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Mesoscopic virial equation for nonequilibrium statistical mechanics

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Abstract

We derive a class of mesoscopic virial equations governing energy partition between conjugate position and momentum variables of individual degrees of freedom. They are shown to apply to a wide range of nonequilibrium steady states with stochastic (Langevin) and deterministic (Nosé–Hoover) dynamics, and to extend to collective modes for models of heat-conducting lattices. A macroscopic virial theorem ensues upon summation over all degrees of freedom. It allows for the derivation of generalised (nonequilibrium) equations of state that involve average dissipative heat flows besides genuine state variables, as exemplified for inertial Brownian motion with solid friction and overdamped active Brownian particles subject to inhomogeneous pressure.

1. Introduction

From equilibrium statistical mechanics we are accustomed to the idea that there is energy equipartition among all quadratic degrees of freedom of classical systems, and that the 'energy bit' corresponds to $k_{\mathrm{B}}T/2$, half of the temperature times the Boltzmann constant. While momenta usually appear with the quadratic contribution of the kinetic energy in the Hamiltonian $\mathcal{H}$, for a position variable q_i one has more generally that it is the average of $q_i\partial_{q_i}\mathcal{H}$ which equals the energy bit. The sum over all degrees of freedom yields the virial theorem [1, 2], which connects the average total kinetic energy with the term $\sum_i\langle q_i\partial_{q_i}\mathcal{H}\rangle$ named virial by Clausius.

Out of equilibrium, the equipartition of energy is not granted. Indeed, recent experiments with heat-conducting metals show intriguing deviations from equipartition, related to enhancements of low-frequency vibrational modes that may become even 'hotter' than the highest boundary temperature [3]. Similar deviations from equipartition are observed for strongly heated cantilevers [4] and Brownian particles [5, 6]. These are some out of many manifestations of nontrivial effects characterizing systems driven far from thermodynamic equilibrium. They imply the need for a critical revisiting of results from equilibrium statistical mechanics, with the aim of finding generalisations to nonequilibrium conditions.

In this work we discuss a generalization of the equipartition theorem, formulated in the context of modern nonequilibrium physics. It takes the form of *mesoscopic virial equations* (MVEs), involving kinetic and dynamical aspects specific to pairs of momentum–position conjugate variables. A MVE determines how thermal energy is distributed between any such pair of variables. For Langevin dynamics, we discuss both the inertial and the overdamped versions of the equation; the former is easily extended to cover Nosé–Hoover dynamics for thermostated simulations. Summation of a MVE over all degrees of freedom generates the virial theorem, which we discuss also for the case of explicitly nonconservative forces. That the virial theorem holds at the microscopic level beyond thermal equilibrium should not come as a surprise, since it is a result derivable in classical mechanics without appealing to statistical arguments[7]. Here we show that one still finds significant virial

[7] In classical mechanics the theorem involves time averages, which are customarily exchanged with ensemble averages under the ergodic assumption [7].

theorems, involving quantities with a clear physical meaning, even if microscopic degrees of freedom are coarse grained as in the mesoscopic models addressed below.

The simple mathematical derivations we employ are slightly different from the conventional line of arguments dating back to Chandrasekhar's work [2, 8]. The main novelty of our approach is that we work consistently in the context of nonequilibrium systems, and that our derivations easily carry over to deterministic thermostats. Moreover, we characterise energy partition even for collective macroscopic variables, such as single normal modes, out of equilibrium. We further show that our results allow for the derivation of generalised equations of state for nonequilibrium steady states. As an illustrative example, we provide a full derivation of the pressure equation for a well-known model of active matter [9].

2. Langevin dynamics

Consider N interacting particles evolving in d dimensions, with generalised coordinates $\{q_i,\ p_i\}$, with $i = 1,\ldots, Nd$. Each degree of freedom has mass m_i and the total energy is given by the Hamiltonian

$$\mathcal{H} = \sum_{i=1}^{Nd} \frac{p_i^2}{2m_i} + U(\{q_i\}), \tag{1}$$

where $U(\{q_i\})$ contains a confining potential energy that allows the system to reach a stationary state in the absence of external, time-dependent driving. In addition, nonconservative forces f_i could also be present. Each degree of freedom is coupled to a Langevin thermostat with damping constant γ_i, so that the general equations of motion read

$$\begin{aligned} \dot{q}_i &= \partial_{p_i}\mathcal{H} = \frac{p_i}{m_i} \equiv v_i, \\ \dot{p}_i &= -\partial_{q_i}\mathcal{H} + f_i - \gamma_i p_i + \xi_i. \end{aligned} \tag{2}$$

Here, the ξ_i represent Gaussian white noise with correlation $\langle \xi_i(t)\xi_j(t')\rangle = 2D_{ij}\delta(t-t')$. We first consider the case of independent heat baths in local equilibrium at temperature T_i, for which the fluctuation–dissipation theorem implies a diagonal diffusivity matrix $D_{ij} = m_i\gamma_i k_B T_i \delta_{ij}$. In section 6 we will show an example of a nondiagonal temperature matrix emerging for the normal modes of coupled oscillators. Note that a space-dependent noise is included in this formalism, since T_i may be a continuous function of the coordinates.

We use the formula for the time derivative of the average of any state observable $\mathcal{O}(t)$,

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle \mathcal{O}\rangle = \langle \mathbb{L}\mathcal{O}\rangle, \tag{3}$$

where $\mathbb{L}$ is the backward generator of the dynamics. For the Langevin equation (2) it can be derived with Itô's formula [10] and is given by

$$\mathbb{L} = \sum_{i=1}^{Nd}\left[\frac{p_i}{m_i}\partial_{q_i} + (f_i - \partial_{q_i}\mathcal{H} - \gamma_i p_i)\partial_{p_i} + \sum_{j=1}^{Nd} D_{ij}\partial_{p_i}\partial_{p_j}\right]. \tag{4}$$

A set of relations emerges immediately from the position–momentum observable[8] $\mathcal{O} = p_i q_i$. Plugging it into (3), we obtain

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle p_i q_i\rangle = \left\langle \frac{p_i^2}{m}\right\rangle + \langle (f_i - \partial_{q_i}\mathcal{H} - \gamma_i p_i) q_i\rangle. \tag{5}$$

Using then $\langle p_i q_i\rangle = m_i\langle \dot{q}_i q_i\rangle = \frac{1}{2}\frac{\mathrm{d}}{\mathrm{d}t}\langle m_i q_i^2\rangle$ and removing all time derivatives by the assumption of stationarity, this is turned into a MVE for the conjugated pairs $q_i,\ p_i$:

$$\left\langle \frac{p_i^2}{m_i}\right\rangle = \langle (\partial_{q_i}\mathcal{H} - f_i) q_i\rangle. \tag{6}$$

The virial theorem follows by applying $\sum_{i=1}^{Nd}$ to both sides of (6). Notice that terms depending on the Langevin thermostat vanish and only mechanical forces survive in (6). Remarkably, (6) retains then the structure that one finds with the classic purely Hamiltonian derivation [1, 2]. As a counterexample, we address the Nosé–Hoover thermostats in section 7. The equipartition theorem is recovered in equilibrium ($f_i = 0$, $T_i = T\ \forall i$), where averages may be performed with the Boltzmann weight $\exp\left(-\frac{\mathcal{H}}{k_B T}\right)$ and all terms in (6) are equal to $k_B T$.

