

Topical Review

Why Noether's theorem applies to statistical mechanics

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Received 8 November 2021, revised 3 March 2022

Accepted for publication 7 March 2022

Published 21 April 2022



Abstract

Noether's theorem is familiar to most physicists due its fundamental role in linking the existence of conservation laws to the underlying symmetries of a physical system. Typically the systems are described in the particle-based context of classical mechanics or on the basis of field theory. We have recently shown (2021 *Commun. Phys.* **4** 176) that Noether's reasoning also applies to thermal systems, where fluctuations are paramount and one aims for a statistical mechanical description. Here we give a pedagogical introduction based on the canonical ensemble and apply it explicitly to ideal sedimentation. The relevant mathematical objects, such as the free energy, are viewed as functionals. This vantage point allows for systematic functional differentiation and the resulting identities express properties of both macroscopic average forces and molecularly resolved correlations in many-body systems, both in and out-of-equilibrium, and for active Brownian particles. To provide further background, we briefly describe the variational principles of classical density functional theory, of power functional theory, and of classical mechanics.

Keywords: statistical mechanics, density functional theory, power functional theory, invariance, Noether's theorem, liquid state theory, sum rules


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

1. Introduction

Symmetries and their breaking in often stunningly beautiful ways are at the core of a broad range of phenomena in physics, from phase transitions in condensed matter to mass generation via the Higgs mechanism. Most readers will be very familiar with the importance of symmetry operations, including complex operations such as CPT-invariance in high energy physics as well as the simple challenge of centering the webcam while having mirroring switched off in a video call.

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The exploitation of the underlying symmetries of a physical system is an important and central concept that allows to simplify the mathematical description and arguably more importantly to gain physical insights and achieve an understanding of the true mechanisms at play. This is what the mathematician Emmy Noether did in her groundbreaking work in functional analysis early in the twentieth century [1].

Noether analyzed carefully the changes that occur upon performing a symmetry operation on a system. Her work solved the then open deep problems of energy conservation in general relativity, as the new theory of gravity that Einstein had just formed. Noether considered the formulation of general relativity via Hilbert's action integral, which is a formal object—a functional—that generates Einstein's field equations. Nowadays Noether's theorems [1–3] are widely known and used to

connect each continuous symmetry of a system with a corresponding conservation law. Noether's work therefore forms a staple of physics, relevant from introductory classical mechanics to advanced theories such as the standard model of high energy particle physics.

In practice the theorems are usually applied to the action functional in a Lagrangian or Hamiltonian theory. This strategy is not of mere historic interest, as much active current research is being carried out, see e.g. recent developments that addressed the action functional for systems that include random forces [4–6] and work that shows, starting from the symmetry of an action functional, that the thermodynamic entropy can be viewed as a Noether invariant [7–9]. However, from a mathematical point of view, Noether's theorem is actually not restricted to the specific case of the action integral. The theorem rather applies to a much more general class of functionals, where it specifies general consequences of invariance under continuous symmetry transformations.

We recall some basics of functional calculus. A functional is a mathematical object that maps an entire function, i.e. the function values together with the corresponding values of the argument, to a single number. A popular introductory example of a functional is the definite integral, say over the unit interval from 0 to 1. When viewed as a functional, the definite integral accepts the integrand (a function) and it returns a number (the area under the curve that the function represents). Although the functional point of view might appear slightly uncommon (or even trivial in this case), the inherent abstract concept allows to formulate very significant insights and use powerful mathematical techniques of variational calculus which can be straightforwardly and widely applied.

The occurrence of functionals in physics is not restricted to the study of behaviour at very large length scales, such as that of the cosmos in the case of general relativity, or to very high energies, as is the case for fundamental theories of elementary particles. In fact the mathematical concept of a functional dependence is very general. Hence there is an according wide variety of objects in physics, such as e.g. the partition sum and the free energy in statistical mechanics that can be viewed as being a functional [10–13]; we give an introduction below. As soon as one is willing to accept this notion, making much headway is possible by analyzing physical properties of the considered system from this formal point of view.

To perform the transfer and use Noether's theorem for thermal systems, from a formal point of view one would need both to identify a suitable functional as well as a symmetry transformation under which this functional is invariant. One primary candidate for the choice of the functional is the partition function, which constitutes an integral over the high-dimensional phase space of classical mechanics. Within this context, phase space describes all degrees of freedom, i.e. the positions and momenta of all particles in the system. The partition sum itself is hence an integral over all these variables. Its integrand is, up to a constant, the Boltzmann factor of the energy function that characterizes the system. So the partition sum actually complies with the nature of a functional as it maps this function to just a number, i.e. the value of the partition sum. (As

detailed below the interesting functional dependence is that on the external potential.) The partition sum is arguably the most fundamental object in statistical physics, as all thermodynamic quantities, such as thermodynamic potentials including the free energy, the equation of state, but also position-resolved correlation functions can be obtained from it, at least in principle.

Within statistical mechanics, where one identifies the free energy with the negative logarithm of the partition sum, ordinary (parametric) derivatives of the free energy with respect to e.g. temperature and other thermodynamic variables generate thermodynamic quantities [11–13]. While the familiar process of building the derivative of a function, as giving a measure of the local slope, is a concept that dates back to Newton and Leibniz, functional differentiation is slightly less common. However, functionals can be differentiated in much the same way that functions can be differentiated. In case of the free energy, functional derivatives give microscopically resolved correlation functions [11–13]. These are quantities, such as the structure factor of a liquid, that are measurable in a lab, say with a scattering apparatus or even with a microscope upon further data processing.

When applying Emmy Noether's thinking to the free energy, one could expect mere abstraction to result, but that is not the case [14]. Consider the invariance under a spatial shift. This classical application of Noether's theorem to the action functional yields the well-known result of momentum conservation. When rather exploiting the invariance of the partition function and hence of the free energy with respect to shifting, what follows are fundamental statements about forces that act in the system [14]. One of them states that the total internal force vanishes. Here the total internal force is that which arises from the interactions only *between* the constituents of the system. The famous Baron Munchausen tale of bootstrapping himself out of the swamp by pulling on his own hair is identified as a fairytale by the Noetherian argument. The impossibility of this feat holds on the scale of his entire body, but also when locally resolving his structure on the molecular scale.

In addition to shifting, one can also consider rotations. In case of the action functional being invariant under rotations Noether's theorem implies that the angular momentum around the rotation axis is conserved. If the free energy has rotational symmetry, fundamental statements about torques emerge [14, 15]. These sum rules express inherent coupling of spin and orbital degrees of freedom. Figuratively speaking, the identities state that a bolt cannot screw itself into the wall and that a Baron Munchausen stuck in mud cannot spontaneously start to rotate by twisting his head.

Recognizing the functional dependence of the free energy allows to build a theory fully founded on a variational principle of thermal systems, as formulated by Mermin [10] and Evans [11, 12]. Their so-called density functional theory is a well-accepted and widely used theory, see reference [13] for a textbook presentation and reference [16] for an overview of recent work. Excellent approximations are available for relevant model fluids, such as for hard spheres [17, 18] (see

reference [19] for recent work addressing hard sphere crystal properties). The density functional approach hence allows explicit calculations to be carried out to predict the behavior of a wide range of physical systems, including solvation [20], hydrophobicity [21–23], critical drying of liquids [24], solvent fluctuations [25], electrolyte solutions near surfaces [26], interpretation of atomic force microscopy data [27], temperature gradients at fluid interfaces [28], and local fluctuations [22–25, 29]. In reference [14] we also apply Noether’s thinking to a very recent variational approach for dynamics, called power functional theory [30, 31], which propels the functional concepts from equilibrium to nonequilibrium [30–45], including the recently popular active Brownian particles [46–52]. The generalization is important, as it shows that not only a dead Munchausen cannot bootstrap himself out of his misery, but that being alive does not help (in this particular case).

In the present contribution we demonstrate that the concepts of reference [14] apply to the canonical ensemble, as is relevant for confined systems [53–55] and for the dynamics [56–58]. Hence having an open system with respect to particle exchange is not necessary for the Noetherian arguments to apply. We give a detailed and somewhat pedagogical derivation of the fundamental concepts and also make much relevant background explicit, which has not been spelled out in reference [14].

