}{2} v_{\text{in}}^2 - \sum \frac{m}{2} v_{\text{out}}^2 = J_{\text{diss}}^{(e)}. \quad (3)$$

As a rough estimate, we replace fluctuating quantities with typical values: $\sum v_{\text{in}} \sim \omega_{\text{col}} v_{\text{th}}$ and $\sum v_{\text{in}}^2 \sim \omega_{\text{col}} v_{\text{th}}^2$, where ω_{col} is the number of collisions per unit time. Similarly, for the outgoing particles, we introduce a typical velocity \bar{v}_{out} . Furthermore, the dissipation is assumed to be so weak that $v_{\text{in}} - v_{\text{out}} \approx 2v_{\text{th}}$. Then, the balance of momentum and energy is expressed in simpler forms

$$F_{\text{MDD}} \approx -\omega_{\text{col}} m (v_{\text{th}} + \bar{v}_{\text{out}}), \quad (4)$$

$$J_{\text{diss}}^{(e)} \approx \omega_{\text{col}} m (v_{\text{th}} + \bar{v}_{\text{out}}) v_{\text{th}}. \quad (5)$$

Eliminating the unknown quantity \bar{v}_{out} , we obtain equation (1) except for the prefactor c which is omitted in the above phenomenological argument since it depends on the system configuration.

Despite the drastically simple derivation, equation (1) agrees with the result of lengthy calculations except for the prefactor. Applying this principle, we are able to explain the adiabatic piston and other phenomena both conceptually and quantitatively [9].

3. Momentum deficiency due to dissipation in hard disc systems

3.1. Basic model

We consider again the NESS case shown in figure 1(b). In order to find explicit expressions, we assume that the gas consists of hard discs which elastically collide with the piston. The temperature of the gas, T , is assumed to be constant and the velocity of the gas particles satisfies the Maxwellian velocity distribution⁵. We assume only binary hard collisions to take place. The piston surface is smooth so that the velocity component parallel to the piston remains the same upon collision. Hereafter, we consider only the velocity component perpendicular to the piston. Momentum and energy are conserved at each collision even when the Brownian object is simultaneously in contact with other baths or external agents, since the hard disc collision is

instantaneous. For the i th collision, the gas particle and piston have the pre-collisional velocity v_i and V_i , respectively, and the corresponding post-collisional velocities u_i and U_i are determined by the momentum and energy conservation laws:

$$m u_i - m v_i = M V_i - M U_i, \quad (6)$$

$$\frac{m}{2} u_i^2 - \frac{m}{2} v_i^2 = \frac{M}{2} V_i^2 - \frac{M}{2} U_i^2. \quad (7)$$

Between successive collisions, the piston interacts with another environment or an external agent and its momentum and energy change by ΔP_i and ΔE_i , respectively. The change in the piston velocity is determined by another set of momentum and energy balance equations:

$$M V_{i+1} - M U_i = \Delta P_i, \quad (8)$$

$$\frac{M}{2} V_{i+1}^2 - \frac{M}{2} U_i^2 = \Delta E_i. \quad (9)$$

Summing up equations (6) and (8) over all n collisions during unit time, we find the net momentum balance:

$$\omega_{\text{col}} (m \langle v \rangle_{\text{col}} - m \langle u \rangle_{\text{col}}) + F_{\text{ext}} = 0, \quad (10)$$

where $F_{\text{ext}} \equiv \sum \Delta P_i$ and we have used the NESS condition $M U_n = M V_1$. The mean value is defined by $\sum v_i = \omega_{\text{col}} \langle v \rangle_{\text{col}}$. Note that $\langle \cdots \rangle_{\text{col}}$ indicates the average over all collisions during unit time (see the [appendix](#)) and it is not the same as a regular thermal average over the Maxwell distribution. The force due to MDD is now expressed as

$$F_{\text{MDD}} = F_{\text{ext}} - pL = -\omega_{\text{col}} m (\langle v \rangle_{\text{col}} + \langle u \rangle_{\text{col}}). \quad (11)$$

Similarly, adding up equation (7) along with equation (9) leads to the net energy balance

$$J_{\text{diss}}^{(e)} = \omega_{\text{col}} \left(\frac{m}{2} \langle u^2 \rangle_{\text{col}} - \frac{m}{2} \langle v^2 \rangle_{\text{col}} \right), \quad (12)$$

where $J_{\text{diss}}^{(e)} \equiv \sum \Delta E_i$. We have used the steady-state condition $M U_n^2 / 2 = M V_1^2 / 2$.