[8] This derivation is formally identical to the one employed in most quantum mechanics textbooks, e.g. [11]. Indeed, $\langle \mathbb{L}\mathcal{O}\rangle = \langle \mathcal{O}\mathbb{W}\rangle = \langle \mathcal{O}\mathbb{W} - \mathbb{W}\mathcal{O}\rangle = \langle [\mathcal{O},\ \mathbb{W}]\rangle$. This relation employs, in order, the definition of the generator of forward time evolution $\mathbb{W}$, the normalization of probabilities, and the definition of the commutator. The correspondence between $\mathbb{W}$ and the quantum generator of time evolution $-\frac{\mathrm{i}}{\hbar}\mathcal{H}$ then gives $\langle [\mathcal{O},\ \mathbb{W}]\rangle = -\frac{\mathrm{i}}{\hbar}\langle [\mathcal{O},\ \mathcal{H}]\rangle$.

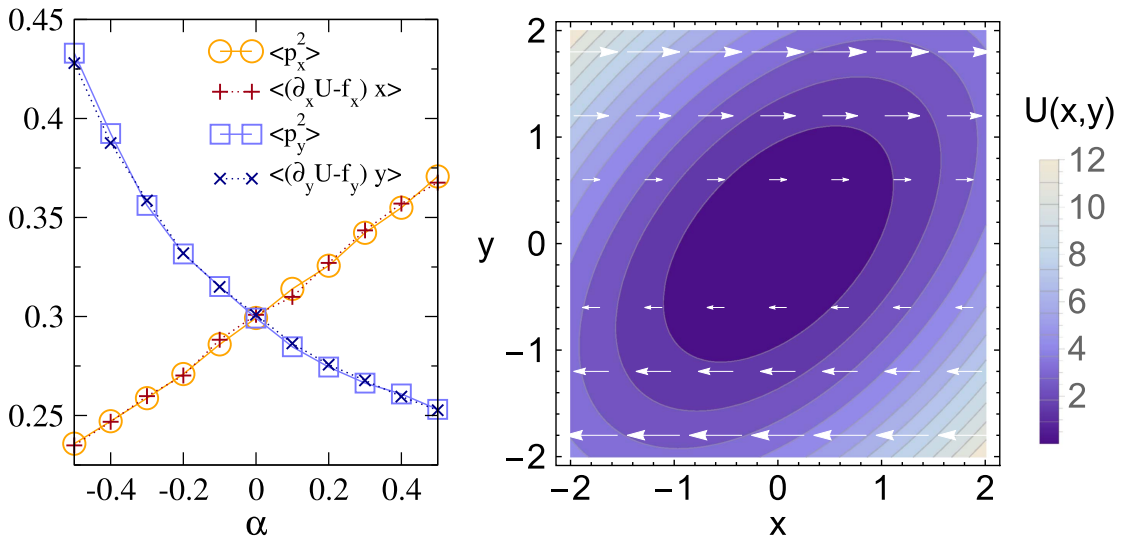

Figure 1. The mesoscopic virial equation (MVE) as a function of the shear force strength α, for each degree of freedom of a particle moving in two dimensions subject to the potential and forces sketched on the right for $\alpha > 0$. The temperature is $T = 0.3$ and the damping constant is $\gamma = 0.2$, in natural units.

As a basic exemplification, consider a unit-mass particle moving in the $\boldsymbol{q} = (x, y)$ plane, subjected to the potential $U(x, y) = x^2 - xy + y^2$ and to the nonconservative shear force $\boldsymbol{f} = \alpha\, y\, \boldsymbol{e}_x$ parallel to the x-axis unit vector $\boldsymbol{e}_x$. Throughout the text we employ α as a dimensional constant measuring the departure from equilibrium. In figure 1(a) we display a numerical validation of the MVE (6). Note that energy equipartition—with virial and (twice) kinetic contributions amounting to $k_B T$—is achieved only in equilibrium (for $\alpha = 0$). This example also illustrates that the system acts as a toy refrigerator: specific degrees of freedom are cooled down under nonequilibrium conditions (for $\alpha \neq 0$) [12], despite energy being constantly supplied to the particle.

3. Generalised equations of state for steady nonequilibrium

Switching to the observable $\mathcal{O} = p_i^2$, equation (3) provides

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle p_i^2\rangle = 2\langle (f_i - \partial_{q_i}\mathcal{H} - \gamma_i p_i)p_i\rangle + 2\langle D_{ii}\rangle. \tag{7}$$

Here $\dot{Q}_i = \left\langle (f_i - \partial_{q_i}\mathcal{H})\frac{p_i}{m_i}\right\rangle$ is recognised as the average heat flow into the ith reservoir, and in a steady state one gets the Harada–Sasa formula [13, 14]

$$\dot{Q}_i = \gamma_i\left(\left\langle \frac{p_i^2}{m_i}\right\rangle - k_B\langle T_i\rangle\right). \tag{8}$$

Combining now the MVE (6) with (8), we find

$$\frac{1}{\gamma_i}\dot{Q}_i + k_B\langle T_i\rangle = \langle(\partial_{q_i}\mathcal{H} - f_i)q_i\rangle. \tag{9}$$