The paper is organized as follows. In section 2 we go into some detail and we present in the following the arguably simplest example of the application of Noether’s theorem to statistical mechanics. We expect the reader to be familiar with Newtonian mechanics and to ideally know about classical mechanics formulated in a more formal setting (we supply some basic notions thereof below). We lay out the canonical ensemble and averages in section 2.1. Forces and their relation to symmetries are addressed in section 2.2. Statistical functionals and their invariances are described in section 2.3. As an example we describe the application to sedimentation in section 2.4. The relationship of the Noether invariance to correlation functions is laid out in section 2.5. We give further background that is relevant for reference [14], such as the details of the grand canonical treatment and the variational principles of density functional theory and of power functional theory, in section 2.6. We present our conclusions in section 3.

2. Theory

2.1. Canonical ensemble and averages

We consider a system with fixed number of particles N . The state of the system is characterized by all positions $\mathbf{r}_1, \dots, \mathbf{r}_N$ and momenta $\mathbf{p}_1, \dots, \mathbf{p}_N$, where the subscript labels the N particles, which we take to all have identical properties. We assume that the total energy consists of kinetic and potential energy contribution, according to

$$H = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m} + u(\mathbf{r}_1, \dots, \mathbf{r}_N) + \sum_{i=1}^N V_{\text{ext}}(\mathbf{r}_i). \quad (1)$$

Here H is the Hamiltonian of the system, with the interparticle interaction potential $u(\mathbf{r}_1, \dots, \mathbf{r}_N)$ and the external one-

body potential $V_{\text{ext}}(\mathbf{r}_i)$ acting on particle i . The equations of motion are generated via $\dot{\mathbf{r}}_i = \partial H / \partial \mathbf{p}_i$ and $\dot{\mathbf{p}}_i = -\partial H / \partial \mathbf{r}_i$, where the overdot indicates a time derivative, m is the particle mass, and the index $i = 1, \dots, N$. Using the explicit form (1) of the Hamiltonian then leads to the equations of motion in the familiar form

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m}, \quad (2)$$

$$\dot{\mathbf{p}}_i = \mathbf{f}_i, \quad (3)$$

where \mathbf{f}_i indicates the force on particle i , which consists of a contribution from all other particles as well as the external force. Explicitly, the force on particle i is given by

$$\mathbf{f}_i = -\nabla_i u(\mathbf{r}_1, \dots, \mathbf{r}_N) - \nabla_i V_{\text{ext}}(\mathbf{r}_i), \quad (4)$$

where ∇_i denotes the derivative with respect to \mathbf{r}_i . (Building the derivative by a vector implies building the derivative with respect to each component of the vector, hence ∇_i can be viewed as building the gradient with respect to \mathbf{r}_i .) Certainly we could have written down the equations of motion (2) and (3) *a priori*. Equation (2) expresses the standard relation of velocity $\dot{\mathbf{r}}_i$ with momentum \mathbf{p}_i , and (3) is Newton’s second law. Hence we have reproduced the Newtonian theory within the Hamiltonian formalism.

So far everything has been deterministic and we were concerned with obtaining a description on the level of individual particles. As our aim is to describe very large systems, we wish to ‘zoom out’ and investigate and describe the macroscopic properties of the system, as they result from the above formulated microscopic picture. Statistical mechanics provides the means for doing so. We will not attempt to give a comprehensive description of the concepts of this theory. Rather we will guide the reader through some essential steps, including in particular how thermal averages are built, to see how Noether’s theorem applies in this context. As we will see, both the physical concept and the outcome are different from the standard application of Noether’s theorem based on the action expressed as a time integral over a Lagrangian that corresponds to (1); we give a brief description of this standard argument at the end of section 2.2.

Statistical mechanics rests on the concept of having a statistical ensemble, in the sense of the collection of microstates $\mathbf{r}_1, \dots, \mathbf{r}_N, \mathbf{p}_1, \dots, \mathbf{p}_N$, i.e. all phase space points. These are transcended beyond classical mechanics by each being assigned a probability for its occurrence. (There is much discussion about who throws the dice here; we recommend Zwanzig’s cool-headed account [59].) The microstate probability distribution is given by a standard Boltzmann form,

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N, \mathbf{p}_1, \dots, \mathbf{p}_N) = \frac{e^{-\beta H}}{Z_N}, \quad (5)$$

where the inverse temperature is $\beta = 1/(k_B T)$, with the Boltzmann constant k_B and absolute temperature T . Here Z_N is the partition sum, and it acts to normalize the probability distribution to unity, when summed up over all microstates. The sum over microstates is in practice a high-dimensional integral over phase space, explicitly given as

$$Z_N = \frac{1}{N!h^{3N}} \int d\mathbf{r}_1 \dots d\mathbf{r}_N d\mathbf{p}_1 \dots d\mathbf{p}_N e^{-\beta H}, \quad (6)$$

where h indicates the Planck constant. Here each position integral and each momentum integral runs over \mathbb{R}^3 . (We are considering systems in three spatial dimensions.) The system volume is rendered finite by confining walls that are modelled by a suitable form of the external potential $V_{\text{ext}}(\mathbf{r})$. As a note on units, recall that h carries energy multiplied by time, i.e. Js, such that the partition sum (6) carries no units.

The purpose of the probability distribution (5) is to build averages. Taking the Hamiltonian (1) as an example, we can express the total energy, averaged over the statistical ensemble, as

$$E = \frac{1}{N!h^{3N}} \int d\mathbf{r}_1 \dots d\mathbf{r}_N d\mathbf{p}_1 \dots d\mathbf{p}_N H\Psi. \quad (7)$$

Here we recall the dependence of the Hamiltonian (1) on the phase space point, and in the notation we have left away the arguments $\mathbf{r}_1, \dots, \mathbf{r}_N, \mathbf{p}_1, \dots, \mathbf{p}_N$ of both H and Ψ .

It is useful to introduce more compact notation, as this reduces clutter and allows to express the structure of the theory more clearly. Let us denote the integral over phase space, together with its normalizing factor in (6) as the ‘classical trace’ operation, hence defined as

$$\text{Tr}_N = \frac{1}{N!h^{3N}} \int d\mathbf{r}_1 \dots d\mathbf{r}_N d\mathbf{p}_1 \dots d\mathbf{p}_N, \quad (8)$$

which is to be understood as acting on an integrand, such as on $H\Psi$ in the example (7) above. Equation (7) can hence be expressed much more succinctly as

$$E = \text{Tr}_N H\Psi. \quad (9)$$

In a similar way we can express other averaged quantities, such as the average external (potential) energy,

$$U_{\text{ext}} = \text{Tr}_N \Psi \sum_{i=1}^N V_{\text{ext}}(\mathbf{r}_i). \quad (10)$$

In order to build some trust for the compact notation, we use (5) and (8) to re-write (10) explicitly as

$$U_{\text{ext}} = \frac{1}{N!h^{3N}} \int d\mathbf{r}_1 \dots d\mathbf{r}_N d\mathbf{p}_1 \dots d\mathbf{p}_N \times \frac{e^{-\beta H}}{Z_N} \sum_{i=1}^N V_{\text{ext}}(\mathbf{r}_i). \quad (11)$$

This allows to see explicitly that U_{ext} depends on the number of particle N and on the temperature T (via the Boltzmann factor and the partition sum). Surely (10) allows to see the physical content, that of an average being carried out, more clearly than (11) and we will continue to use the compact notation. (Readers who wish to familiarize themselves more intimately with these benefits are encouraged to put pen to scratch paper and re-write the following material in explicit notation.)

2.2. Forces and symmetries

Before continuing with thermal concepts, such as the free energy, we take a detour from standard paths in statistical mechanics, and return to forces. After all, it was the microscopically and particle-resolved forces \mathbf{f}_i in (4) that formed the starting point for the description of the coupled system. As an example, let us hence consider the total external force that acts on the system, in the sense that we sum up the external force that acts on each individual particle, $-\nabla_i V_{\text{ext}}(\mathbf{r}_i)$. This accounting results in $-\sum_i \nabla_i V_{\text{ext}}(\mathbf{r}_i)$. Note that this expression still applies per microstate, or in other words, the total external force varies in general across phase space. As a cautionary note on terminology, we use throughout the term ‘total’ in the above sense of denoting a global, macroscopic, extensive quantity. This usage is different from the also frequent meaning of total referring to the sum of intrinsic and external contributions.

