

## The law of action and reaction for the effective force in a non-equilibrium colloidal system

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2006 J. Phys.: Condens. Matter 18 2825

(<http://iopscience.iop.org/0953-8984/18/10/008>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 28/05/2010 at 09:06

Please note that [terms and conditions apply](#).

# The law of action and reaction for the effective force in a non-equilibrium colloidal system

Kumiko Hayashi<sup>1</sup> and Shin-ichi Sasa

Department of Pure and Applied Sciences, University of Tokyo, Komaba, Tokyo 153-8902, Japan

E-mail: [hayashi@jiro.c.u-tokyo.ac.jp](mailto:hayashi@jiro.c.u-tokyo.ac.jp)

Received 25 October 2005, in final form 27 January 2006

Published 20 February 2006

Online at [stacks.iop.org/JPhysCM/18/2825](http://stacks.iop.org/JPhysCM/18/2825)

## Abstract

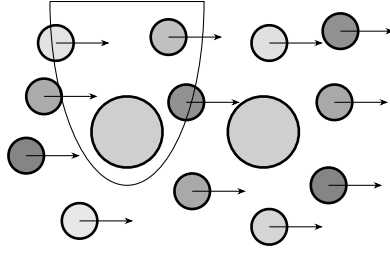
We study a non-equilibrium Langevin many-body system containing two ‘test’ particles and many ‘background’ particles. The test particles are spatially confined by a harmonic potential, and the background particles are driven by an external driving force. Using numerical simulations of the model, we formulate an effective description of the two test particles in a non-equilibrium steady state. In particular, we investigate several different definitions of the effective force acting between the test particles. We find that the law of action and reaction does not hold for the total mechanical force exerted by the background particles, but that it does hold for the thermodynamic force defined operationally on the basis of an idea used to extend the first law of thermodynamics to non-equilibrium steady states.

## 1. Introduction

Colloids are microscopic particles suspended in liquid. Generally, they are of the order of micrometres in size, and thus they are much larger than molecules but still small enough to exhibit Brownian motion. Colloids are convenient to study experimentally because, unlike molecules, they can be easily observed with ordinary microscopes. In recent years, as the technology used in their manipulation has developed, experimental studies of colloids have advanced greatly [1–6].

In colloidal many-body systems, melting, freezing, glass transitions and non-equilibrium statistical mechanics have been studied. Among the studies of non-equilibrium steady states (NESSs), that of Dzubeilla *et al* investigated a model that describes two fixed colloidal particles (test particles) in an environment containing many driven particles (background particles). They reported that in a NESS, the effective interaction forces they defined between the two fixed particles violate the law of action and reaction [7]. This result implies that an effective potential seems not to be constructed in NESS.

<sup>1</sup> Author to whom any correspondence should be addressed.



**Figure 1.** Schematic representation of the model we study. Note that the background particles are not driven in the equilibrium case.

The effective interaction force defined in [7] represents the two-body effect of the total force exerted by the background particles, which is extracted by subtracting from it the total force in the case when there are only colloidal particles. Although their definition seems plausible because of its simplicity, we expect that there is room to define a different type of effective force in NESS. With this motivation, we attempt to provide another idea for an effective interaction force between the two fixed particles.

In this paper we reconsider effective forces in NESSs by studying a system similar to that used in [7]. First, we review the concept of effective forces in equilibrium from three points of view: statistical mechanics, mechanics and thermodynamics. Next, we investigate effective forces for non-equilibrium systems by considering the results of numerical experiments. In particular, we demonstrate that in the NESS we consider the law of action and reaction holds for the effective force defined according to a conjectured thermodynamic relation applied to NESSs.

## 2. Model

The model we study describes a system in which two ‘test’ particles are trapped side by side in the centre of the system by a harmonic potential, and  $N$  ‘background’ particles are driven by an external force (see figure 1). The test particles are unaffected by the driving force, and the background particles are unaffected by the trapping potential. Hereafter, we refer to the test particles as particle **1** and particle **2**.

For the sake of simplicity, we consider the idealized situation of a two-dimensional system of length  $L_x$  and  $L_y$  in the  $x$  and the  $y$  directions, with periodic boundary conditions in both directions. Then, letting  $\vec{R}_1$  and  $\vec{R}_2$  be the positions of particle **1** and particle **2**, we consider particle **2** fixed for simplicity, with particle **1** trapped by the harmonic potential

$$V_t(\vec{R}_1) = \frac{k}{2}(\vec{R}_1 - \vec{R}_c)^2, \quad (1)$$

where  $\vec{R}_c$  corresponds to the centre of the potential and  $k$  is a spring constant chosen to be sufficiently large that particle **1** can be regarded as almost fixed. It is important to note that although it may seem simpler to fix particle **1** the dynamical degrees of freedom of particle **1** must be taken into account when we consider the distribution function of the effective description in which the degrees of freedom of the background particles are integrated. (If particle **1** is also fixed, no variable remains in the distribution function of the effective description (see the next section).) As a further simplification, it is assumed that there is no direct interaction between particles **1** and **2** and that there is no direct interaction among the background particles. Then, we stipulate that the interaction between particle **1** or particle **2**

and a background particle is represented by a short-ranged potential function  $V_{\text{int}}(\vec{R}_i - \vec{r}_k)$ , where  $\vec{r}_k$  is the position of the  $k$ th background particle ( $k = 1, \dots, N$ ), of the form

$$V_{\text{int}}(\vec{r}) = V_0 \exp\left[-2\left|\frac{\vec{r}}{\sigma}\right|^2\right]. \quad (2)$$

With the system as described above, the motion of particle **1** is described by the Langevin equation

$$\gamma \dot{\vec{R}}_1 = -k(\vec{R}_1 - \vec{R}_c) - \sum_{k=1}^N \frac{\partial V_{\text{int}}(\vec{R}_1 - \vec{r}_k)}{\partial \vec{R}_1} + \vec{\xi}(t), \quad (3)$$

where  $\gamma$  is a friction constant and  $\vec{\xi}(t) = (\xi_x(t), \xi_y(t))$  represents Gaussian white noise that satisfies

$$\langle \xi_\alpha(t) \xi_{\alpha'}(t') \rangle = 2\gamma T \delta(t - t') \delta_{\alpha, \alpha'}. \quad (4)$$