For incoming particles, we find that $\langle v \rangle_{\text{col}} = \sqrt{\pi/2} v_{\text{th}}$ and $\langle v^2 \rangle_{\text{col}} / \langle v \rangle_{\text{col}}^2 = 4/\pi$ (see the [appendix](#)). We do not have the exact statistics of the outgoing particles. However, when the dissipation is weak, we can assume that $\langle u \rangle_{\text{col}} \approx -\langle v \rangle_{\text{col}}$ and $\langle v^2 \rangle_{\text{col}} / \langle v \rangle_{\text{col}}^2 \approx \langle u^2 \rangle_{\text{col}} / \langle u \rangle_{\text{col}}^2$. Using this approximation, equation (12) is reduced to

$$J_{\text{diss}}^{(e)} = \sqrt{\frac{8}{\pi}} v_{\text{th}} \omega_{\text{col}} m (\langle v \rangle_{\text{col}} + \langle u \rangle_{\text{col}}). \quad (13)$$

Comparing equations (11) and (13), we obtain formula (1) with a prefactor $c = \sqrt{\pi/8}$.

3.2. Shared Brownian pistons

Now, we introduce a more concrete NESS model shown in figure 2(a), so that we can evaluate the dissipation rate. The upper cylinder is the same as the basic model (figure 1(b)) and the gas in it has temperature T_1 . An NESS condition is generated by linking the piston to another piston in the second cylinder filled with another gas at a different temperature T_2 . These two pistons are rigidly connected and move together. Unlike the upper one, the lower cylinder is periodic, so that

⁴ Maxwell struggled to explain it until near the end of his life. See [12].

⁵ In general, this assumption does not hold under non-equilibrium conditions. Following the previous models [4, 7, 10, 11], we assume that the incoming particles leave a thermostated region and directly hit the Brownian object. The outgoing particles, lower in kinetic energy on average, travel back to the thermostated area before colliding with the incoming particles, and thus the incoming particles follow the Maxwellian distribution. However, this situation is possible only when the distance between the Brownian object and the thermostated region is not larger than the mean free path.

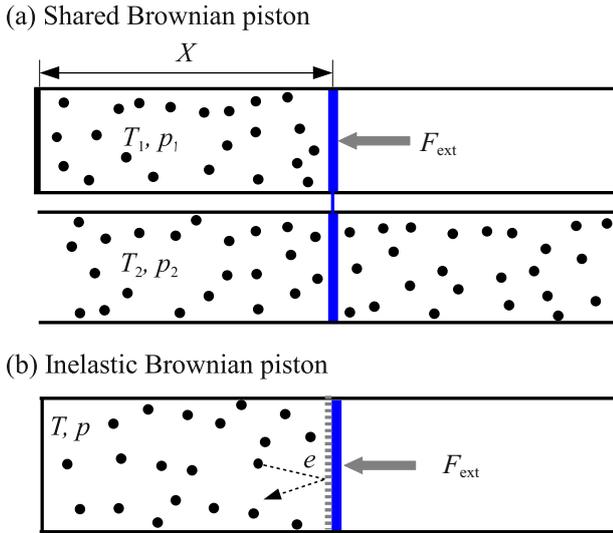


Figure 2. Models with two different types of dissipation. (a) The shared Brownian piston: the piston is in contact with the second gas. When two gases have different temperatures, heat flows from the upper gas to the lower one through fluctuations of the piston. (b) The inelastic Brownian piston: the collision between the gas particles and the piston is inelastic. The energy dissipates into the internal degrees of freedom in the piston and gas particles.

the particle density does not change as the piston moves. Accordingly, when the piston moves, the pressure of the upper gas, p_1 , changes while the pressure p_2 of the lower gas remains constant.

It is known that when $T_1 > T_2$, heat flows from the upper gas to the lower gas through the fluctuations of the Brownian object [13]. The heat dissipation through a shared piston is understood at the level of standard Langevin theory [14]. Using the friction coefficients for the upper and lower pistons, $\gamma_1 = \sqrt{8/\pi} \rho_1 L \sqrt{k_B T_1}$ and $\gamma_2 = 2\sqrt{8/\pi} \rho_2 L \sqrt{k_B T_2}$, we find that the dissipation rate is

$$J_{\text{diss}}^{(e)} = \sqrt{\frac{\pi}{8}} \frac{k_B T_1 - k_B T_2}{M(\gamma_1^{-1} + \gamma_2^{-1})}. \quad (14)$$

Substituting this dissipation rate and the prefactor $c = \sqrt{\pi/8}$ into equation (1), we obtain an explicit expression of the force due to MDD:

$$F_{\text{MDD}} = -\frac{2\rho_1\rho_2 L m}{\rho_1 + 2\rho_2 M} (k_B T_1 - k_B T_2). \quad (15)$$