In order to obtain the macroscopic description we need to trace over phase space and respect the probability for the occurrence of each given microstate. Hence the average total external force is given by

$$\mathbf{F}_{\text{ext}}^0 = -\text{Tr}_N \Psi \sum_{i=1}^N \nabla_i V_{\text{ext}}(\mathbf{r}_i). \quad (12)$$

Due to the structure of (12), $\mathbf{F}_{\text{ext}}^0$ depends on the number of particles N (via the upper limit of the sum and the dimensionality of the phase space integrals), on temperature T (via the thermal distribution Ψ , cf (5) and (6)), and it of course also depends on the form of the function $V_{\text{ext}}(\mathbf{r})$. Note that the function $V_{\text{ext}}(\mathbf{r})$ appears both explicitly in the gradient in (12) as well as in a more hidden form in the probability distribution Ψ , cf (5) and (1).

Let us halt for a moment and ponder the physics. Imagine having a vessel with impenetrable walls, such that the system stays confined inside of the vessel. Furthermore, to add some flavour, imagine an external field such as gravity acting on the system. Then the external potential consists of two contributions, i.e. the potential energy that the container walls exert on each given particle plus the gravitational energy. In an equilibrium situation, what would we expect the total external force to be like? Surely, it should not change in time. (Technically any time evolution had been superseded by the ensemble, which is a static one in the present case.) The reader might expect that

$$\mathbf{F}_{\text{ext}}^0 = 0, \quad (13)$$

because otherwise the system would surely start to move! However, as for any given microstate the total external force will in general *not* vanish, (13), if true, is a nontrivial property of thermal equilibrium. See figure 1 for an illustration of this concept, based on a system confined in a spherical cavity. Hence we wish to address carefully in the following whether we can prove (13) from first principles.

In the following we give two derivations of (13), which both rest on spatial translations of the system. The first derivation only requires vector calculus. The second derivation shows the Noetherian symmetry argument based on the functional

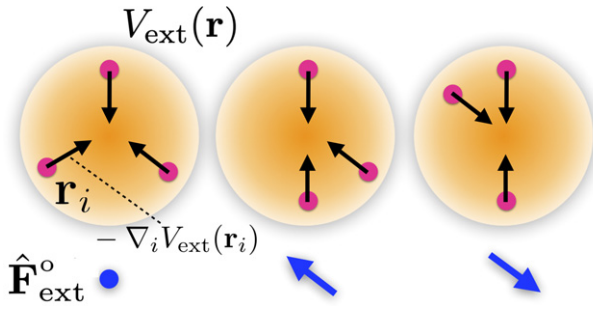


Figure 1. Three representative microstates \mathbf{r}^N for $N = 3$ particles inside of a spherical cavity modelled by a confining external potential $V_{\text{ext}}(\mathbf{r})$ (orange). Shown are the particle positions \mathbf{r}_i (pink dots) and the respective external force $-\nabla_i V_{\text{ext}}(\mathbf{r}_i)$ acting on particle i (black arrows). The resulting total external force $\hat{\mathbf{F}}_{\text{ext}}^{\circ} = -\sum_i \nabla_i V_{\text{ext}}(\mathbf{r}_i)$ is shown for each microstate (blue arrows and blue dot, the later indicating zero). Although $\hat{\mathbf{F}}_{\text{ext}}^{\circ}$ for each microstate is in general nonzero, the average over the thermal ensemble vanishes, $\mathbf{F}_{\text{ext}}^{\circ} = \langle \hat{\mathbf{F}}_{\text{ext}}^{\circ} \rangle = 0$.

setting. This requires to adopt the notion of functional dependencies, which we have used only implicitly so far. In the following we make these relationships and dependencies explicit. We also supply the necessary methodology of functional differentiation and will attempt to convince the reader that their background in ordinary calculus can be flexed in order to follows these steps.

The fundamental ingredients to both derivations are identical though. We use the free energy and we monitor its changes upon spatial displacement of the system. The free energy, and more generally thermodynamic potentials, are central to thermal physics, and the following material can be viewed as a demonstration why this indeed is the case.

The free energy F_N , or more precisely: the total Helmholtz free energy is given by

$$F_N = -k_B T \ln Z_N, \quad (14)$$

where Z_N is the partition sum, as defined in (6). One can show that the relation of free energy and internal energy is given by the thermodynamic identity $F_N = E - TS$, where S is the entropy, here defined on a microscopic basis and the internal energy E is given by (9). One can surely be surprised by the promotion of the rather banal normalization factor Z_N to such a prominent and as we show decisive role. We demonstrate in the following that Z_N had been a dark horse, and that its status to generate the free energy via (14) is well-deserved.

Besides the free energy, the second ingredient that we require is a spatial shift of the entire system according to a displacement vector ϵ of the system. We hence displace the external potential spatially by a constant vector ϵ . (Although we Taylor expand in ϵ below, the displacement ϵ can be finite and arbitrary.) The displaced system is then under the influence of an external potential which has changed according to

$$V_{\text{ext}}(\mathbf{r}) \rightarrow V_{\text{ext}}(\mathbf{r} + \epsilon). \quad (15)$$

Formally, the free energy of the displaced system will depend on the displacement vector, i.e.

$$F_N \rightarrow F_N(\epsilon), \quad (16)$$

where F_N is the free energy (14) expressed in the original coordinates, and the new free energy is given by

$$F_N(\epsilon) = -k_B T \ln Z_N(\epsilon). \quad (17)$$

Here the partition sum of the shifted system is

$$Z_N(\epsilon) = \text{Tr}_N \exp \left[-\beta \left(H_{\text{int}} + \sum_i V_{\text{ext}}(\mathbf{r}_i + \epsilon) \right) \right], \quad (18)$$

where the intrinsic part H_{int} of the Hamiltonian consists of kinetic energy and interparticle interaction potential energy only, i.e. $H_{\text{int}} = \sum_i \mathbf{p}_i^2 / (2m) + u(\mathbf{r}_1, \dots, \mathbf{r}_N)$.

We proceed by first recognizing that the shift does not change the value of the free energy (in other words, the choice of origin of the coordinate system does not matter). We can see this explicitly by performing a coordinate transformation $\mathbf{r}_i \rightarrow \mathbf{r}_i - \epsilon$. This leaves H_{int} invariant, as the momenta are unaffected and the internal interaction potential is unaffected. Recall that the interparticle energy only depends on relative particle positions, which remain invariant under the transformation: $\mathbf{r}_i - \mathbf{r}_j \rightarrow (\mathbf{r}_i - \epsilon) - (\mathbf{r}_j - \epsilon) = \mathbf{r}_i - \mathbf{r}_j$. Furthermore, due to the simplicity of the coordinate transformation that the shift represents, the phase space integral, of the classical trace (8), is unaffected as the Jacobian of the transformation is unity. Note that in the shifting operation, the momenta are unaffected and their behaviour remains governed by the Maxwell distribution throughout. Hence we have shown that the original free energy is identical to the free energy of the shifted system

$$F_N = F_N(\epsilon), \quad (19)$$

for any value of the displacement vector ϵ .