Here, the Boltzmann constant is set to unity, and  $T (=1/\beta)$  is the temperature of the environment. The motion of the  $k$ th background particle is described by

$$\gamma \dot{\vec{r}}_k = \vec{f} - \sum_{i=1}^2 \frac{\partial V_{\text{int}}(\vec{R}_i - \vec{r}_k)}{\partial \vec{r}_k} + \vec{\xi}_k(t), \quad (5)$$

where  $\vec{f} = (f, 0)$  is an external driving force and  $\vec{\xi}_k(t) = (\xi_{k,x}(t), \xi_{k,y}(t))$  is Gaussian white noise that satisfies

$$\langle \xi_{k,\alpha}(t) \xi_{k',\alpha'}(t') \rangle = 2\gamma T \delta_{k,k'} \delta(t - t') \delta_{\alpha, \alpha'}. \quad (6)$$

Below, all the quantities are converted into dimensionless forms by normalizing  $\sigma$ ,  $\gamma$  and  $T$  to unity. We set the parameters used for our numerical experiments as  $L_x = 11$ ,  $L_y = 6$ ,  $N = 200$ ,  $k = 50$ ,  $V_0 = 7$ ,  $0 \leq f \leq 0.3$ ,  $\vec{R}_c = (3, 3)$  and  $\vec{R}_2 = (4.5, 3)$ . Also, all the numerical results in this paper are obtained using a finite difference method of the Langevin equations with a time step  $2.5 \times 10^{-4}$ .

### 3. Equilibrium case

#### 3.1. Review of the effective description

Before analysing non-equilibrium cases, we review the *effective description* of particles **1** and **2** in equilibrium, in which the stationary distribution function of the model is the canonical distribution

$$p_c(\vec{R}_1, \{\vec{r}_k\}; \vec{R}_2) = \frac{\exp\{-\beta[V_1(\vec{R}_1) + \sum_{i=1}^2 \sum_{k=1}^N V_{\text{int}}(\vec{R}_i - \vec{r}_k)]\}}{Z}, \quad (7)$$

where  $Z$  is a normalization constant. In the equilibrium case, employing the well-established framework of statistical mechanics, we can derive the effective Hamiltonian of particles **1** and **2** by integrating (7) over the degrees of freedom of the background particles.

For the canonical distribution  $p_c(\vec{R}_1, \{\vec{r}_k\}; \vec{R}_2)$  given by (7) and the interaction given by (2), there exists a function  $\vec{R}_1 - \vec{R}_2$ , which we write  $V_{\text{eff}}(\vec{R}_1 - \vec{R}_2)$ , satisfying the equation

$$\exp\{-\beta[V_{\text{eff}}(\vec{R}_1 - \vec{R}_2) + V_1(\vec{R}_1)]\} = \int \prod_{k=1}^N d\vec{r}_k p_c(\vec{R}_1, \{\vec{r}_k\}; \vec{R}_2). \quad (8)$$

It is natural to refer to the function  $V_{\text{eff}}(\vec{R}_1 - \vec{R}_2)$  as the effective interaction potential. The fact that this effective interaction potential depends only on the relative displacement  $\vec{R}_1 - \vec{R}_2$  is

due to the spatial symmetry of the system. Then, as the left-hand side of (8) depends only on  $\vec{R}_1$  and  $\vec{R}_2$ , it is interpreted as the steady-state distribution for the effective description:

$$P_{\text{eff}}(\vec{R}_1; \vec{R}_2) = \exp\{-\beta[V_t(\vec{R}_1) + V_{\text{eff}}(\vec{R}_1 - \vec{R}_2)]\}. \quad (9)$$

Clearly the effective potential  $V_{\text{eff}}(\vec{R}_1 - \vec{R}_2)$  obtained in the above manner is properly defined, as this  $P_{\text{eff}}(\vec{R}_1; \vec{R}_2)$  is in canonical form.

With the above argument establishing the proper definition of  $V_{\text{eff}}(\vec{R}_1 - \vec{R}_2)$ , the *statistical mechanical force* between particles **1** and **2** is defined naturally by

$$\vec{F}_i^{\text{stat}} \equiv -\frac{\partial V_{\text{eff}}(\vec{R}_1 - \vec{R}_2)}{\partial \vec{R}_i}, \quad (10)$$

with  $i = 1, 2$ . Because  $V_{\text{eff}}(\vec{R}_1 - \vec{R}_2)$  is a function of the relative displacement  $\vec{R}_1 - \vec{R}_2$ , we immediately find the relation

$$\vec{F}_1^{\text{stat}} = -\vec{F}_2^{\text{stat}}, \quad (11)$$

which represents the law of action and reaction for statistical mechanical forces in equilibrium. The statistical mechanical force defined above is closely related to the *mechanical force* exerted by all the background particles:

$$\vec{F}_i^{\text{mec}} \equiv \sum_{k=1}^N \frac{\partial V_{\text{int}}(\vec{R}_i - \vec{r}_k)}{\partial \vec{r}_k}. \quad (12)$$

Indeed, using (8) and (10), we can prove the relation

$$\langle \vec{F}_i^{\text{stat}} \rangle_{f=0}^{\text{s}} = \langle \vec{F}_i^{\text{mec}} \rangle_{f=0}^{\text{s}}, \quad (13)$$

where  $\langle \rangle_{f=0}^{\text{s}}$  represents the statistical average in the steady state with  $f = 0$  (see section 3.1 for the proof of (13)). From (11) and (13), we obtain the law of action and reaction for  $\vec{F}_i^{\text{mec}}$ :

$$\langle \vec{F}_1^{\text{mec}} \rangle_{f=0}^{\text{s}} = -\langle \vec{F}_2^{\text{mec}} \rangle_{f=0}^{\text{s}}. \quad (14)$$