If the system is in thermal equilibrium, then $\dot{Q}_i = 0\ \ \forall\, i$, and (9) constitutes the starting point for deriving equations of state. Specifically, we recall the standard derivation of the mechanical one [15]. For interacting particles, labelled by $n = 1,\ldots, N$ and having spatial coordinates $\boldsymbol{r}_n$ within a container of volume $\mathcal{V}$, it is useful to separate the contribution of the external conservative forces $\boldsymbol{F}_{\mathrm{ext}}$ (comprising confining wall forces $\boldsymbol{F}_{\mathrm{w}}$, gravity, etc) from that of the inter-particle interactions $\boldsymbol{F}_{\mathrm{int}}$. The sum over all degrees of freedom of $\langle\partial_{q_i}\mathcal{H}q_i\rangle$ gives both the *internal* virial $C_{\mathrm{int}} = -\sum_{i=1}^{Nd}\langle F_{\mathrm{int},i}\, q_i\rangle$ [1] and the *external* virial $-\sum_{i=1}^{Nd}\langle F_{\mathrm{ext},i}q_i\rangle$. The latter can be related to the pressure. Using the local particle density $\rho(\boldsymbol{r}) = \langle\sum_{n=1}^{N}\delta(\boldsymbol{r} - \boldsymbol{r}_n)\rangle$ we write

$$-\sum_{n=1}^{N}\langle \boldsymbol{F}_{\mathrm{ext}}(\boldsymbol{r}_n)\cdot\boldsymbol{r}_n\rangle = -\int_{\mathcal{V}}\mathrm{d}\boldsymbol{r}\boldsymbol{F}_{\mathrm{ext}}(\boldsymbol{r})\cdot\boldsymbol{r}\rho(\boldsymbol{r}). \tag{10}$$

Since the local stress tensor $\boldsymbol{\sigma}$ is defined by the steady-state equation expressing momentum conservation [15],

$$\nabla_{\boldsymbol{r}} \cdot \boldsymbol{\sigma}(\boldsymbol{r}) = \boldsymbol{F}_{\rm ext}(\boldsymbol{r})\rho(\boldsymbol{r}) \tag{11}$$

an integration by parts of (10) yields

$$-\sum_{i=1}^{Nd} \langle F_{{\rm ext},i}\, q_i \rangle = \bar{P}_{\mathcal{V}} \mathcal{V} d. \tag{12}$$

Here the volume-averaged pressure $\bar{P}_{\mathcal{V}}$ is defined through the trace of the stress tensor $\bar{P}_{\mathcal{V}} \equiv \frac{1}{{\rm d}\mathcal{V}} \int_{\mathcal{V}} {\rm d}\boldsymbol{r} {\rm Tr}\boldsymbol{\sigma}(\boldsymbol{r})$. If the external force is just the confining force $\boldsymbol{F}_{\rm w}$ of the wall, the system clearly has a homogeneous pressure $\bar{P}_{\mathcal{V}} = P$. Under equilibrium conditions, from (9) thus descends

$$N k_{\rm B} T = P\mathcal{V} + C_{\rm int}/d, \tag{13}$$

which can for example be used to derive the van der Waals equation [16].

The validity of (12) in not restricted to equilibrium systems, though. For simplicity, we may think about systems with equal particles and homogeneous dissipation ($T_i = T$ and $\gamma_i = \gamma \ \forall\, i$). The nonequilibrium stationary states are maintained, as in the case of figure 1(a), by the action of the nonconservative forces, which contribute the additional nonequilibrium virial term $C_{\rm ne} \equiv -\sum_{i=1}^{Nd} \langle f_i q_i \rangle$ to (9). Two different cases should be distinguished, depending on the nature of f_i.

If f_i is an external driving, such as the shear force of section 2, $C_{\rm ne}$ combines with the conservative external forces in (11) to produce the pressure,

$$-\sum_{i=1}^{Nd} \langle (F_{{\rm ext},i} + f_i) q_i \rangle = \bar{P}_{\mathcal{V}} \mathcal{V} d. \tag{14}$$

This can be easily shown noting that the momentum balance equation (11) under this nonequilibrium stationary condition becomes [17]

$$\nabla_{\boldsymbol{r}} \cdot \boldsymbol{\sigma}(\boldsymbol{r}) = (\boldsymbol{F}_{\rm ext}(\boldsymbol{r}) + \boldsymbol{f}(\boldsymbol{r}))\rho(\boldsymbol{r}) - m\gamma \boldsymbol{u}(\boldsymbol{r})\rho(\boldsymbol{r}), \tag{15}$$

where $\boldsymbol{u}(\boldsymbol{r})\rho(\vec{\boldsymbol{r}}) = \langle \sum_{n=1}^{N} \boldsymbol{v}_n \delta(\boldsymbol{r} - \boldsymbol{r}_n) \rangle$ is the local particle current, which vanishes only at equilibrium ($\boldsymbol{v}_n$ is the velocity of particle n). When integrated over the whole system, the additional friction term in (15) does not contribute to (12) thanks to the stationary continuity equation $\nabla_{\boldsymbol{r}} \cdot (\boldsymbol{u}\rho) = 0$, namely

$$\begin{aligned} -\sum_{n=1}^{N} \langle (\boldsymbol{F}_{\rm ext}(\boldsymbol{r}_n) + \boldsymbol{f}(\boldsymbol{r}_n)) \cdot \boldsymbol{r}_n \rangle &= -\int_{\mathcal{V}} {\rm d}\boldsymbol{r} (\nabla_{\boldsymbol{r}} \cdot \boldsymbol{\sigma}(\boldsymbol{r}) + m\gamma \boldsymbol{u}(\boldsymbol{r})\rho(\boldsymbol{r})) \cdot \boldsymbol{r} \\ &= \bar{P}_{\mathcal{V}} \mathcal{V} d + m\gamma \int_{\mathcal{V}} {\rm d}\boldsymbol{r}\, \frac{\boldsymbol{r}^2}{2} \nabla_{\boldsymbol{r}} \cdot (\boldsymbol{u}(\boldsymbol{r})\rho(\boldsymbol{r})) \\ &= \bar{P}_{\mathcal{V}} \mathcal{V} d. \end{aligned} \tag{16}$$

Hence the equation of state (13) is generalised to

$$\frac{1}{\gamma}\dot{Q} + N k_{\rm B} T d = \bar{P}_{\mathcal{V}} \mathcal{V} d + C_{\rm int}, \tag{17}$$

where $\dot{Q} = \sum_i \dot{Q}_i$ is the mean rate of total heat dissipation into the reservoirs. Indeed, $\dot{Q}$ is the constant housekeeping heat flux necessary to maintain the nonequilibrium stationary state.