At this point one could conclude mission accomplished. This is not what Emmy Noether did in her mathematical formulation of the problem—we hint at her variational techniques below. The way forward at this point is to rather ignore (19) and return to the explicit expression (17) for the free energy in the shifted system. We consider small displacements ϵ and Taylor expand to first order,

$$F_N(\epsilon) = F_N + \left. \frac{\partial F_N(\epsilon)}{\partial \epsilon} \right|_{\epsilon=0} \cdot \epsilon, \quad (20)$$

where quadratic and higher order terms in ϵ have been omitted. The partial derivative in (20) can be calculated explicitly:

$$\frac{\partial F_N(\epsilon)}{\partial \epsilon} = -\frac{k_B T}{Z_N(\epsilon)} \frac{\partial}{\partial \epsilon} Z_N(\epsilon) \quad (21)$$

$$= -\frac{k_B T}{Z_N(\epsilon)} \text{Tr}_N \frac{\partial}{\partial \epsilon} e^{-\beta H(\epsilon)} \quad (22)$$

$$= -\frac{k_B T}{Z_N(\epsilon)} \text{Tr}_N e^{-\beta H(\epsilon)} \frac{\partial}{\partial \epsilon} (-\beta) \sum_{i=1}^N V_{\text{ext}}(\mathbf{r}_i - \epsilon), \quad (23)$$

where in the first step (21) the partition sum in the denominator arises from the derivative of the logarithm in (17) and in the

second step (22) we have interchanged the phase space integration (as notated by Tr_N , cf (8)) and the ϵ -derivative. The third step (23) follows directly from the structure of the Hamiltonian (1) and the fact that H_{int} is independent of ϵ . We continue to obtain

$$\frac{\partial F_N(\epsilon)}{\partial \epsilon} = \text{Tr}_N \frac{e^{-\beta H(\epsilon)}}{Z_N(\epsilon)} \sum_{i=1}^N \frac{\partial}{\partial \epsilon} V_{\text{ext}}(\mathbf{r}_i - \epsilon) \quad (24)$$

$$= -\text{Tr}_N \Psi(\epsilon) \sum_{i=1}^N \frac{\partial}{\partial \mathbf{r}_i} V_{\text{ext}}(\mathbf{r}_i - \epsilon), \quad (25)$$

where in (24) we have pulled the partition sum as a constant inside of phase space integral and have moved the ϵ -derivative inside the sum over all particles. In (25) we have combined the Boltzmann factor with the partition sum in order to express the many-body probability distribution function in the shifted system, $\Psi(\epsilon) = \exp(-\beta H(\epsilon))/Z_N(\epsilon)$, in generalization of (5). Furthermore the spatial derivative of the external potential is re-written via using $\partial/\partial \epsilon = -\partial/\partial \mathbf{r}_i$ (which is valid due to the dependence on only the difference $\mathbf{r}_i - \epsilon$). Considering the case $\epsilon = 0$ allows us to conclude that

$$\left. \frac{\partial F_N(\epsilon)}{\partial \epsilon} \right|_{\epsilon=0} = -\text{Tr}_N \Psi \sum_{i=1}^N \frac{\partial}{\partial \mathbf{r}_i} V_{\text{ext}}(\mathbf{r}_i). \quad (26)$$

Remarkably the right-hand side is the average total external force as previously defined in (12). The left-hand side is identically zero, as ϵ is arbitrary in (20) and the linear order (as well as all higher orders) need to vanish in the Taylor expansion (20) by virtue of the invariance (19) of the free energy upon spatial displacement. Hence

$$-\text{Tr}_N \Psi \sum_{i=1}^N \frac{\partial}{\partial \mathbf{r}_i} V_{\text{ext}}(\mathbf{r}_i) = 0, \quad (27)$$

which proves constructively the anticipated vanishing (13) of the average total external force (12).

As a preliminary summary, we have shown that the invariance of a global thermodynamic potential, the Helmholtz free energy expressed in the canonical ensemble, against spatial displacement (as generated by a shift of the external potential) leads to the non-trivial force identity of vanishing total external force. This identity holds true for any value of the number of particles in the system, at arbitrary temperature, and most notably irrespective of the precise form of the external potential. Hence we refer to statements such as $\mathbf{F}_{\text{ext}}^0 = 0$, cf (13), as a Noether identity or Noether sum rule. Clearly the concept is general, as both the symmetry operation can be altered (rotations are considered in reference [14]) as well as the type of thermodynamic object can be changed (the grand potential and the excess free energy density functional are considered in reference [14] and we shift the total external energy U_{ext} below in section 2.5).

We have presented here the shifting from the point of view that the actual physical system is moved to a different location. Alternatively, one could adopt a ‘passive’ point of view and displace only the origin of the coordinate system,

in the sense of using shifted coordinates that still describe an unchanged physical system. Then going through a chain of arguments analog to those given above yields identical results.

For completeness we contrast the present statistical mechanical treatment with the standard application of Noether’s theorem to deterministic dynamics. We keep the same N -body classical many-body system as before, i.e. with Hamiltonian H given by (1). The equations of motion (2) and (3) follow from the action integral $\mathcal{S} = \int_{t_1}^{t_2} dt L$, where the Lagrangian L is obtained via $L = \sum_i \mathbf{p}_i \dot{\mathbf{r}}_i - H$ and t_1 and t_2 are two fixed points in time. We apply the global shifting transformation $\mathbf{r}_i \rightarrow \mathbf{r}_i - \epsilon$, as before, to all particle coordinates in the system and at all times. As a consequence, the Lagrangian acquires a corresponding dependence on ϵ . Taylor expanding the action to first order in ϵ then yields

$$\mathcal{S}(\epsilon) = \mathcal{S} + \left. \frac{\partial \mathcal{S}(\epsilon)}{\partial \epsilon} \right|_{\epsilon=0} \cdot \epsilon \quad (28)$$

$$= \mathcal{S} + \int_{t_1}^{t_2} dt \left. \frac{\partial L}{\partial \epsilon} \right|_{\epsilon=0} \cdot \epsilon \quad (29)$$

$$= \mathcal{S} - \int_{t_1}^{t_2} dt \sum_i \left. \frac{\partial L}{\partial \mathbf{r}_i} \right|_{\epsilon=0} \cdot \epsilon \quad (30)$$

$$= \mathcal{S} - \int_{t_1}^{t_2} dt \sum_i \frac{d\mathbf{p}_i}{dt} \cdot \epsilon \quad (31)$$

$$= \mathcal{S} - \sum_i \mathbf{p}_i \Big|_{t_1}^{t_2} \cdot \epsilon, \quad (32)$$

where $\mathcal{S} = \mathcal{S}(\epsilon = 0)$ is the action in the original unshifted system; we have used the representation of $\mathcal{S}(\epsilon)$ as the time integral of the Lagrangian in the derivation of (29), the identity $\partial L/\partial \epsilon = -\sum_i \partial L/\partial \mathbf{r}_i$ to obtain (30), the Lagrangian equations of motion $d\mathbf{p}_i/dt = \partial L/\partial \mathbf{r}_i$ to derive (31), and the fact that the integrand of (31) is a total time differential to obtain (32).

Suppose now that the system is invariant under the displacement, such that $\mathcal{S} = \mathcal{S}(\epsilon)$ for any value of ϵ and the second term in (32) needs to vanish. This implies that the global momentum $\mathbf{P}^0 = \sum_i \mathbf{p}_i$ is conserved, i.e. $\mathbf{P}^0(t_2) = \mathbf{P}^0(t_1)$.

2.3. Functionals and invariances

The abstraction that is yet to be performed and that allows to see the above statistical mechanical force result in an even wider setting, is based on functional methods. As we had hinted at in the introduction, integrals often allow for direct interpretation as functionals as they map their integrand (or part thereof) to the value of the quadrature. In the specific case at hand, we stay with the canonical free energy F_N and observe that its value certainly depends on the form of the external potential $V_{\text{ext}}(\mathbf{r})$, cf its occurrence in the Hamiltonian (1), which via the partition sum (6) enters the free energy (14). Hence we have $F_N[V_{\text{ext}}]$, where we indicate the functional dependence by square brackets (and leave away in the

notation the position argument \mathbf{r} , despite the fact that the functional depends on the entire function). In order to highlight this point of view, we rewrite (14) and (6), respectively, in the form

$$F_N[V_{\text{ext}}] = -k_B T \ln Z_N[V_{\text{ext}}], \quad (33)$$

$$Z_N[V_{\text{ext}}] = \text{Tr}_N \exp \left(-\beta H_{\text{int}} - \beta \sum_{i=1}^N V_{\text{ext}}(\mathbf{r}_i) \right), \quad (34)$$

where still the partition sum, viewed now as a functional of the external potential, $Z_N[V_{\text{ext}}]$ is given by its elementary form, i.e. the right-hand side of (6). In a more compact form, eliminating $Z_N[V_{\text{ext}}]$ as a standalone object, we have

$$F_N[V_{\text{ext}}] = -k_B T \ln \text{Tr}_N \exp \left(-\beta H_{\text{int}} - \beta \sum_{i=1}^N V_{\text{ext}}(\mathbf{r}_i) \right). \quad (35)$$

We dwell on the functional concept and demonstrate some practical consequences. As an analogy, viewing the functional dependence in (35) akin to the dependence of an ordinary function $f(x)$ on its argument x brings concepts of calculus immediately to mind, such as building the derivative $f'(x)$ and investigating its properties.