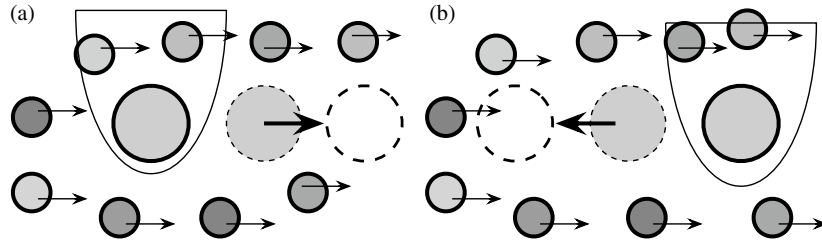
The statistical mechanical force in equilibrium can also be understood within a thermodynamic framework by considering the case in which an operation is performed on the system. We now explain this understanding. As an example, we consider the simple operation of shifting the position of particle **2** as  $\vec{R}_2 \rightarrow \vec{R}_2 + \Delta \vec{R}_2$  instantaneously at time  $t = 0$  (see figure 2(a) depicting the case  $f = 0$ ). After the application of this operation, the system is left until a new equilibrium state is realized. Then, the work done by the external agent carrying out this operation,  $W^{\text{op1}}$ , satisfies the first law of thermodynamics:

$$W^{\text{op1}} = \langle Q_1 \rangle_{f=0}^{\text{op1}} + \langle Q_b \rangle_{f=0}^{\text{op1}} + \langle \Delta V_t(\vec{R}_1) \rangle_{f=0}^{\text{op1}} + \left\langle \sum_{i=1}^2 \sum_{k=1}^N \Delta V_{\text{int}}(\vec{R}_i - \vec{r}_k) \right\rangle_{f=0}^{\text{op1}}. \quad (15)$$

Here  $\langle \rangle_f^{\text{op1}}$  represents the statistical average with respect to this operation. The quantities  $Q_1$  and  $Q_b$  are the energies transferred to the heat bath from the degrees of freedom of particle **1** and the background particles. We refer to each of these transferred quantities of energy as *heat*. According to [8], the quantities

$$J_1 \equiv (\gamma \dot{\vec{R}}_1 - \vec{\xi}) \circ \dot{\vec{R}}_1, \quad (16)$$

$$J_b \equiv \sum_{k=1}^N (\gamma \dot{\vec{r}}_k - \vec{\xi}_k) \circ \dot{\vec{r}}_k \quad (17)$$



**Figure 2.** (a) A simple operation shifting the position of particle 2 as  $\vec{R}_2 \rightarrow \vec{R}_2 + \Delta\vec{R}_2$  instantaneously at time  $t = 0$ . Note that the background particles are not driven in the equilibrium case. (b) A simple operation in which the roles of particles 1 and 2 in (a) are exchanged.

represent the heat transferred per unit time, and therefore  $Q_1$  and  $Q_b$  can be defined as

$$Q_1 \equiv \int_0^\infty dt J_1(t), \tag{18}$$

$$Q_b \equiv \int_0^\infty dt J_b(t). \tag{19}$$

The symbol  $\circ$  in (16) and (17) indicates that the product here is the stochastic Stieltjes integral in the Stratonovich sense [8].

Now, using the work  $W^{\text{op1}}$ , we define the *thermodynamic force* by

$$\vec{F}_2^{\text{thermo}} \equiv \lim_{|\Delta\vec{R}_2| \rightarrow 0} \left( -\frac{W^{\text{op1}}}{\Delta(\vec{R}_2)_x}, -\frac{W^{\text{op1}}}{\Delta(\vec{R}_2)_y} \right). \tag{20}$$

Then, integrating the Langevin equations (3) and (5), and using the expression

$$\dot{\vec{R}}_2 = \Delta\vec{R}_2\delta(t) \tag{21}$$

to represent the operation, we can prove the relation

$$\vec{F}_2^{\text{thermo}} = \left\langle \vec{F}_2^{\text{mec}} \right\rangle_{f=0}^s, \tag{22}$$

(see section 3.2 for the proof of (22)).

In the same manner that we used to define the thermodynamic force  $\vec{F}_2^{\text{thermo}}$ , we can also define  $\vec{F}_1^{\text{thermo}}$  by exchanging the roles of particles 1 and 2 (see figure 2(b) depicting the case  $f = 0$ ). That is, particle 1 is fixed, while particle 2 is trapped by the harmonic potential. Because this exchange is equivalent to the spatial reflection with respect to  $\vec{R}_2/2$ , we find

$$\vec{F}_1^{\text{thermo}} = -\vec{F}_2^{\text{thermo}}. \tag{23}$$

Then, from (14), (22) and (23), we derive

$$\vec{F}_1^{\text{thermo}} = \left\langle \vec{F}_1^{\text{mec}} \right\rangle_{f=0}^s. \tag{24}$$

From the above results, we conclude that in the equilibrium case, because  $\langle \vec{F}_i^{\text{stat}} \rangle_{f=0}^s = \langle \vec{F}_i^{\text{mec}} \rangle_{f=0}^s = \vec{F}_i^{\text{thermo}}$ , we can regard any one of these quantities as the *effective interaction force* between particles 1 and 2.