If instead f_i is a dissipative interaction force between particles (e.g. describing binary inelastic collisions in granular gases [18]), then it is not present in (15), so that (12) holds true. As a result, the nonequilibrium virial $C_{\rm ne}$ figures explicitly in the generalised equation of state

$$\frac{1}{\gamma}\dot{Q} + N k_{\rm B} T d = \bar{P}_{\mathcal{V}} \mathcal{V} d + C_{\rm int} + C_{\rm ne}. \tag{18}$$

Interestingly, (17) and (18) include not only equilibrium thermodynamic variables but also the unusual average heat-flow $\dot{Q} = \left\langle \sum_i f_i \dot{q}_i \right\rangle$, which stems solely from the nonconservative driving because stationarity implies $\left\langle \sum_i \dot{q}_i \partial_{q_i} \mathcal{H} \right\rangle = \frac{\rm d}{{\rm d}t} \langle U \rangle = 0$. Mind the distinction between the steady state conditions addressed throughout the paper are distinct to path-dependent thermodynamics protocols. They are the reason why dissipative fluxes can be put on equal footing with state variables. We note that dissipative fluxes are upgraded to the status of state variables also in a phenomenological theory of extended irreversible thermodynamics [19].

As a simple illustration of the role of the mean heat flux, consider N independent particles with unitary mass, again in the xy-plane. Each particle is subjected to a Langevin bath of uniform temperature T, to a confining potential $U_{\rm w}(x, y) = \frac{1}{12}(x^{12} + y^{12})$ so that $\boldsymbol{F}_{\rm w} = -\boldsymbol{\nabla} U_{\rm w}$, and to an additional solid friction $\boldsymbol{f} = -\alpha\, \boldsymbol{v}/|\boldsymbol{v}|$ of constant magnitude $\alpha \geqslant 0$ [20, 21]. In the presence of this nonconservative friction, a steady state is generated in which heat is continuously taken from the Langevin bath and delivered to the substrate ($\dot{Q} < 0$). However, the symmetry of the problem implies that $C_{\rm ne}$ is zero. In view of the particles' mutual independency, also $C_{\rm int}$ is

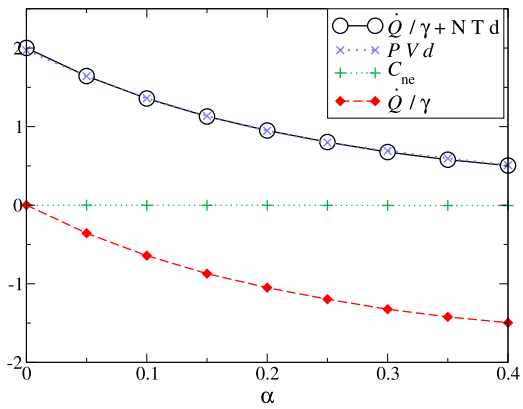

Figure 2. Contributions in the generalised equation of state (18) for a spatially confined Langevin particle at temperature $T = 1$ (natural dimensionless units), subjected to an extra dry friction $\boldsymbol{f} = -\alpha\, \boldsymbol{v}/|\boldsymbol{v}|$. The negative sign of the mean heat flow into the reservoir, $\dot{Q} < 0$, is consistent with a positive heat absorbed on average by the system when solid friction dissipates energy ($\alpha > 0$).

exactly zero, and each of the remaining terms in (18) amounts to N times the single-particle contribution. In figure 2, we display each term in (18) as obtained from single-particle simulations for various α, finding $\dot{Q} = 0$ in equilibrium ($\alpha = 0$), while out of equilibrium $\dot{Q}$ is negative and gives an important contribution that guarantees the validity of the generalised equation of state (18).

4. Overdamped dynamics

If one considers time scales much larger than the characteristic relaxation times of momenta, i.e. $\gamma_i \mathrm{d}t \to \infty$ [10], then $\dot{Q}_i/\gamma_i \to 0$ and (9) reduces to the overdamped MVE[9]

$$k_{\mathrm{B}} T_i = \left\langle \left(\frac{\partial U}{\partial q_i} - f_i \right) q_i \right\rangle. \tag{19}$$

This corresponds to (6) after the substitution $\langle p_i^2/m_i \rangle \mapsto k_{\mathrm{B}} T_i$, as it should be expected, since momentum is instantaneously thermalised by its own thermal bath in the overdamped limit. Of course, this relation can be derived directly by taking the overdamped limit of the diffusion equation (2):

$$\dot{q}_i = \mu_i(-\partial_{q_i} U + f_i) + \hat{\xi}_i, \tag{20}$$

where $\mu_i = (m_i \gamma_i)^{-1}$ is the mobility, $\langle \hat{\xi}_i(t) \hat{\xi}_j(t') \rangle = 2\hat{D}_{ij}\, \delta(t - t')$ with $\hat{D}_{ij} = \mu_i k_{\mathrm{B}} T_i \delta_{ij}$, and the Hamiltonian $\mathcal{H}$ boils down to the potential energy U. The backward generator of the dynamics becomes $\mathbb{L} = \sum_i \mu_i (f_i - \partial_{q_i} U) \partial_{q_i} + \sum_{ij} \hat{D}_{ij} \partial_{q_i} \partial_{q_j}$, and $\mathcal{O} = q_i^2$ is the appropriate observable to plug in (3) to retrieve (19).

These results hold under the assumption that the dissipative force f_i acts effectively on time scales much longer than $1/\gamma_i$. If instead f_i is of order $O(\gamma_i)$, energy dissipation interferes with the thermalization process of momenta, so that $\langle p_i^2/m_i \rangle \neq k_{\mathrm{B}} T_i$. For example, a solid friction (see section 3) of order $O(\alpha_i) \sim O(\gamma_i \sqrt{\langle p_i^2 \rangle})$ renders (8) in the form

$$\left\langle \frac{p_i^2}{2m_i} \right\rangle = k_{\mathrm{B}} T_i - \frac{\alpha_i \sqrt{\langle p_i^2 \rangle}}{\gamma_i m_i}, \tag{21}$$

and thus yields an overdamped MVE which features nonequilibrium corrections to the bath temperature, of the form

$$k_{\mathrm{B}} T_i - \frac{\alpha_i \sqrt{\langle p_i^2 \rangle}}{\gamma_i m_i} = \left\langle \left(\frac{\partial U}{\partial q_i} - f_i \right) q_i \right\rangle. \tag{22}$$

Active Brownian particles (see more details in the next section) can be taken as another example. In the overdamped limit, they are often modelled as colloidal particles driven by a propulsion force $f_{\mathrm{p},i}$ that is counterbalanced by an associated viscous drag force $-\alpha_i p_i$. Together they combine into the nonequilibrium force $f_i = -\alpha_i p_i + f_{\mathrm{p},i}$. If the friction forces are comparable in magnitude, that is $\alpha_i/\gamma_i = \mathrm{const}$ in the limit

[9] To avoid the issues related to the interpretation of the overdamped stochastic equations hereafter we consider additive noise only.