We have checked the above results using hard disc MD simulation. The detailed simulation method will be written somewhere else. Initially, the system is in thermal equilibrium with $T_1 = T_2 = 1.0$. The mean position of the piston X_0 remains constant since $F_{\text{ext}} + p_1 L = 0$. Figure 3 shows that when the temperature of the lower gas is reduced to $T_2 = 0.5$, the upper gas is compressed although the temperature is fixed at $T_1 = 1.0$. The displacement of the piston indicates that the force exerted on the piston by the gas is *not* the pressure times the surface area. Similarly, when T_2 is raised above T_1 , the upper gas expands.

When the system reaches an NESS, the piston is settled at a new position and a new pressure p'_1 is established. Assuming

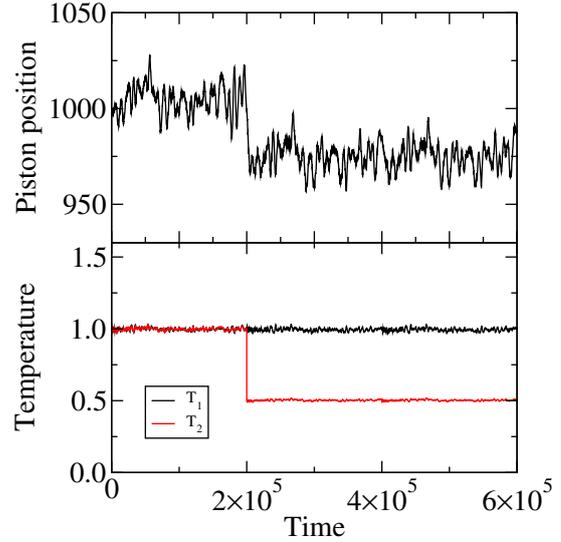


Figure 3. MD simulation of MDD using the model illustrated in figure 2(a). The upper panel shows the position of the piston and the lower panel the temperature of two gases. Initially, the two gases have the same temperature $T_1 = T_2 = 1.0$. When the temperature of the lower gas is reduced to $T_2 = 0.5$, the upper gas is compressed owing to F_{MDD} . The values of the system parameters are $L = 300$, $M/m = 20$, $X_0 = 1000$ and $\rho_1 = \rho_2 = 0.00333$ where the diameter of the gas particle is a unit of the length. The mean-free path in this configuration is about 150. The data are averaged over 300 realizations.

that the gas obeys the ideal gas law and the displacement ΔX is much smaller than X_0 , the missing force is estimated by

$$F_{\text{MDD}} = (p_1 - p'_1)L = p_1 L \frac{\Delta X}{X_0}. \quad (16)$$

In figure 4, we plot F_{MDD} obtained in three different ways: equation (16) with the measured displacement of the piston, equation (1) using the dissipation rate measured in the MD simulation and the full theoretical result (15). All three estimations agree very well, implying the validity of equation (1).

4. MDD in granular systems: the inelastic piston

In order to demonstrate the generality of equation (1), we consider a different type of dissipation. In the model illustrated in figure 2(b), energy dissipates into the internal degrees of freedom of the piston and gas particles through inelastic collisions between them. Using a standard collision rule used for granular systems, post-collisional velocities are related to the pre-collisional velocities as $u_i - U_i = -e(v_i - V_i)$, where e is a coefficient of restitution ($0 < 1 - e \ll 1$). The momentum is always conserved and thus equation (6) is still valid. The energy balance for this model is

$$\frac{m}{2} v_i^2 - \frac{m}{2} u_i^2 = \frac{M}{2} U_i^2 - \frac{M}{2} V_i^2 + \frac{1-e^2}{2} \frac{mM}{m+M} (V_i - v_i)^2. \quad (17)$$

Unlike the previous case, there is no dissipation between collisions; hence $V_{i+1} = U_i$. Summing up equation (17) for all collisions during unit time, we obtained equation (12) again