### 3.2. Proofs of (13) and (22)

*Proof of (13).* The differentiation of (8) with respect to  $\vec{R}_2$  yields

$$\begin{aligned} & \frac{\partial V_{\text{eff}}(\vec{R}_1 - \vec{R}_2)}{\partial \vec{R}_2} \exp\{-\beta[V_{\text{eff}}(\vec{R}_1 - \vec{R}_2) + V_t(\vec{R}_1)]\} \\ &= \int \prod_{k=1}^N d\vec{r}_k \sum_{k=1}^N \frac{\partial V_{\text{int}}(\vec{R}_2 - \vec{r}_k)}{\partial \vec{R}_2} p_c(\vec{R}_1, \vec{r}_k; \vec{R}_2). \end{aligned} \quad (25)$$

Integrating this with respect to  $\vec{R}_1$ , we derive

$$\left\langle \frac{\partial V_{\text{eff}}(\vec{R}_1 - \vec{R}_2)}{\partial \vec{R}_2} \right\rangle_{f=0}^s = \left\langle \sum_{k=1}^N \frac{\partial V_{\text{int}}(\vec{R}_2 - \vec{r}_k)}{\partial \vec{R}_2} \right\rangle_{f=0}^s \quad (26)$$

$$= - \left\langle \sum_{k=1}^N \frac{\partial V_{\text{int}}(\vec{R}_2 - \vec{r}_k)}{\partial \vec{r}_k} \right\rangle_{f=0}^s. \quad (27)$$

Using the definitions (10) and (12), we obtain (13).

*Proof of (22).* From (3) and (5) with  $f = 0$ , we obtain the energy balance equations:

$$(\gamma \dot{\vec{R}}_1 - \dot{\vec{\xi}}) \circ \dot{\vec{R}}_1 = - \frac{\partial V_t(\vec{R}_1)}{\partial \vec{R}_1} \circ \dot{\vec{R}}_1 - \sum_{k=1}^N \frac{\partial V_{\text{int}}(\vec{R}_1 - \vec{r}_k)}{\partial \vec{R}_1} \circ \dot{\vec{R}}_1 \quad (28)$$

$$(\gamma \dot{\vec{r}}_k - \dot{\vec{\xi}}_k(t)) \circ \dot{\vec{r}}_k = - \sum_{i=1}^2 \frac{\partial V_{\text{int}}(\vec{R}_i - \vec{r}_k)}{\partial \vec{r}_k} \circ \dot{\vec{r}}_k, \quad (29)$$

where  $k = 1, \dots, N$ . The addition of (28) and (29) with  $k = 1, \dots, N$  leads to

$$J_1 + J_b = - \sum_{i=1}^2 \sum_{k=1}^N \dot{V}_{\text{int}}(\vec{R}_i - \vec{r}_k) - \dot{V}_t(\vec{R}_1) + \sum_{k=1}^N \frac{\partial V_{\text{int}}(\vec{R}_2 - \vec{r}_k)}{\partial \vec{R}_2} \cdot \Delta \vec{R}_2 \delta(t), \quad (30)$$

where we have used (21). Here, we perform the time integration and consider its statistical average. Noting that the third term on the right-hand side of (30) becomes  $-\langle \vec{F}_2^{\text{mec}} \rangle_{f=0}^s \cdot \Delta \vec{R}_2$ , we obtain

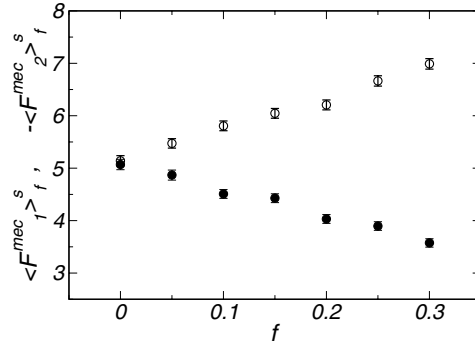
$$-\langle \vec{F}_2^{\text{mec}} \rangle_{f=0}^s \cdot \Delta \vec{R}_2 = \langle Q_1 \rangle_{f=0}^{\text{op1}} + \langle Q_b \rangle_{f=0}^{\text{op1}} + \left\langle \sum_{i=1}^2 \sum_{k=1}^N \Delta V_{\text{int}}(\vec{R}_i - \vec{r}_k) \right\rangle_{f=0}^{\text{op1}} + \langle \Delta V_t(\vec{R}_1) \rangle_{f=0}^{\text{op1}}. \quad (31)$$

Comparing this with the definition of  $F_2^{\text{thermo}}$  given in (15), we obtain

$$\vec{F}_2^{\text{thermo}} = \langle \vec{F}_2^{\text{mec}} \rangle_{f=0}^s. \quad (32)$$

## 4. Non-equilibrium case

In this section, which consists of three subsections, we study the non-equilibrium case. We first note that the canonical distribution cannot be employed in the derivation of an effective description for a NESS, in contrast to the equilibrium case. In the case of NESSs, the relationships between  $\vec{F}_i^{\text{stat}}$ ,  $\vec{F}_i^{\text{mec}}$  and  $\vec{F}_i^{\text{thermo}}$  are not yet understood. In this section, we investigate these three forces as defined above in the non-equilibrium,  $f \neq 0$  case. We hope that this will allow us to obtain a proper effective description of particles **1** and **2** in a NESS. We



**Figure 3.**  $\langle F_1^{\text{mec}} \rangle_f^s$  (open symbols) and  $-\langle F_2^{\text{mec}} \rangle_f^s$  (solid symbols) are plotted as functions of  $f$ .

first present the numerically computed results determining  $\vec{F}_i^{\text{mec}}$  and  $\vec{F}_i^{\text{thermo}}$  as defined in (12) and (20) for a NESS. Then, we derive  $\vec{F}_i^{\text{stat}}$  from the expression of the steady-state distribution and compare this  $\vec{F}_i^{\text{stat}}$  with  $\vec{F}_i^{\text{mec}}$  and  $\vec{F}_i^{\text{thermo}}$ .

Throughout this section, we consider only the case of forces in the  $x$  direction and denote the  $x$  component of  $\vec{F}_i^{\text{mec}}$ ,  $\vec{F}_i^{\text{thermo}}$  and  $\vec{F}_i^{\text{stat}}$  as  $F_i^{\text{mec}}$ ,  $F_i^{\text{thermo}}$  and  $F_i^{\text{stat}}$ .