$\gamma_i \to \infty$, equation (8) in the overdamped limit reads

$$\left\langle \frac{p_i^2}{2m_i} \right\rangle = \frac{k_B T_i}{1 + \frac{\alpha_i}{\gamma_i}}, \tag{23}$$

which implies a renormalised temperature for the overdamped MVE

$$\frac{k_B T_i}{1 + \frac{\alpha_i}{\gamma_i}} = \left\langle \left(\frac{\partial U}{\partial q_i} - f_i \right) q_i \right\rangle. \tag{24}$$

5. Overdamped active matter

Active Brownian particles are often employed as an overdamped model for the collective behaviour of motile bacteria and self-propelled colloids [22]. Their phase behaviour is currently much studied [9, 23–28]. In this regard, the utility of the virial theorem was pointed out in [27]. Here we fully exploit the generalised virial theorem and show how our approach leads to a pressure equation for active particles confined by hard walls of arbitrary geometry.

We describe an ensemble of identical active Brownian spheres moving in a two-dimensional volume $\mathcal{V}$ in terms of their positions $\boldsymbol{r}_n = (x_n, y_n)$ and velocity orientations θ_n (hence, $\{\boldsymbol{q}_n\} = \{\boldsymbol{r}_n, \theta_n\}$). Their overdamped equations of motion are

$$\begin{aligned} \dot{\boldsymbol{r}}_n &= v_0 \boldsymbol{u}(\theta_n) + \mu \boldsymbol{F}_w(\boldsymbol{r}_n) + \sum_{m \neq n} \mu \boldsymbol{F}_{int}(\boldsymbol{r}_n - \boldsymbol{r}_m) + \hat{\boldsymbol{\xi}}_n^{(r)}, \\ \dot{\theta}_n &= \hat{\xi}_n^{(\theta)}. \end{aligned} \tag{25}$$

The active velocity of modulus v_0 is directed along the unit vector $\boldsymbol{u}(\theta_n) = (\cos\theta_n, \sin\theta_n)$, and can be formally interpreted as another realization of the nonconservative force $\boldsymbol{f}_n = v_0 \boldsymbol{u}(\theta_n)/\mu$ that breaks detailed balance. Each particle experiences the others through the two-body force $\boldsymbol{F}_{int}$. No special symmetry is assumed for the confining hard walls acting via $\boldsymbol{F}_w(\boldsymbol{r}_n)$ at the container surface $\mathcal{S}$. The Gaussian translational noise $\hat{\boldsymbol{\xi}}_n^{(r)}$ is characterised by $\langle \hat{\boldsymbol{\xi}}_n^{(r)}(t) \hat{\boldsymbol{\xi}}_m^{(r)}(t') \rangle = 2\mu k_B T \delta_{mn} \mathbf{1}\, \delta(t - t')$ and the Gaussian rotational noise $\hat{\xi}_n^{(\theta)}$ by $\langle \hat{\xi}_n^{(\theta)}(t) \hat{\xi}_m^{(\theta)}(t') \rangle = 2\hat{D}^{(\theta)} \delta_{mn}\, \delta(t - t')$. The backward generator $\mathbb{L}$ is thus

$$\mathbb{L} = \sum_{n=1}^{N} \left[\left(v_0 \boldsymbol{u}(\theta_n) + \mu \boldsymbol{F}_w(\boldsymbol{r}_n) + \mu \sum_{m \neq n} \boldsymbol{F}_{int}(\boldsymbol{r}_n - \boldsymbol{r}_m) \right) \cdot \nabla_{\boldsymbol{r}_n} + \mu k_B T \nabla_{\boldsymbol{r}_n}^2 + \hat{D}^{(\theta)} \partial_{\theta_n}^2 \right], \tag{26}$$

and the choice of the observable $\mathcal{O} = \boldsymbol{r}_n^2$ in (3) yields the overdamped MVE

$$2k_B T = -\left\langle \left(\frac{1}{\mu} v_0 \boldsymbol{u}(\theta_n) + \boldsymbol{F}_w(\boldsymbol{r}_n) + \sum_{m \neq n} \boldsymbol{F}_{int}(\boldsymbol{r}_n - \boldsymbol{r}_m) \right) \cdot \boldsymbol{r}_n \right\rangle. \tag{27}$$

In the presence of activity one expects the pressure to be nonuniform due to particle aggregation at the boundaries [29–31] and phase separation [32], unless highly symmetric geometries are considered [9]. Note that in the momentum balance, which takes the form (11), the only external force is the wall interaction. Consistently with the assumption of a constant active speed v_0, the self-propulsion force and the corresponding fluid friction balance each other and hence do not appear on the right hand side of (11).

For the special case of hard walls, we prove in the appendix that the external virial is proportional to the surface-averaged density $\bar{\rho}_{\mathcal{S}}$, namely $-\sum_{n=1}^{N} \langle \boldsymbol{F}_w(\boldsymbol{r}_n) \cdot \boldsymbol{r}_n \rangle = 2\mathcal{V} k_B T \bar{\rho}_{\mathcal{S}}$ [33, 34]. Moreover, inter-particle interactions do not contribute to the momentum flux across the wall, so that the surface-averaged pressure $\bar{P}_{\mathcal{S}}$ can only have a kinetic contribution [34, 35], $\bar{P}_{\mathcal{S}} = k_B T \bar{\rho}_{\mathcal{S}}$. The latter equilibrium result was recently rederived in the field of active matter [36]. It can be employed here since, in the overdamped description, momenta are assumed to be thermalised at the temperature T—by the choice of the translational noise's correlation. Therefore one arrives at the important result that the external virial gives the mean force per unit area exerted on the container

$$-\sum_{n=1}^{N} \langle \boldsymbol{F}_w(\boldsymbol{r}_n) \cdot \boldsymbol{r}_n \rangle = 2\bar{P}_{\mathcal{S}} \mathcal{V}. \tag{28}$$

Combining (28) with the general result $-\sum_{n=1}^{N} \langle \boldsymbol{F}_w(\boldsymbol{r}_n) \cdot \boldsymbol{r}_n \rangle = 2\bar{P}_{\mathcal{V}} \mathcal{V}$, which holds when $\boldsymbol{F}_w$ is the only net external force acting on the system, we obtain the equality of average surface and volume pressure, $\bar{P}_{\mathcal{S}} = \bar{P}_{\mathcal{V}}$.