This analogy extends to functionals and their derivatives with respect to the argument function, in a process referred to as functional differentiation. For the present case, functionally deriving $F_{\text{ext}}[V_{\text{ext}}]$ with respect to $V_{\text{ext}}(\mathbf{r})$ can be viewed as monitoring the change of the value of the functional upon changing its argument function at position \mathbf{r} . The change will in general depend on position \mathbf{r} , hence building functional derivatives creates position dependence. (The result of the functional derivative is again a functional, as the dependence on the argument function persists.) Functional calculus is in many ways similar to ordinary multi-variable calculus. We do not attempt to give a tutorial here (see e.g. the appendix of reference [31] for a very brief one), but rather present a single example that is relevant for the present physics of invariance operations applied to many-body systems.

We use standard notation and denote the functional derivative with respect to the function $V_{\text{ext}}(\mathbf{r})$ as $\delta/\delta V_{\text{ext}}(\mathbf{r})$. Applying this procedure to the free energy (33) yields

$$\frac{\delta F_N[V_{\text{ext}}]}{\delta V_{\text{ext}}(\mathbf{r})} = -k_B T \frac{\delta}{\delta V_{\text{ext}}(\mathbf{r})} \ln Z_N[V_{\text{ext}}] \quad (36)$$

$$= -\frac{k_B T}{Z_N[V_{\text{ext}}]} \frac{\delta}{\delta V_{\text{ext}}(\mathbf{r})} Z_N[V_{\text{ext}}], \quad (37)$$

where in the first step we have taken the multiplicative constant $-k_B T$ out of the derivative and in the second step have used the ordinary chain rule, which also holds for functional differentiation. We next use the explicit form (34) to obtain

$$\frac{\delta F_N[V_{\text{ext}}]}{\delta V_{\text{ext}}(\mathbf{r})} = -\frac{k_B T}{Z_N[V_{\text{ext}}]} \text{Tr}_N \frac{\delta}{\delta V_{\text{ext}}(\mathbf{r})} e^{-\beta H} \quad (38)$$

$$= -\frac{k_B T}{Z_N[V_{\text{ext}}]} \text{Tr}_N e^{-\beta H} \frac{\delta}{\delta V_{\text{ext}}(\mathbf{r})} (-\beta H) \quad (39)$$

$$= \frac{1}{Z_N[V_{\text{ext}}]} \text{Tr}_N e^{-\beta H} \frac{\delta}{\delta V_{\text{ext}}(\mathbf{r})} \sum_{i=1}^N V_{\text{ext}}(\mathbf{r}_i), \quad (40)$$

where we have first exchanged the order of the functional derivative and the phase space integral, i.e. moved the derivative inside of the trace in (38), then in the second step (39) have used the chain rule to differentiate the exponential, and in the last step (40) have exploited the structure (1) of the Hamiltonian. Moving the derivative inside of the sum over i and identifying the many-body probability distribution function Ψ according to (5) yields the final result

$$\frac{\delta F_N[V_{\text{ext}}]}{\delta V_{\text{ext}}(\mathbf{r})} = \text{Tr}_N \Psi \sum_i \delta(\mathbf{r} - \mathbf{r}_i) \equiv \rho(\mathbf{r}), \quad (41)$$

where we have used one central rule of functional differentiation: differentiating a function by itself gives $\delta V_{\text{ext}}(\mathbf{r}_i)/\delta V_{\text{ext}}(\mathbf{r}) = \delta(\mathbf{r} - \mathbf{r}_i)$, where the result $\delta(\cdot)$ is the Dirac delta distribution (here in three dimensions, as its argument is a three-dimensional vector).

Notably in (41) we have arrived at the form of a thermal average over the statistical ensemble; recall the generic form exemplified by the average internal energy (9). Rather than the expectation value of the Hamiltonian, the present case represents the average of the microscopically resolved density operator $\sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i)$, which can be viewed as an indicator function that measures whether any particle resides at the given position \mathbf{r} . The result of the average is the one-body density distribution, or in short the density profile $\rho(\mathbf{r})$. That functional differentiation yields useful, spatially-resolved ('correlation') functions is a general mechanism. See e.g. [13] for much background on correlation functions and their generation via functional differentiation. Reference [14] carries this concept much further than we do here.

We return to the shifting symmetry operation of above, but now monitor the system response via tracking the changes in the function $V_{\text{ext}}(\mathbf{r})$ that are induced by the spatial shifting. Recall the elementary Taylor expansion

$$V_{\text{ext}}(\mathbf{r} + \boldsymbol{\epsilon}) = V_{\text{ext}}(\mathbf{r}) + \boldsymbol{\epsilon} \cdot \nabla V_{\text{ext}}(\mathbf{r}), \quad (42)$$

where ∇ indicates the derivative (gradient) with respect to \mathbf{r} and we have truncated at linear order. See figure 2 for an illustration. The first order term in (42) can be viewed as a local change in the external potential, $\delta V_{\text{ext}}(\mathbf{r})$, which is given by

$$\delta V_{\text{ext}}(\mathbf{r}) \equiv \boldsymbol{\epsilon} \cdot \nabla V_{\text{ext}}(\mathbf{r}). \quad (43)$$

In order to capture the resulting effect on the functional, we can functionally Taylor expand the dependence of the free energy on $V_{\text{ext}}(\mathbf{r}) + \delta V_{\text{ext}}(\mathbf{r})$ around the function $V_{\text{ext}}(\mathbf{r})$. To linear order in $\delta V_{\text{ext}}(\mathbf{r})$ the functional Taylor expansion reads

$$F_N[V_{\text{ext}} + \delta V_{\text{ext}}] = F_N[V_{\text{ext}}] + \int d\mathbf{r} \frac{\delta F_N[V_{\text{ext}}]}{\delta V_{\text{ext}}(\mathbf{r})} \delta V_{\text{ext}}(\mathbf{r}) \quad (44)$$

$$= F_N[V_{\text{ext}}] + \int d\mathbf{r} \rho(\mathbf{r}) \boldsymbol{\epsilon} \cdot \nabla V_{\text{ext}}(\mathbf{r}), \quad (45)$$

where in (45) we have used the explicit form (43) of $\delta V_{\text{ext}}(\mathbf{r})$ as it arises from the fact that the variation in the shape of the

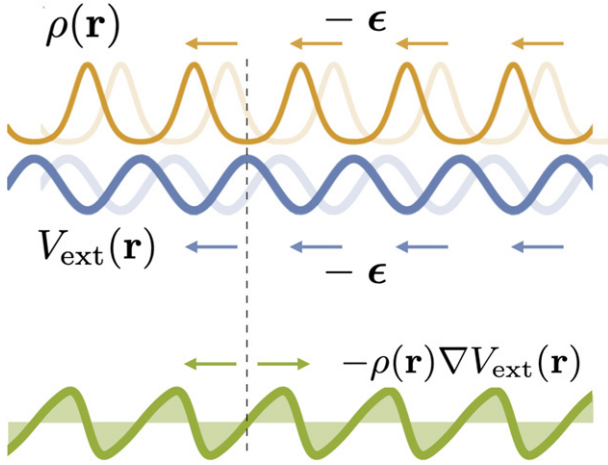


Figure 2. Illustration of the shifting. A sinusoidal external potential $V_{\text{ext}}(\mathbf{r})$ (blue lines) is spatially displaced by a displacement $-\epsilon$ (blue arrows). The density profile $\rho(\mathbf{r})$ (amber lines) measures the local probability to find a particle; it hence has e.g. peaks at the troughs of the external potential and it is shifted accordingly (amber arrows). Also shown is the magnitude of the external force density $-\rho(\mathbf{r})\nabla V_{\text{ext}}(\mathbf{r})$ (green line); the green arrows represent its local direction. The horizontal dashed line is a guide that indicates the position of locally vanishing external force density.

external potential is specifically generated by a spatial displacement, cf (42). Furthermore we have used (41) to identify the functional derivative in (44) as the density profile.