#### 4.1. Mechanical forces exerted by the background particles

In figure 3,  $\langle F_1^{\text{mec}} \rangle_f^s$  and  $-\langle F_2^{\text{mec}} \rangle_f^s$  are plotted as functions of  $f$ . In the case  $f = 0$ , it is seen that  $\langle F_1^{\text{mec}} \rangle_{f=0}^s = -\langle F_2^{\text{mec}} \rangle_{f=0}^s$ , which is consistent with (14). However, it is seen that for  $f \neq 0$ , these quantities are not equal, and indeed the discrepancy between them increases monotonically as a function of  $f$ . Hence, the law of action and reaction does not hold with respect to  $\langle F_1^{\text{mec}} \rangle_f^s$  and  $\langle F_2^{\text{mec}} \rangle_f^s$  in the non-equilibrium case, unlike in the equilibrium case. This asymmetry is interpreted as follows. Particle 2 is partially shielded from the effect of the background particles by particle 1 in the case  $f > 0$  (see figure 1).

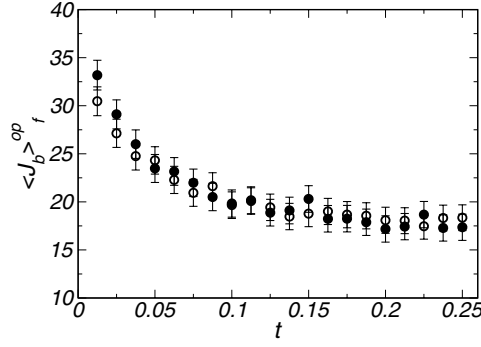
#### 4.2. Thermodynamic definition

Let us now reconsider the first law of thermodynamics represented by (15), which provides the definition of  $\vec{F}_i^{\text{thermo}}$  ( $i = 1, 2$ ). In contrast to equilibrium cases, (15) cannot be employed directly for NESSs because  $J_b$ , defined by (17), takes a non-zero value even when there is no operation applied to the system, and hence  $Q_b$  becomes infinite. (Recall that the background particles are driven by the external driving force,  $f$ .)

In order to extend thermodynamic considerations to NESSs, we introduce the idea of the *net heat* generated by an operation, following the framework of *steady-state thermodynamics* proposed by Oono and Paniconi [9]. In this framework, the heat necessary to maintain a steady state (the so-called *housekeeping heat*) is regarded as being independent of the change undergone by the system caused by the operation, and the *excess heat* is defined by subtracting the housekeeping heat from the total heat dissipated to the heat bath. They conjecture that thermodynamics can be extended to NESSs by using this excess heat.

Here, as one example, in figure 4  $\langle J_b(t) \rangle_f^{\text{op1}}$  is plotted as a function of time for the case that  $\Delta \vec{R}_2 = (\Delta R_2, 0) = (0.25, 0)$  and  $f = 0.3$ . This graph shows that  $\langle J_b(t) \rangle_f^{\text{op1}}$  reaches a steady-state value,  $J_b(\infty)$ , a sufficiently long time after the application of the operation. Then,





**Figure 4.**  $\langle J_b(t) \rangle_f^{op1}$  (open symbols) and  $\langle J_b(t) \rangle_f^{op2}$  (solid symbols) as functions of time  $t$  in the non-equilibrium case with  $f = 0.3$ . Here,  $\Delta R_2 = 0.25$  and  $\Delta R_1 = 0.25$ .  $\langle J_b(t) \rangle_f^{op1}$  and  $\langle J_b(t) \rangle_f^{op2}$  are computed in the situations described in figures 2(a) and (b), respectively.

employing the idea of the excess heat, it is reasonable to define

$$\tilde{Q}_b \equiv \int_0^\infty dt (J_b(t) - J_b(\infty)). \quad (33)$$

By replacing  $Q_b$  in (15) with  $\tilde{Q}_b$ , we hypothesize the following, an extended form of the first law of thermodynamics:

$$W^{op1} = \langle Q_1 \rangle_f^{op1} + \langle \tilde{Q}_b \rangle_f^{op1} + \langle \Delta V_t(\vec{R}_1) \rangle_f^{op1} + \left\langle \sum_{i=1}^2 \sum_{k=1}^N \Delta V_{\text{int}}(\vec{R}_i - \vec{r}_k) \right\rangle_f^{op1}. \quad (34)$$

Using this  $W^{op1}$ , we define the *thermodynamic force* in the present NESS by (20).

In figures 5 and 6, we plot  $\langle \Delta V_t \rangle_f^{op1}$  and  $\langle \sum_{i=1}^2 \sum_{k=1}^N \Delta V_{\text{int}}(\vec{R}_i - \vec{r}_k) \rangle_f^{op1}$  as functions of  $\Delta R_2$  in the case  $f = 0.3$ . It is seen that these quantities depend linearly on  $\Delta R_2$  in the range plotted. This implies that  $\Delta R_2 = 0.25$  is sufficiently small to be used in (20) to numerically compute the force. Using this value, we obtain  $\langle \tilde{Q}_b \rangle_f^{op1} = 0.61$ ,  $\langle \Delta V_t(\vec{R}_1) \rangle_f^{op1} = -0.11$ ,  $\langle \sum_{i=1}^2 \sum_{k=1}^N \Delta V_{\text{int}}(\vec{R}_i - \vec{r}_k) \rangle_f^{op1} = 0.79$ . Also, we find that  $\langle Q_1 \rangle_f^{op1}$  is sufficiently small to be ignored (within the numerical accuracy of our simulations). Using these values, we estimate

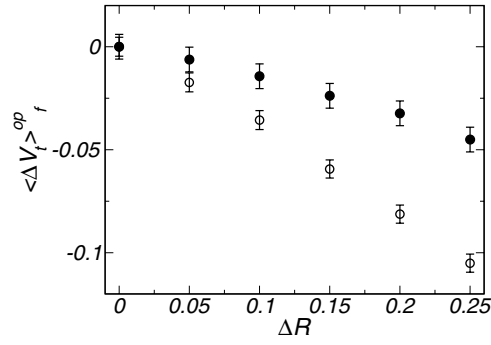
$$F_2^{\text{thermo}} = -5.2. \quad (35)$$