In the bulk, the interaction term in (27) gives a contribution analogous to the corrections to the ideal gas pressure in an equilibrium system. Indeed, for large N,

$$\sum_{n,m\neq n}\langle \boldsymbol{F}_{\rm int}(\boldsymbol{r}_n-\boldsymbol{r}_m)\cdot\boldsymbol{r}_n\rangle=-\frac{N^2}{2\mathcal{V}^2}\int_{\mathcal{V}}\mathrm{d}\boldsymbol{r}'\int_{\mathcal{V}}\mathrm{d}\boldsymbol{r}''r\frac{\partial U_{\rm int}}{\partial r}g(\boldsymbol{r}',\boldsymbol{r}''),\tag{29}$$

where $\boldsymbol{F}_{\rm int}=-\nabla U_{\rm int}$, $r\equiv|\boldsymbol{r}'-\boldsymbol{r}''|$, and g is the nonequilibrium pair density correlation function. In general, g cannot be reduced to a function of the relative pair position, since the system is inhomogeneous [37]. The explicit nonequilibrium contribution in (27) (the term containing v_0) gives rise to the so-called swim pressure [29, 32]. Using (3), this time with $\mathcal{O}=\boldsymbol{r}_n\cdot\boldsymbol{u}(\theta_n)$, and summing over n, we readily obtain

$$\begin{aligned}v_0\hat{D}^{(\theta)}\sum_n\langle\boldsymbol{r}_n\cdot\boldsymbol{u}(\theta_n)\rangle=Nv_0^2+v_0\mu\sum_n\langle\boldsymbol{F}_{\rm w}(\boldsymbol{r}_n)\cdot\boldsymbol{u}(\theta_n)\rangle\\+v_0\mu\sum_{n,m\neq n}\langle\boldsymbol{F}_{\rm int}(\boldsymbol{r}_n-\boldsymbol{r}_m)\cdot\boldsymbol{u}(\theta_n)\rangle.\end{aligned}\tag{30}$$

The first average on the right-hand side involves the particle polarization at the wall, while the second one represents the correlation between interactions and polarization. The constant term v_0^2 is an enhancement of the kinetic 'ideal gas' contribution due to the particles' activity. Putting everything together, we obtain the generalised equation of state

$$\begin{aligned}\bar{P}_{\mathcal{S}}\mathcal{V}=Nk_{\rm B}T-\frac{N^2}{4\mathcal{V}^2}\int_{\mathcal{V}}\mathrm{d}\boldsymbol{r}'\int_{\mathcal{V}}\mathrm{d}\boldsymbol{r}''r\frac{\partial U_{\rm int}}{\partial r}g(\boldsymbol{r},\boldsymbol{r}')\\+\frac{Nv_0^2}{2\mu\hat{D}^{(\theta)}}+\frac{v_0}{2\hat{D}^{(\theta)}}\sum_{n,m\neq n}\langle\boldsymbol{F}_{\rm int}(\boldsymbol{r}_n-\boldsymbol{r}_m)\cdot\boldsymbol{u}(\theta_n)\rangle+\frac{v_0}{2\hat{D}^{(\theta)}}\sum_n\langle\boldsymbol{F}_{\rm w}(\boldsymbol{r}_n)\cdot\boldsymbol{u}(\theta_n)\rangle.\end{aligned}\tag{31}$$

This result is valid irrespective of the confining geometry, thus extending the results of [27] and substantiating the numerical evidence for the equality of (average) wall and bulk pressure in large systems [29, 30]. Equation (31) is a mesoscopic generalised state equation that depends explicitly on the interaction with the wall through its last term. In equilibrium ($v_0=0$), the latter vanishes so that the pressure equation does not explicitly depend on $\boldsymbol{F}_{\rm w}$, for every system size. Out of equilibrium, the thermodynamic limit ($N,\mathcal{V}\to\infty$ with $N/\mathcal{V}$ constant) can be taken in order to get rid of this surface term, which is a peculiarity of torque-free active Brownian particles with constant self-propulsion. When aligning interactions are added into the model, the active particle pressure appears to depend explicitly on the interactions with the boundaries and not only on thermodynamic properties (temperature, density, etc) [25]. Of course, the framework based on the MVE is unaffected by such dynamical details and can be applied even to models qualitatively different from (25) (see [38]).

6. Normal modes of coupled oscillators

The derivation of the MVE does not rely on the diagonality of the matrix D_{ij}, that is (6) also holds for systems in which the noise components are cross-correlated. An instance of such a situation is offered by the analysis of the normal modes of a system with local reservoirs. For harmonic lattices [7], depending on the details of the forcing and on boundary conditions, the energy stored in long wavelength vibrational modes may be either enhanced or reduced compared to the average. Here, we illustrate the MVE in modes' space for a one-dimensional chain of N point masses coupled with quadratic–quartic interactions, thus going beyond the harmonic approximation. The stochastic equation of the normal modes, obtained by applying a linear transformation to the equation (2) for the oscillators' position and velocity [39], is

$$\ddot{X}_k=-\gamma\dot{X}_k-\omega_k^2X_k-\epsilon\sum_{l,r,s}\mathcal{B}_{klrs}X_lX_rX_s+\eta_k,\tag{32}$$

where ω_k^2 is the squared eigenfrequency of the kth mode and $\epsilon\,\mathcal{B}_{klrs}$ is a tensor that emerges from the quartic interactions. The noise terms η_k are mutually correlated according to

$$\langle\eta_k(t)\eta_l(t')\rangle=2\gamma k_{\rm B}\mathcal{T}_{kl}\delta(t-t').\tag{33}$$

The symmetric matrix $\mathcal{T}_{kl}$ of *mode temperatures* [12], is in general not diagonal unless the system is in equilibrium.

Without the anharmonic coupling, $\epsilon=0$, the average kinetic and potential energy of the modes satisfy

$$\langle\dot{X}_k^2\rangle=\omega_k^2\langle X_k^2\rangle=k_{\rm B}\mathcal{T}_{kk},\tag{34}$$

where the first equality is analogous to (6), and the second amounts to (9) specialised to the present analysis. Notice that the kinetic and potential energy coincide for a given mode, but differ in general for different modes, thus breaking full equipartition. With $\epsilon\neq0$ the modes' dynamics is coupled via the tensor $\mathcal{B}_{klrs}$ and the MVE (6) becomes