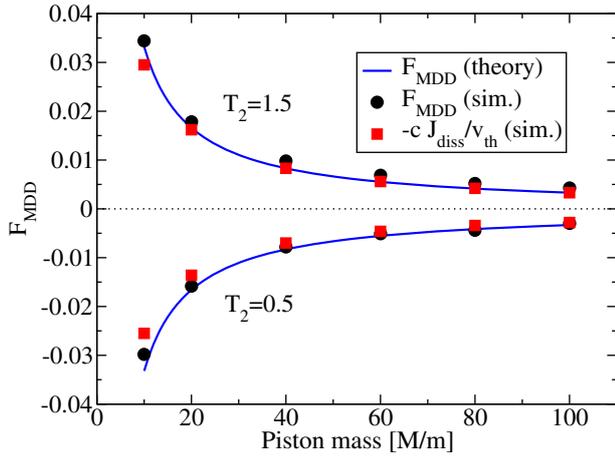


Figure 4. MD simulation of MDD using the model illustrated in figure 2(a). The black solid circle shows the force measured in the simulation through equation (16). The red solid square plots the force estimated from equation (1) using the observed heat flow. The full theoretical prediction equation (15) is plotted with a solid line. The upper curves show the case when the temperature of the second gas ($T_2 = 1.5$) is higher than that of the upper gas, whereas the lower curves show the opposite case where the lower gas has $T_2 = 0.5$. See figure 3 for the values of the system parameters.

with a different dissipation rate:

$$J_{\text{diss}}^{(e)} = \frac{1 - e^2}{2} \frac{mM}{m + M} \omega_{\text{col}} \langle (V - v)^2 \rangle_{\text{col}}. \quad (18)$$

Although the actual expression of $J_{\text{diss}}^{(e)}$ is different, the momentum and energy conservation laws are universal, and hence the general expression (1) is valid also for this model.

Now, we evaluate the dissipation rate (18). Assuming that the piston obeys the Maxwellian distribution with a kinetic temperature T_{kin} , the mean value in equation (18) is given by

$$\langle (v - V)^2 \rangle_{\text{col}} = \frac{2k_B T}{m} + \frac{2k_B T_{\text{kin}}}{M}, \quad (19)$$

as shown in the appendix. The dissipation rate is divided into two parts: one proportional to the mean kinetic energy of the gas particles (the first term) and the other proportional to the mean kinetic energy of the piston (the second term). We shall call the former as housekeeping dissipation ($J_{\text{diss,hk}}$) and the latter as excess dissipation ($J_{\text{diss,ex}}$) as coined in [15]. Using the mean values used in the previous section and $\omega_{\text{col}} = \rho L v_{\text{th}} / \sqrt{2\pi}$ (see the appendix), we obtain

$$J_{\text{diss,hk}} = (1 - e) \sqrt{\frac{2}{\pi}} v_{\text{th}} p L, \quad (20)$$

$$J_{\text{diss,ex}} = (1 - e) \frac{\gamma}{M} \frac{k_B T}{2}, \quad (21)$$

where we assumed that $m/M \ll 1$, $(1 - e^2) \approx 2(1 - e)$ and $T_{\text{kin}} \approx T \times (1 + e)/2$ [16]. Through our basic principle (1) and the prefactor $c = \sqrt{\pi}/8$, these dissipation rates lead to $F_{\text{MDD}} = F_{\text{MDD,hk}} + F_{\text{MDD,ex}}$ where

$$F_{\text{MDD,hk}} = -\frac{1}{2}(1 - e)pL, \quad (22)$$

$$F_{\text{MDD,ex}} = -\frac{m}{M}(1 - e)pL. \quad (23)$$

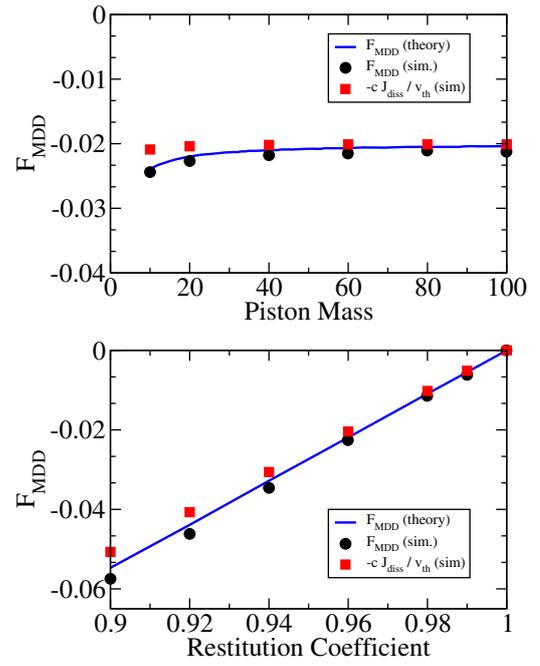


Figure 5. F_{MDD} on the inelastic piston shown in figure 2(b) is plotted as a function of the piston mass (the upper panel) and of the restitution coefficient (the lower panel). The force was evaluated in three different ways: the black circle indicates the force measured from the displacement of the piston in the MD simulation using equation (16). The red square shows formula (1) using the dissipation rate observed in the MD simulation. The solid line plots the theoretical value, the sum of equations (22) and (23). In the upper panel, $e = 0.96$ and in the lower panel, $M/m = 20$ are used. See figure 3 for other parameter values.