Next, by exchanging the roles of particles 1 and 2 (see figure 2(b)), we can define  $F_1^{\text{thermo}}$  in the same way:

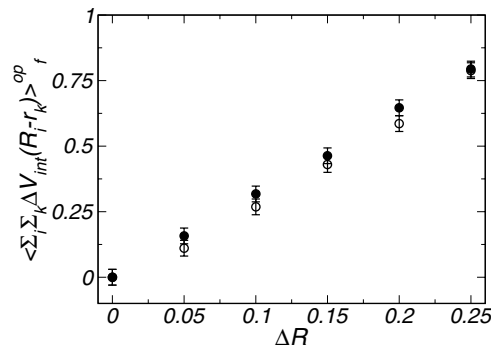
$$\begin{aligned} -F_1^{\text{thermo}} \Delta R_1 &= \langle Q_2 \rangle_f^{op2} + \langle \tilde{Q}_b \rangle_f^{op2} + \langle \Delta V_t(\vec{R}_2) \rangle_f^{op2} \\ &+ \left\langle \sum_{i=1}^2 \sum_{k=1}^N \Delta V_{\text{int}}(\vec{R}_i - \vec{r}_k) \right\rangle_f^{op2} + O(\Delta R_1^2). \end{aligned} \quad (36)$$

In figures 5 and 6, we plot  $\langle \Delta V_t \rangle_f^{op2}$  and  $\langle \sum_{i=1}^2 \sum_{k=1}^N \Delta V_{\text{int}}(\vec{R}_i - \vec{r}_k) \rangle_f^{op2}$  as functions of  $\Delta R_1$  for the case of  $f = 0.3$ . Also, in figure 4,  $\langle J_b(t) \rangle_f^{op2}$  is plotted as a function of time for the case of  $\Delta R_1 = 0.25$ . Then, obtaining  $\langle \tilde{Q}_b \rangle_f^{op2} = 0.64$ ,  $\langle \Delta V_t(\vec{R}_1) \rangle_f^{op2} = -0.05$ ,  $\langle \sum_{i=1}^2 \sum_{k=1}^N \Delta V_{\text{int}}(\vec{R}_i - \vec{r}_k) \rangle_f^{op2} = 0.79$ , and ignoring the small contribution from  $\langle Q_2 \rangle_f^{op2}$ , we estimate

$$F_2^{\text{thermo}} = 5.5. \quad (37)$$



**Figure 5.**  $\langle \Delta V_f \rangle_f^{op1}$  as a function of  $\Delta R_2$ , and  $\langle \Delta V_f \rangle_f^{op2}$  as a function of  $\Delta R_1$ . The open symbols and the solid symbols represent the quantities obtained in the situations described in figures 2(a) and (b), respectively.



**Figure 6.**  $\langle \sum_{i=1}^2 \sum_{k=1}^N \Delta V_{int}(\vec{R}_i - \vec{r}_k) \rangle_f^{op1}$  as a function of  $\Delta R_2$ , and  $\langle \sum_{i=1}^2 \sum_{k=1}^N \Delta V_{int}(\vec{R}_i - \vec{r}_k) \rangle_f^{op2}$  as a function of  $\Delta R_1$ . The open symbols and the solid symbols represent the quantities obtained in the situations described in figures 2(a) and (b), respectively.

The numerical results given in (35) and (37) are consistent with the law of action and reaction with respect to  $F_1^{\text{thermo}}$  and  $F_2^{\text{thermo}}$ . While it is desirable to obtain more precise results (the uncertainty on the values of  $F_i^{\text{thermo}}$  is due mainly to the difficulty in determining  $\langle \tilde{Q}_b \rangle_f^{op1}$  and  $\langle \tilde{Q}_b \rangle_f^{op2}$  (see figure 4)), it is clear from the present results that even if the law of action and reaction is violated for  $F_i^{\text{thermo}}$  in the NESS we consider, the extent of this violation is much less than that in the case of  $F_i^{\text{mec}}$  (recall that we found  $\langle F_1^{\text{mec}} \rangle_f^s = 7.0$  while  $\langle F_2^{\text{mec}} \rangle_f^s = -3.6$  (see figure 3)).

#### 4.3. Statistical mechanical definition

In this subsection, we investigate the interaction force between particles **1** and **2** in a NESS from a statistical mechanical point of view, employing the steady-state distribution function,  $p_s(\vec{R}_1, \{\vec{r}_k\}; \vec{R}_2)$ . It is known that  $p_s(\vec{R}_1, \{\vec{r}_k\}; \vec{R}_2)$  is given by

$$p_s(\vec{R}_1, \{\vec{r}_k\}; \vec{R}_2) = \lim_{\tau \rightarrow \infty} p_c(\vec{R}_1, \{\vec{r}_k\}; \vec{R}_2) \overline{\exp(-\beta \Sigma_\tau)}, \quad (38)$$

with

$$\Sigma_\tau = \int_0^\tau dt \sum_{k=1}^N \vec{f} \cdot \dot{\vec{r}}_k, \quad (39)$$

where  $\overline{A}$  denotes the statistical average of  $A$  over noise histories under the condition that the initial condition  $(\vec{R}_1(0), \{\vec{r}_k(0)\})$  is fixed as the argument  $(\vec{R}_1, \{\vec{r}_k\})$  of the distribution function  $p_s(\vec{R}_1, \{\vec{r}_k\}; \vec{R}_2)$ . The expression (38) indicates that the deviation of  $p_s(\vec{R}_1, \{\vec{r}_k\}; \vec{R}_2)$  from the canonical distribution,  $p_c(\vec{R}_1, \{\vec{r}_k\}; \vec{R}_2)$ , is represented by the entropy production  $\beta\Sigma_\tau$ . This form of the steady-state distribution is similar to that obtained by Zubarev and McLennan [10, 11]. (Regarding the derivation for stochastic systems, see section 4.2 of [12].)