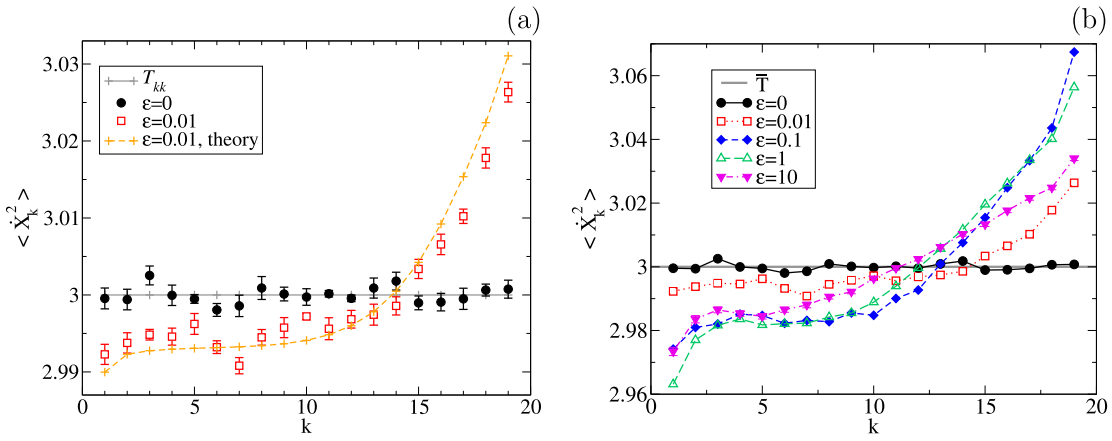

Figure 3. Kinetic energy of the normal modes for a chain of $N = 20$ unit masses coupled via quadratic–quartic potential (harmonic constant $\kappa = 1$, quartic $\epsilon = 0$,..., 10) and immersed in heat baths characterised by the (global) friction constant $\gamma = 0.1$ and the local temperatures T_i, which grow linearly with i from $T_0 = 1$ to $T_{N-1} = 5$ (in natural dimensionless units). (a) Comparison between the analytic expansion (37) (+) and the numerically estimated $\langle \dot{X}_k^2 \rangle$ (□) obtained by integration of the oscillators' stochastic dynamics. (b) Numerically estimated mode kinetic energies also for strongly anharmonic chains. Errors are of the order of symbol sizes.

$$\langle \dot{X}_k^2 \rangle = \omega_k^2 \langle X_k^2 \rangle + \epsilon \sum_{l,r,s} \mathcal{B}_{klrs} \langle X_k X_l X_r X_s \rangle \tag{35}$$

containing no explicit sign of the nondiagonal $\mathcal{T}_{kl}$, as anticipated above. Similarly, the heat-flux equation (8) becomes

$$\langle \dot{X}_k^2 \rangle = k_B \mathcal{T}_{kk} + \frac{\epsilon}{\gamma} \sum_{l,r,s} \mathcal{B}_{klrs} \langle \dot{X}_k X_l X_r X_s \rangle. \tag{36}$$

This represents the perfect starting point for studying perturbative corrections to mode energies, given the Gaussian statistics of the X_k's for $\epsilon = 0$. In equilibrium ($T_i = T \ \forall \, i$), where the modes' position and velocity are on average uncorrelated, the last term disappears, so that (36) implies the equipartition for velocities $\langle \dot{X}_k^2 \rangle = k_B T$. Under nonequilibrium conditions, the nonzero heat flux modifies the mode kinetic energy in (36). For small ϵ we can expand (36) as

$$\langle \dot{X}_k^2 \rangle = k_B \mathcal{T}_{kk} + \frac{3\epsilon}{\gamma} \sum_{l,r,s} \mathcal{B}_{klrs} \langle \dot{X}_k X_l \rangle_{\epsilon=0} \langle X_r X_s \rangle_{\epsilon=0} + O(\epsilon^2). \tag{37}$$

Here we used the symmetry of the tensor $\mathcal{B}$ together with Wick's theorem to break up the Gaussian correlations $\langle ... \rangle_{\epsilon=0}$ evaluated in the harmonic system [12].

An illustration of (37) is provided in figure 3(a) for a one-dimensional lattice with fixed boundaries immersed in a linear temperature profile. For purely harmonic couplings ($\epsilon = 0$), the modes enjoy a peculiar full energy equipartition [12] at the average temperature $\mathcal{T}_{kk} = \overline{T} \equiv \frac{1}{N} \sum_{i=0}^{N-1} T_i$, which is due to the symmetry in the T_i's and in the boundary conditions. The anharmonic terms allow energy to leak into the higher, more localised modes. The same qualitative behaviour is found numerically for increasing values of ϵ (figure 3(b)). The energy repartition among modes is thus robust against the introduction of nonlinearities and fairly well approximated by a first order perturbative calculation. Note that the total kinetic energy is insensitive to ϵ, namely $\sum_{k=0}^{N-1} \langle \dot{X}_k^2 \rangle = k_B \sum_{k=0}^{N-1} \mathcal{T}_{kk} \, \forall \, \epsilon$, since the total flux appearing in (36) sum up to zero under stationary conditions, thanks to the potential nature of the interaction:

$$\sum_{k,l,r,s} \mathcal{B}_{klrs} \langle \dot{X}_k X_l X_r X_s \rangle = \sum_{k=0}^{N-1} \langle \dot{X}_k (\partial_k U - \omega_k^2 X_k) \rangle = \frac{\mathrm{d}}{\mathrm{d}t} \left(\langle U \rangle - \sum_{k=0}^{N-1} \frac{\omega_k^2}{2} \langle X_k^2 \rangle \right) = 0. \tag{38}$$

7. Deterministic thermostats

The relations derived above for stochastic inertial systems remain valid in the zero-noise limit, where the dynamics becomes deterministic. Stationarity is then ensured by coupling the system to suitably defined thermostats. Examples are Nosé–Hoover thermostats, where extra degrees of freedom act as frictional couplings for the physical ones [40]. Similarly to Langevin dynamics, they guarantee canonical thermalization in cases of uniform temperatures, and they lead to nonzero heat fluxes if different temperatures are imposed on different degrees of freedom of the system. For lattices of oscillators interacting only via conservative forces and coupled

to Nosé–Hoover thermostats at various temperatures, the existence of local energy equipartition is a common assumption needed for the local definition of temperature [41]. So far, it has only been observed in simulations for the masses not directly driven by Nosé–Hoover thermostats [42]. Here we provide a formal proof. We consider statistical averages with respect to the invariant density, which, in general, may or may not coincide with time averages. Equality is assured by the use of Nosé–Hoover chains of thermostats [43].