Figure 5 shows the result of MD simulation. We again plot F_{MDD} evaluated in three different ways: equation (16), equation (1) using the measured dissipation rate and the full theoretical value with equations (22) and (23). All three estimations agree well.

As discussed in [9], these forces explain the driving of inelastic pistons [10] and granular ratchets [11]. For the granular pistons, the housekeeping force (22) is dominant and agrees with the perturbative results [10]. On the other hand, the driving force of the granular ratchets is the excess-dissipation force (23) since the net housekeeping force vanishes in this model.

5. Conclusions

We examined the MDD using various hard disc models. The explicit expressions of the force due to MDD are obtained for two different models: the shared Brownian piston and the inelastic Brownian piston. Despite the different dissipation processes, the general principle (1) is valid for both the cases. MD simulations agree well with theoretical predictions for both the cases.

Acknowledgments

We thank the organizers of NonEqSM2011 and the European Science Foundation for providing us (KS and RK) the opportunity to work on this project at NORDITA. RK also thanks the members of Physico-Chimie Théorique at ESPCI

for their kind hospitality and stimulating discussion during his sabbatical stay. KS acknowledges RIKEN for financial support under contract no. CNRS: 30020830.

Appendix. Collision statistics

Here, we briefly explain the calculation of the average over collision events. We assume that the incoming gas particles obey Maxwell's velocity distribution $f_g(v) = \sqrt{m/2\pi k_B T} e^{-mv^2/2k_B T}$ with temperature T . Under non-equilibrium conditions, the velocity distribution of the piston is not necessarily Maxwellian. However, when the piston is under an NESS not far from equilibrium, the piston approximately follows Maxwell's velocity distribution $f_p(V) = \sqrt{M/2\pi k_B T_{\text{kin}}} e^{-MV^2/2k_B T_{\text{kin}}}$ but with a kinetic temperature T_{kin} that is different from the temperature of the gas. Under these assumptions, the velocity distribution of gas particles colliding with the piston moving at a velocity V is given by

$$\Phi(v; V) = \frac{L\rho(v-V)}{\omega_{\text{col}}} f_g(v) f_p(V) \Theta(v-V), \quad (\text{A.1})$$

where $\Theta(\cdot)$ is the Heaviside step function and the normalization constant ω_{col} is the total number of collisions per unit time, defined by

$$\begin{aligned} \omega_{\text{col}} &= L\rho \int_{-\infty}^{\infty} dV \int_{-\infty}^{\infty} dv (v-V) f_g(v) f_p(V) \\ &= L\rho \sqrt{\frac{k_B T}{2\pi m}} \sqrt{1 + \frac{mT_{\text{kin}}}{MT}} \approx L\rho \frac{v_{\text{th}}}{\sqrt{2\pi}}, \end{aligned} \quad (\text{A.2})$$

where $m \ll M$ is assumed.

Using the probability distribution (A.1), we obtain the first and second moments:

$$\begin{aligned} \langle v \rangle_{\text{col}} &= \int_{-\infty}^{\infty} dV \int_{-\infty}^{\infty} dv v \Phi(v; V) \\ &= \sqrt{\frac{\pi k_B T}{2m}} \left(1 + \frac{mT_{\text{kin}}}{MT}\right)^{-\frac{1}{2}} \approx \sqrt{\frac{\pi}{2}} v_{\text{th}}, \end{aligned} \quad (\text{A.3})$$

$$\begin{aligned} fI \langle v^2 \rangle_{\text{col}} &= \int_{-\infty}^{\infty} dV \int_{-\infty}^{\infty} dv v^2 \Phi(v; V) \\ &= \frac{k_B T}{m} \cdot \frac{mT_{\text{kin}} + 2MT}{mT_{\text{kin}} + MT} \approx 2v_{\text{th}}^2. \end{aligned} \quad (\text{A.4})$$

Similarly, the second moment of the relative velocity is computed as

$$\begin{aligned} \langle (v-V)^2 \rangle_{\text{col}} &= \int_{-\infty}^{\infty} dV \int_{-\infty}^{\infty} dv (v-V)^2 \Phi(v; V) \\ &= \frac{2k_B T}{m} + \frac{2k_B T_{\text{kin}}}{M}, \end{aligned} \quad (\text{A.5})$$

which is exact under the present assumption.

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