Now, referring to the equilibrium case, we define an effective potential  $V_{\text{eff}}(\vec{R}_1; \vec{R}_2)$  by

$$\exp[-\beta(V_{\text{eff}}(\vec{R}_1; \vec{R}_2) + V_1(\vec{R}_1))] = \lim_{\tau \rightarrow \infty} \int \prod_{k=1}^N d\vec{r}_k p_c(\vec{R}_1, \{\vec{r}_k\}; \vec{R}_2) \overline{\exp(-\beta\Sigma_\tau)}. \quad (40)$$

With this effective potential, we define the statistical mechanical force as

$$\vec{F}_2^{\text{stat}} \equiv -\frac{\partial V_{\text{eff}}(\vec{R}_1; \vec{R}_2)}{\partial \vec{R}_2}. \quad (41)$$

Then, differentiating (40) with respect to  $\vec{R}_2$ , assuming that the relation

$$\frac{\partial}{\partial \vec{R}_2} \overline{\exp(-\beta\Sigma_\tau)} = -\beta \left( \frac{\partial}{\partial \vec{R}_2} \overline{\Sigma_\tau} \right) \overline{\exp(-\beta\Sigma_\tau)} \quad (42)$$

holds, we derive

$$\left\langle \vec{F}_2^{\text{stat}} \right\rangle_f^s = \left\langle \vec{F}_2^{\text{mec}} \right\rangle_f^s - \lim_{\tau \rightarrow \infty} \int d\vec{R}_1 \prod_{k=1}^N d\vec{r}_k p_s(\vec{R}_1, \{\vec{r}_k\}; \vec{R}_2) \frac{\partial}{\partial \vec{R}_2} \overline{\Sigma_\tau}. \quad (43)$$

Note that (42) is valid to linear order in  $\vec{f}$  because the both sides of (42) become

$$-\beta \frac{\partial}{\partial \vec{R}_2} \overline{\Sigma_\tau} + O(|\vec{f}|^2). \quad (44)$$

We expect that (42) might be approximately valid even for large  $\vec{f}$ , due to many-body effects. In the argument below we assume (42).

On the other hand, using the energy balance equation obtained from the Langevin equations (3) and (5), we can rewrite (34) as

$$F_2^{\text{thermo}} \Delta R_2 = \left\langle F_2^{\text{mec}} \right\rangle_f^s \Delta R_2 - \lim_{\tau \rightarrow \infty} \vec{f} \cdot \left( \left\langle \int_0^\tau dt \sum_{k=1}^N \dot{\vec{r}}_k \right\rangle_f^{\text{opl}} - \left\langle \int_0^\tau dt \sum_{k=1}^N \dot{\vec{r}}_k \right\rangle_f^s \right). \quad (45)$$

Then, recalling that  $\langle \rangle_f^{\text{opl}}$  is the statistical average with respect to the instantaneous shift  $\vec{R}_2 \rightarrow \vec{R}_2 + \Delta \vec{R}_2$  at  $t = 0$ , we can write

$$\begin{aligned} & \left\langle \int_0^\tau dt \sum_{k=1}^N \dot{\vec{r}}_k \right\rangle_f^{\text{opl}} - \left\langle \int_0^\tau dt \sum_{k=1}^N \dot{\vec{r}}_k \right\rangle_f^s \\ &= \int d\vec{R}_1 \prod_{k=1}^N d\vec{r}_k p_s(\vec{R}_1, \{\vec{r}_k\}; \vec{R}_2) \frac{\partial}{\partial \vec{R}_2} \int_0^\tau dt \sum_{k=1}^N \dot{\vec{r}}_k \Delta \vec{R}_2 + O(|\Delta \vec{R}_2|^2). \end{aligned} \quad (46)$$

Substituting this result into (45) and comparing the obtained expression with (43), we find

$$F_2^{\text{thermo}} = \left\langle F_2^{\text{stat}} \right\rangle_f^s. \quad (47)$$

Thus, the equality  $F_1^{\text{thermo}} = -F_2^{\text{thermo}}$  observed numerically in the last subsection suggests that  $\vec{F}_1^{\text{stat}}$  defined by

$$\vec{F}_1^{\text{stat}} \equiv -\frac{\partial V_{\text{eff}}(\vec{R}_2; \vec{R}_1)}{\partial \vec{R}_1} \quad (48)$$

satisfies the relation

$$\vec{F}_1^{\text{stat}} = -\vec{F}_2^{\text{stat}}. \quad (49)$$

We further assume that

$$V_{\text{eff}}(\vec{R}_1; \vec{R}_2) = V_{\text{eff}}(\vec{R}_2; \vec{R}_1). \quad (50)$$

Then, (49) and (50) imply that there exists a function  $\tilde{V}_{\text{eff}}(\vec{R}_1 - \vec{R}_2)$  such that

$$\begin{aligned} \tilde{V}_{\text{eff}}(\vec{R}_1 - \vec{R}_2) &= V_{\text{eff}}(\vec{R}_1; \vec{R}_2) \\ &= V_{\text{eff}}(\vec{R}_2; \vec{R}_1). \end{aligned} \quad (51)$$

It is for future work to develop a theoretical argument for the suggestion (49).

## 5. Discussion

In this paper we have studied three types of force,  $F_i^{\text{stat}}$ ,  $F_i^{\text{mec}}$  and  $F_i^{\text{thermo}}$ , in a NESS. In equilibrium, these forces satisfy the relations  $\langle F_i^{\text{stat}} \rangle_{f=0}^s = \langle F_i^{\text{mec}} \rangle_{f=0}^s = F_i^{\text{thermo}}$ . From the results of our numerical simulations, we found that in the NESS that we study  $F_1^{\text{thermo}} = -F_2^{\text{thermo}}$  but  $\langle F_1^{\text{mec}} \rangle_f^s \neq -\langle F_2^{\text{mec}} \rangle_f^s$ , and hence the law of action and reaction holds for forces of the former kind but not the latter. We also demonstrated that  $F_i^{\text{thermo}}$  defined with respect to a form of the first law of thermodynamics hypothesized to hold for our NESS is equal to  $\langle F_i^{\text{stat}} \rangle_f^s$  derived from the expression for the steady-state distribution under the assumption represented by (42).