The result (45) is based on the properties of functional calculus alone. Hence the identity is general and holds, to linear order in ϵ , irrespective of any invariance properties. For the case of the total free energy, which as we have shown above in (19) is invariant under spatial displacement, we have

$$F_N[V_{\text{ext}}] = F_N[V_{\text{ext}} + \delta V_{\text{ext}}], \quad (46)$$

where $\delta V_{\text{ext}}(\mathbf{r})$ is generated from the spatial displacement of the system, cf (43). Hence (43) together with (46) express in functional language the translational symmetry properties of the free energy.

From the identity (46) and the linear Taylor expansion (45) we can conclude that the correction term needs to vanish,

$$\int d\mathbf{r} \rho(\mathbf{r}) \epsilon \cdot \nabla V_{\text{ext}}(\mathbf{r}) = 0. \quad (47)$$

The displacement vector ϵ is arbitrary, as there was no restriction on the direction of the shift. Hence the above expression can only identically vanish provided that [14, 66]

$$\mathbf{F}_{\text{ext}}^{\text{o}} = - \int d\mathbf{r} \rho(\mathbf{r}) \nabla V_{\text{ext}}(\mathbf{r}) = 0, \quad (48)$$

where we have multiplied by -1 in order to identify the one-body expression for the total external force $\mathbf{F}_{\text{ext}}^{\text{o}}$; the equivalence with the many-body form (12) is straightforward to show upon using the definition of the density profile (41). See figure 2 for an illustration of the local force density profile, i.e. the integrand of (48).

2.4. Application to sedimentation

We exemplify the general result (48) using the concrete example of a thermal system under gravity, such that sedimentation-diffusion equilibrium is reached. Recall that we consider systems at finite temperature, where entropic effects compete with ordering generated by the potential energy. We first omit the interparticle interactions, and hence consider the classical monatomic ideal gas. We assume that the external potential consists of a gravitational contribution, mgz , where g indicates the gravitational acceleration and z is the height variable. Furthermore due to the presence of a lower container wall, there is a repulsive contribution, which we take to be a harmonic potential with spring constant α acting ‘inside’ the wall, i.e. at altitudes $z < 0$. Hence the specific form of the total external potential is

$$V_{\text{ext}}(z) = mgz + \frac{\alpha z^2}{2} \Theta(-z), \quad (49)$$

where $\Theta(\cdot)$ indicates the Heaviside (unit step) function, which ensures that the parabolic potential only acts for $z < 0$. There is no need for the presence of an upper wall to close the system, as gravity alone already ensures that $V_{\text{ext}} \rightarrow \infty$ for $z \rightarrow \infty$. The magnitude of the external force field is obtained as $-V'_{\text{ext}}(z) = -mg - \alpha z \Theta(-z)$, see figure 3 for an illustration (blue line).

The density distribution of the isothermal ideal gas is given by the generalized barometric law [13],

$$\rho(z) = \Lambda^{-3} e^{-\beta(V_{\text{ext}}(z) - \mu)}, \quad (50)$$

where Λ is the thermal de Broglie wavelength which arises from carrying out the momentum integrals in Tr_N (this is analytically possible due to the simple kinetic energy part of the Boltzmann factor). The chemical potential μ in (50) is a constant that ensures the correct normalization, $\int dz \rho(z) = N/A$, where A is the lateral system size (i.e. the area perpendicular to the z -direction). That the value of the chemical potential μ controls the number of particles in the system is universal. However, the mathematical formulation in the grand ensemble, where the particle number in the system can fluctuate, is very different from the present canonical treatment. (Some basics of the grand canonical description, as used in reference [14], are described below in section 2.6.)

The general expression for the total external force (48) together with the specific density profile (50) gives

$$\mathbf{F}_{\text{ext}}^{\text{o}} = - \frac{A \mathbf{e}_z}{\Lambda^3} \int_{-\infty}^{\infty} dz e^{-\beta(V_{\text{ext}}(z) - \mu)} V'_{\text{ext}}(z) \quad (51)$$

$$= \frac{A \mathbf{e}_z}{\Lambda^3 \beta} \left[e^{-\beta(V_{\text{ext}}(z) - \mu)} \right]_{-\infty}^{\infty} \quad (52)$$

$$= 0, \quad (53)$$

where \mathbf{e}_z is the unit vector pointing into the positive z -direction and the prime denotes differentiation with respect to the argument, hence $\nabla V_{\text{ext}}(\mathbf{r}) = V'_{\text{ext}}(z) \mathbf{e}_z$. The integrand in (51) is a total differential, $d e^{-\beta(V_{\text{ext}} - \mu)} / dz$, which upon integration gives

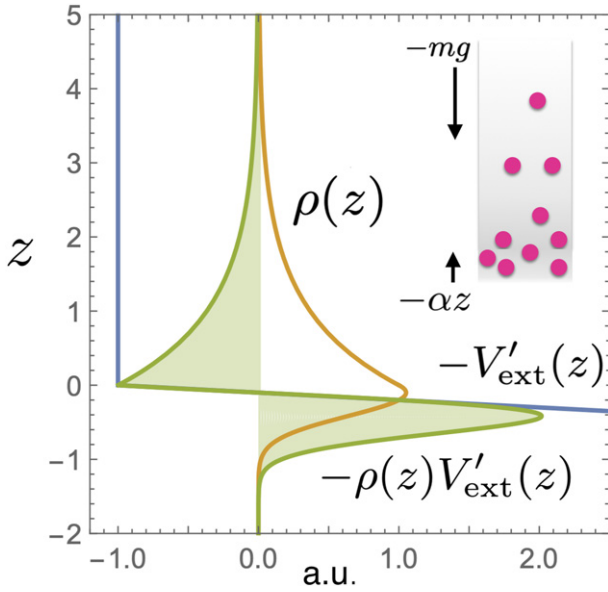


Figure 3. Illustration of sedimentation of a fluid against a lower soft wall represented by a harmonic potential. The total external potential is $V_{\text{ext}}(z) = mgz + \Theta(-z)\alpha z^2/2$. The resulting external force field is $-V'_{\text{ext}}(z) \equiv -\partial V_{\text{ext}}(z)/\partial z = -mg - \Theta(-z)\alpha z$ (blue line). The direction of both force contributions is indicated in the inset (arrows), where pink dots represent particles. In the main plot the density profile $\rho(z)$ (amber line) decays for large and for small values of z . The external force density is the product $-\rho(z)V'_{\text{ext}}(z)$ (green line). The total external force (per unit area) is the integral $-\int dz V'_{\text{ext}}(z)\rho(z) = 0$; note that the shaded green areas cancel each other. Representative values of the parameters are chosen; the unit of length is the sedimentation length $k_B T/(mg)$ and all energies are scaled with $k_B T$.

(52); for (53) we have exploited that for $z \rightarrow \pm\infty$ the external potential $V_{\text{ext}} \rightarrow \infty$, leading to vanishing Boltzmann factor. We have hence shown explicitly the vanishing of the total external force acting on a bounded ideal gas in thermal equilibrium under gravity. Figure 3 illustrates the density profile $\rho(z)$ and the force density profile $-V'_{\text{ext}}(z)\rho(z)$ for representative values of the parameters.

We briefly sketch the effect of interparticle interactions. On a formal level, and returning to the general case of arbitrary form of $V_{\text{ext}}(\mathbf{r})$, the density profile is given by a modified form of (50), which reads

$$\rho(\mathbf{r}) = \Lambda^{-3} e^{-\beta(V_{\text{ext}}(\mathbf{r})-\mu)+c_1(\mathbf{r})}, \quad (54)$$

where the so-called one-body direct correlation function [11, 13] $c_1(\mathbf{r})$ contains the effects of the interparticle interactions. The total interparticle force density is then given by

$$\mathbf{F}_{\text{int}}^0 = k_B T \int d\mathbf{r} \rho(\mathbf{r}) \nabla c_1(\mathbf{r}) = 0. \quad (55)$$

Here the vanishing of the total internal force can be viewed as a consequence of Newton's third law *actio equals reactio*; see reference [14] for the derivation. Note the formal similarity of the total external and total intrinsic force Noether sum rules, cf (48) and (55). The no-bootstrap theorem (55) holds beyond equilibrium, as shown in reference [14], and it hence debunks any swamp escape myths.