The Nosé–Hoover dynamics for unit masses is given by

$$\dot{q}_i = p_i, \qquad \dot{p}_i = -\partial_{q_i} U - \Theta_i \zeta_i p_i, \qquad \dot{\zeta}_i = \frac{1}{\tau^2}\left(\frac{p_i^2}{k_B T_i} - 1\right), \tag{39}$$

where Θ_i is an indicator function, which is 1 or 0 depending on whether the mass i is coupled or not to a thermostat. The auxiliary feedback variable ζ_i aims at thermalizing p_i at the temperature T_i on a timescale τ. The backward generator associated to (39) is

$$\mathbb{L} = \sum_{i=1}^{Nd}\left\{p_i\partial_{q_i} - \partial_{q_i}U\partial_{p_i} + \Theta_i\left[-\zeta_i p_i\partial_{p_i} + \frac{1}{\tau^2}\left(\frac{p_i^2}{k_B T_i} - 1\right)\partial_{\zeta_i}\right]\right\}.$$

Following the scheme outlined above, we find the generalised MVE

$$\langle p_i^2\rangle = \langle q_i\,\partial_{q_i}U\rangle + \Theta_i\langle\zeta_i p_i q_i\rangle, \tag{40}$$

which includes the formal justification for the mentioned numerical observation of local energy equipartition if restricted to masses without a local thermostat [42], corresponding to $\Theta_i = 0$. The term

$$\langle\zeta_i p_i q_i\rangle = -\frac{1}{2\tau^2}\left\langle\left(\frac{p_i^2}{k_B T_i} - 1\right)q_i^2\right\rangle, \tag{41}$$

stemming from the thermostat's force (that can be seen as another realization of the nonconservative force f_i), is identically zero in equilibrium, where momentum and position are uncorrelated and $\langle p_i^2\rangle = k_B T_i$ holds also for the degrees of freedom coupled to thermostats.

8. Conclusions

For a wide class of nonequilibrium systems in steady states, including stochastic and deterministic thermostated dynamics, we have shown that the kinetic energy of a given degree of freedom is on average equal to the corresponding virial of the forces. An integration over all degrees of freedom of such MVE yields the standard (macroscopic) virial theorem and a variety of useful results for general nonequilibrium systems. It is indeed possible to follow the path valid for equilibrium systems, using the virial theorem as a tool for the derivation of generalised equations of state that involve pressure, temperature and other observables. For inertial systems with dissipative dynamics, this leads to an intriguing relation between the virial, the temperature of the heat baths, and the heat flux into them. Similarly, for active Brownian particles a generalised equation of state valid for arbitrary container geometries ensues. A direct experimental verification of the fundamental mesoscopic virial relations (underlying all these results) would therefore be desirable. In boundary driven systems with conservative internal forces, such verification amounts to checking energy equipartition between momentum–position type conjugate variables.

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Appendix. Pressure on a hard wall

In section 5 we argued that the external virial given by the a hard wall force is proportional to the pressure averaged over the wall surface. To prove this point, we basically collect and repeat the arguments of [33, 34], as they assume stationarity and require the particle momenta to be thermalised to the bath temperature T, only. For the local stress tensor $\boldsymbol{\sigma}$ this leads to the splitting

$$\nabla_{\boldsymbol{r}}\cdot\boldsymbol{\sigma} = k_B T\nabla_{\boldsymbol{r}}\rho + \nabla_{\boldsymbol{r}}\cdot\boldsymbol{\sigma}_{\rm int}. \tag{A.1}$$

Recall that $\boldsymbol{\sigma}(\boldsymbol{r})$ gives the momentum exchanged across a surface placed in $\boldsymbol{r}$. Hence, the two terms on the right-hand side of (A.1) represent, respectively, the momentum transferred kinetically by particles crossing the surface and the momentum exchanged between particles separated by the surface itself. Using (A.1), multiplying the momentum balance equation (15) (with $f=0$) by $\boldsymbol{r}$ and integrating over $\mathcal{V}_-$, defined as an inner volume infinitesimally smaller than $\mathcal{V}$, yields

$$\int_{\mathcal{V}_-} \mathrm{d}\vec{r}\ (\nabla_{\boldsymbol{r}}\cdot\boldsymbol{\sigma}_{\mathrm{int}})\cdot\boldsymbol{r} + \mathrm{m}\gamma\int_{\mathcal{V}_-}\mathrm{d}\vec{r}\ \boldsymbol{u}\rho\cdot\boldsymbol{r} = \mathrm{d}k_{\mathrm{B}}T(\bar{\rho}_{\mathcal{V}}-\bar{\rho}_{\mathcal{S}}). \tag{A.2}$$

Here we have used that $\boldsymbol{F}_{\mathrm{w}}(\boldsymbol{r})=0$ for $\boldsymbol{r}\in\mathcal{V}_-$, and $\mathcal{S}$ indicates the surface of $\mathcal{V}_-$. On the other hand, using that the particle density vanishes identically on the hard wall, an integration over the whole system gives

$$\int_{\mathcal{V}} \mathrm{d}\vec{r}\ (\nabla_{\boldsymbol{r}}\cdot\boldsymbol{\sigma}_{\mathrm{int}})\cdot\boldsymbol{r} + \mathrm{m}\gamma\int_{\mathcal{V}}\mathrm{d}\vec{r}\ \boldsymbol{u}\rho\cdot\boldsymbol{r} = \int_{\mathcal{V}}\mathrm{d}\vec{r}\,\boldsymbol{F}_{\mathrm{w}}\rho\cdot\boldsymbol{r} + \mathrm{d}k_{\mathrm{B}}T\bar{\rho}_{\mathcal{V}}. \tag{A.3}$$

The left-hand side of (A.2) and (A.3) are equal, since the integrands are finite everywhere in the system and the integration domains only differ in a set of zero measure. Hence, we conclude that the external virial for hard walls is only proportional to the surface averaged density

$$-\sum_{n=1}^{N}\langle\boldsymbol{F}_{\mathrm{w}}(\boldsymbol{r}_n)\cdot\boldsymbol{r}_n\rangle = 2\mathcal{V}k_{\mathrm{B}}T\bar{\rho}_{\mathcal{S}}. \tag{A.4}$$

Then, one applies the rationale behind (A.1) to the momentum exchanged at the wall, which is by definition the surface averaged pressure $\bar{P}_{\mathcal{S}}$. Namely, it may consist of the kinetic contribution $k_{\mathrm{B}}T\bar{\rho}_{\mathcal{S}}$ and a configurational term coming from inter-particle interactions. Yet, the latter is identically zero on a hard wall, since no configuration is allowed with particles on both side of the wall surface. Therefore, plugging $\bar{P}_{\mathcal{S}} = k_{\mathrm{B}}T\bar{\rho}_{\mathcal{S}}$ into (A.4), we arrive at the sought result (28).

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