The law of action and reaction holds for any force given by the derivative of a potential function. Thus, the fact that this law holds with respect to the thermodynamic force defined by (34) implies that in the NESS we considered, there may exist a potential function associated with this force. It is important to clarify the physical conditions under which the thermodynamic force obtained using the method employed in this paper is indeed a potential force.

In equilibrium, a potential function is related to the thermodynamic free energy. For this reason, it is natural to conjecture that even in a NESS, the potential force measured experimentally is related to thermodynamics. Such a conjecture led us to introduce the thermodynamic force based on the idea of Oono and Paniconi [9]. Here we remark that the framework proposed by Oono and Paniconi is embodied in the non-equilibrium Langevin model [13]. In that work, Hatano and Sasa derived an identity which yields an extended second law relating the Shannon entropy to the excess heat they defined. Recently, the validity of this identity was confirmed experimentally for a bead system [14]. In the analysis employed in the present paper, we conjecture that  $\tilde{Q}_b$  defined in (33) has a certain connection with the excess heat defined in [13]. However, we do not yet understand this relation, though apparently the quantity  $\tilde{Q}_b$  employed here takes a simpler form than that proposed by Hatano and Sasa.

As another important subject related to the present work, we now consider the problem of *force decomposition*. As seen in section 4.1 (see figure 3), the law of action and reaction does not hold for the total mechanical force acting on the test particle,  $\langle \vec{F}_i^{\text{mec}} \rangle_f^s$ . If the potential force in a NESS can be defined properly on the basis of thermodynamic considerations, it might be possible to decompose  $\langle \vec{F}_i^{\text{mec}} \rangle_f^s$  into its potential and non-potential parts. Furthermore, because

$\vec{F}_i^{\text{mec}}$  fluctuates in time, we would like to decompose  $\vec{F}_i^{\text{mec}}$  into a fluctuating dissipative force, a fluctuating interaction potential force and the remaining part.

With regard to the decomposition of fluctuating forces, recently a significant result has been obtained for a model of a Brownian particle that is driven by an external driving force and subject to a spatially periodic potential. As this particle is driven in one direction, it experiences repeated ‘collisions’ with the periodic potential barriers. Studying a finite time average of the force exerted by the periodic potential under non-equilibrium conditions, we have found that a simple orthogonality condition provides a proper force decomposition of the time averaged force into a dissipative force and a non-dissipative part [15]. This result has led us to construct a mathematical technique for re-expressing a Langevin equation in a form in which the response function appears explicitly [16]. Using this technique, an interesting equality that connects energy dissipation with the violation of a fluctuation-response relation has been proved [17]. Considering these developments, the problem of decomposing  $\langle \vec{F}_i^{\text{mec}} \rangle_f^s$  can be regarded as a natural extension of the study presented in [15], involving the elimination of the dynamical degrees of freedom.

To summarize the most important point of this work, we have found that the law of action and reaction with respect to thermodynamic forces has a deep connection with fundamental aspects of non-equilibrium statistical mechanics. We believe that the numerical findings reported in this paper will stimulate further theoretical and experimental studies.

## Acknowledgments

This work was supported by grants from JSPS Research Fellowships for Young Scientists (grant no. 1711222) and the Ministry of Education, Science, Sports and Culture of Japan (grant no. 16540337).

## References

- [1] Leunissen M E, Christove C G, Hynnien A P, Royall C P, Cambell A I, Imhof A, Dijkstra M, Roij R V and Blaaderen A V 2005 *Nature* **437** 235
- [2] Brunner M, Bechinger C, Streep W, Lobaskin V and von Grünberg H H 2002 *Europhys. Lett.* **58** 926
- [3] Brunner M, Bechinger C, Herz U and von Grünberg H H 2003 *Europhys. Lett.* **63** 791
- [4] Anderson V A and Lekkerkerker H N W 2002 *Nature* **416** 811
- [5] Pham K N, Puertas A M, Bergenholtz J, Egelhaaf S U, Moussaïd A, Pusey P N, Schofield A B, Cates M E, Fuchs M and Poon W C K 2002 *Science* **296** 104
- [6] Harada T and Yoshikawa K 2004 *Phys. Rev. E* **69** 031113
- [7] Dzubiella J, Löwen H and Likos C N 2003 *Phys. Rev. Lett.* **91** 248301
- [8] Sekimoto K 1997 *J. Phys. Soc. Japan* **66** 1234
- [9] Oono Y and Paniconi M 1998 *Prog. Theor. Phys. Suppl.* **130** 29
- [10] Zubarev D N 1974 *Nonequilibrium Statistical Thermodynamics* (New York: Consultants Bureau)
- [11] McLennan J A 1989 *Introduction to Nonequilibrium Statistical Mechanics* (Englewood Cliffs, NJ: Prentice-Hall)
- [12] Hayashi K and Sasa S 2005 *Preprint cond-mat/0507719*
- [13] Hatano T and Sasa S 2001 *Phys. Rev. Lett.* **86** 3463
- [14] Trepangnier E H, Jarzynski C, Ritort F, Crooks G E, Bustamante C J and Liphardt J 2004 *Proc. Natl Acad. Sci. USA* **101** 15038
- [15] Hayashi K and Sasa S 2005 *Phys. Rev. E* **71** 020102(R)
- [16] Harada T, Hayashi K and Sasa S 2005 *J. Phys. A: Math. Gen.* **38** 3799
- [17] Harada T and Sasa S 2005 *Phys. Rev. Lett.* **95** 130602