An alternative derivation of (55) rests on the Noether invariance of the free energy, where the latter is constructed to be a functional of the density profile; we refer the reader to reference [14] for a description of these considerations and comment briefly on the embedding into the frameworks of classical density functional theory and power functional theory below in section 2.6.

2.5. Relationship to correlation functions

Global identities, such as the sum rules of vanishing external force (48) and of vanishing internal force (55), can be used as a starting point to obtain position-resolved identities. Functional differentiation with respect to an appropriate field creates dependence on position. Integrating over these additional variables (or 'root points' [13]) then yields novel global identities. While we refer the reader to reference [14] for this treatment, we wish to demonstrate here the direct derivation of such global identities.

We stick to the canonical ensemble and as a specific case return to our initial example of a thermal average, i.e. the global external potential energy U_{ext} , as equivalently expressed in compact notation (10) or the explicitly written out phase space integral (11). Let us shift! The external energy in the new system is then given by

$$U_{\text{ext}}(\epsilon) = \text{Tr}_N \frac{e^{-\beta H(\epsilon)}}{Z_N(\epsilon)} \sum_{i=1}^N V_{\text{ext}}(\mathbf{r}_i - \epsilon). \quad (56)$$

We Taylor expand to first order,

$$U_{\text{ext}}(\epsilon) = U_{\text{ext}} + \left. \frac{\partial U_{\text{ext}}(\epsilon)}{\partial \epsilon} \right|_{\epsilon=0} \cdot \epsilon. \quad (57)$$

Here the derivative of (56) can be calculated via the product rule as

$$\begin{aligned} \left. \frac{\partial U_{\text{ext}}(\epsilon)}{\partial \epsilon} \right|_{\epsilon=0} &= \text{Tr} \frac{\partial \Psi(\epsilon)}{\partial \epsilon} \sum_{i=1}^N V_{\text{ext}}(\mathbf{r}_i) \\ &\quad - \text{Tr} \Psi \sum_{i=1}^N \nabla_i V_{\text{ext}}(\mathbf{r}_i). \end{aligned} \quad (58)$$

We can recognize the second term as the average external force, which we have proven to vanish, cf (27). The first term in (58) requires carrying out the derivative of $\Psi(\epsilon)$ with respect to the displacement ϵ , which yields

$$\left. \frac{\partial U_{\text{ext}}(\epsilon)}{\partial \epsilon} \right|_{\epsilon=0} = -\text{Tr} \Psi \sum_{i=1}^N \beta V_{\text{ext}}(\mathbf{r}_i) \sum_{j=1}^N \nabla_j V_{\text{ext}}(\mathbf{r}_j). \quad (59)$$

Here an additional term, generated by the derivative, vanishes: $-\beta U_{\text{ext}} \mathbf{F}_{\text{ext}}^0 = 0$, again due to (27).

Clearly (59) is the correlator of the global external potential energy and the global external force. Using the by now familiar invariance argument, we argue that the value of $U_{\text{ext}}(\epsilon)$ is an invariant under the displacement, and that hence the first order

term in (57) needs to be zero. As ϵ is arbitrary, we conclude

$$-\text{Tr} \Psi \sum_{i=1}^N V_{\text{ext}}(\mathbf{r}_i) \sum_{j=1}^N \nabla_j V_{\text{ext}}(\mathbf{r}_j) = 0, \quad (60)$$

where we have divided by β . Hence the global external potential, $\sum_i V_{\text{ext}}(\mathbf{r}_i)$, and the global external force, $-\sum_j \nabla_j V_{\text{ext}}(\mathbf{r}_j)$, are uncorrelated with each other. The sum rule (60) is derived in reference [14] via the route of integration over free position variables (root points), cf (5) in reference [14] for the order $n = 2$ of the sum rule hierarchy. An important distinction in the presentation though lies in the choice of ensemble, which is an issue to which we turn in the next subsection.

As a final comment, when applied to the above example of sedimentation against a lower harmonic wall, (60) can be explicitly verified by carrying out the z -integral, which yields $-A \int_{-\infty}^{\infty} dz \rho(z) V_{\text{ext}}(z) V'_{\text{ext}}(z) = 0$.

2.6. Density functional and power functional

In all of the above, we have described the thermal system on the basis of the canonical ensemble, as specified by the classical phase space, the probability distribution (5) and the canonical partition sum (6). Hence the system is coupled to a heat bath at temperature T , where the value of T determines the mean energy E in the system, cf the form of E as an expectation value (7). The system is thermally open, and hence energy fluctuations occur between system and bath.

Corresponding fluctuations in particle number N can be implemented in the grand canonical ensemble where the system is furthermore coupled to a particle bath. The particle bath sets the value of the chemical potential μ , which then determines the average number of particles \bar{N} in the system. (This mechanism is analogous to the relationship of T and E described above.) Although the grand canonical formalism poses this additional level of abstraction, and the bare formulae increase somewhat in complexity due to the average over N , in typical theoretical developments this framework is significantly more powerful and more straightforward to use. (There is no need having to implement $N = \text{const}$, which in practice can be awkward.) We briefly sketch the essentials of the grand ensemble as they underlie reference [14].

The grand canonical ensemble consists of the microstates given by phase space points of N particles, with N being a non-negative integer, which is treated as a random variable. The corresponding probability distribution is

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N, \mathbf{p}_1, \dots, \mathbf{p}_N, N) = \frac{e^{-\beta(H-\mu N)}}{\Xi}, \quad (61)$$

where the grand partition sum is given by

$$\Xi = \text{Tr} e^{-\beta(H-\mu N)}, \quad (62)$$

with the grand canonical trace operation defined by

$$\text{Tr} = \sum_{N=0}^{\infty} \text{Tr}_N \quad (63)$$

$$= \sum_{N=0}^{\infty} \frac{1}{h^{3N} N!} \int d\mathbf{r}_1 \dots d\mathbf{r}_N d\mathbf{p}_1 \dots d\mathbf{p}_N, \quad (64)$$

where we have obtained (64) by using the explicit form (8) for the canonical trace. The thermodynamic potential which is fundamental for the grand ensemble is the grand potential (also referred to as the grand canonical free energy) and it is given by

$$\Omega = -k_B T \ln \Xi, \quad (65)$$

with the grand partition sum Ξ according to (62). Note the strong formal analogy with the corresponding canonical expressions for: the probability distribution (5) with (61); the partition sum (6), i.e. $Z_N = \text{Tr}_N e^{-\beta H}$, with (62); the trace (8) with (63); and the free energy (14) with (65).

Despite the system being open to particle exchange, Noether's reasoning continues to hold [14]. Briefly, the grand potential is a functional of the external potential, $\Omega[V_{\text{ext}}]$ (we suppress the dependence on the thermodynamic parameters μ, T), and $\Omega[V_{\text{ext}}]$ is invariant under spatial displacements according to (15). As a consequence, the sum rule of vanishing external force (13) emerges, expressed in the form (27) with Tr_N replaced by Tr , as is appropriate for the open system.

Why is the functional point of view important? In what we have presented above it had played the role of adding abstraction and re-deriving results that we could obtain via more elementary arguments. The importance of the variational formulation stems from two sources, one being that it provides a mechanism for the generation of correlation functions via functional differentiation, in extension of the generation of the density profile via (41), see e.g. references [13] for a comprehensive account. The second point lies in the variational principle itself which formulates the many-body problem in a way that allows to systematically introduce approximations and make much headway in identifying and studying physical mechanisms in complex, coupled many-body problems. While giving a self-contained overview of these concepts is beyond the scope of the present contribution (see reference [31] for a recent account), we wish to briefly describe certain central points, to—hopefully—provide motivation for further study.

We hence sketch the two variational principles as they are relevant for equilibrium (classical density functional theory) and for the dynamics (power functional theory); these form the basis of reference [14]. Classical density functional theory is based on treating the density profile $\rho(\mathbf{r})$, rather than the external potential $V_{\text{ext}}(\mathbf{r})$, as the fundamental variational field. The grand potential, when viewed as a density functional [11, 12], has the form

$$\Omega[\rho] = F[\rho] + \int d\mathbf{r} \rho(\mathbf{r})(V_{\text{ext}}(\mathbf{r}) - \mu), \quad (66)$$

where $F[\rho]$ is the intrinsic Helmholtz free energy functional. Crucially, $F[\rho]$ is independent of the external potential, which

features solely in the second term in (66). Here $\rho(\mathbf{r})$ is conceptually treated as a variable; its true form as the equilibrium density profile is that which minimizes $\Omega[\rho]$ and for which hence the functional derivative vanishes,

$$\frac{\delta\Omega[\rho]}{\delta\rho(\mathbf{r})} = 0 \quad (\text{min}). \quad (67)$$

Inserting the split form (66) of the grand potential into the minimization condition (67) and using the splitting into ideal gas and excess (over ideal gas) free energy contributions, $F[\rho] = k_B T \int d\mathbf{r} \rho(\mathbf{r}) [\ln(\rho(\mathbf{r})\Lambda^3) - 1] + F_{\text{exc}}[\rho]$, yields upon exponentiating the modified barometric law (54). Here the one-body direct correlation function $c_1(\mathbf{r})$ is identified as the functional derivative of the excess free energy functional, i.e. $c_1(\mathbf{r}) = -\beta\delta F_{\text{exc}}[\rho]/\delta\rho(\mathbf{r})$. As the functional dependence on the density profile persists upon building the derivative, i.e. in more explicit notation $c_1(\mathbf{r}, [\rho])$, equation (54) constitutes a self-consistency condition for the determination of the equilibrium density profile; determining the solution thereof requires to have an approximation for $F_{\text{exc}}[\rho]$ and typically involves numerical work.

Power functional theory generalizes the variational concept of working on the level of one-body correlation functions to nonequilibrium. For overdamped Brownian motion, as is a simple model for the description for the temporal behaviour of mesoscopic particles that are suspended in a liquid, the free power is a functional of both the time-dependent density profile $\rho(\mathbf{r}, t)$ and of the locally resolved current distribution $\mathbf{J}(\mathbf{r}, t)$, where t indicates time. The power functional has the form

$$R_t[\rho, \mathbf{J}] = \dot{F}[\rho] + P_t[\rho, \mathbf{J}] - \int d\mathbf{r} (\mathbf{J}(\mathbf{r}, t) \cdot \mathbf{f}_{\text{ext}}(\mathbf{r}, t) - \rho(\mathbf{r}, t) \dot{V}_{\text{ext}}(\mathbf{r}, t)), \quad (68)$$

where $\dot{F}[\rho]$ is the time derivative of the intrinsic free energy functional, $P_t[\rho, \mathbf{J}]$ consists of an ideal gas and a superadiabatic part, where the latter arises from the internal interactions in the nonequilibrium situation, $\mathbf{f}_{\text{ext}}(\mathbf{r}, t)$ is a time-dependent external one-body force field, which in general consists of a (conservative) gradient term $-\nabla V_{\text{ext}}(\mathbf{r}, t)$ and an additional rotational (non-gradient, non-conservative) contribution, and $\dot{V}_{\text{ext}}(\mathbf{r}, t)$ is the time derivative of the external potential. The density profile and the current distribution are linked by the continuity equation, $\partial\rho(\mathbf{r}, t) = -\nabla \cdot \mathbf{J}(\mathbf{r}, t)$, which is sharply resolved on the microscopic scale. The dynamic variational principle states that $R_t[\rho, \mathbf{J}]$ is minimized, at time t , by the physically realized current,

$$\frac{\delta R_t[\rho, \mathbf{J}]}{\delta \mathbf{J}(\mathbf{r}, t)} = 0 \quad (\text{min}). \quad (69)$$

Inserting the splitting (68) of the total free power into the minimization condition (69) yields the formally exact force density relationship,

$$\gamma \mathbf{J}(\mathbf{r}, t) = -k_B T \nabla \rho(\mathbf{r}, t) + \mathbf{F}_{\text{int}}(\mathbf{r}, t) + \rho(\mathbf{r}, t) \mathbf{f}_{\text{ext}}(\mathbf{r}, t), \quad (70)$$

where γ is the friction constant of the overdamped motion, such that the left-hand side constitutes the (negative) friction force density at position \mathbf{r} and time t . The right-hand side of (70) consists of an ideal, an internal and an external driving contribution, with $\mathbf{F}_{\text{int}}(\mathbf{r}, t)$ being the internal force density distribution, as it arises from the effect of all interparticle interactions that act on a given particle at position \mathbf{r} and time t . The internal force density $\mathbf{F}_{\text{int}}(\mathbf{r}, t)$ consists of an adiabatic contribution, which follows from the excess free energy functional via $\mathbf{F}_{\text{ad}}(\mathbf{r}, t) = -\rho(\mathbf{r}, t) \nabla \delta F[\rho]/\delta\rho(\mathbf{r}, t)$ and an additional genuine nonequilibrium contribution, i.e. the superadiabatic force density, $\mathbf{F}_{\text{sup}}(\mathbf{r}, t)$. Honoring its functional dependence on the kinematic fields $\rho(\mathbf{r}, t)$ and $\mathbf{J}(\mathbf{r}, t)$ forms the basis for much recent work in nonequilibrium statistical mechanics based on the power functional concept. See reference [31] for an overview.

As a comment on terminology, we note that sometimes the term Euler–Lagrange equation is applied generically to refer to the vanishing of the first functional derivative of the given variational problem, i.e. equation (67) for the case of DFT and equation (69) for PFT, which respectively turn into the explicit forms (54) and (70). This terminology is different from the also frequent use of referring specifically to the Euler–Lagrange equations of motion of classical mechanics, as they result from Hamilton’s principle, i.e. the stationarity of the action functional (see e.g. the appendix of reference [31] for a description of the functional methods involved).

3. Conclusions

In conclusion, we have demonstrated on an elementary level how fundamental symmetries in statistical mechanics lead to exact statements (sum rules) about average forces when considering translations. These considerations also apply to torques when considering rotations [14]. We have based our presentation on the canonical ensemble, as is relevant in a variety of contexts [53–58]. While the canonical ensemble avoids the complexity of particle number fluctuations that occur grand canonically, nevertheless an open system is retained with respect to energy exchange with a heat bath. As we have shown, treating such fluctuating systems is well permissible on the basis of Noetherian arguments. The arguably simplest Noether sum rule is that of vanishing average total external force in thermal equilibrium. As an application we have presented the case of a fluid confined inside of a container and subject to the effect of gravity. While we have selected this example for its relative simplicity, the influence of gravity on mesoscopic soft matter is also a topic of relevance for studying e.g. complex phase behaviour in colloidal mixtures; see e.g. reference [60] for recent work that addresses colloidal liquid crystals. Our derivations imply that the symmetry operation is applied to the entire system. Here the system must be enclosed by an external potential that represents confinement by e.g. walls. The shift then applies also to these walls. In cases where system boundaries are open (as can be suitable for a periodically repeated system like that shown in figure 2), Noether’s theorem remains applicable upon taking account of additional

boundary terms, see reference [14] for a detailed discussion of such treatment.

In the presented considerations, we have started on the basis of arguably the most fundamental statistical mechanical object, i.e. the partition sum, as it enters the elementary definition of the (here canonical) free energy. Investigating invariance properties of further statistical objects, such as the global external energy, is also worthwhile, as then Noether's reasoning leads to the correlator identity (60) of vanishing correlation between global external force and global external potential. Investigating the outcome of invariance applied in this way constitutes an interesting task for future work.

Statistical mechanical derivations often rely on very similar reasoning; reference [14] gives an overview. A particularly insightful example is the work by Bryk *et al* on hard sphere fluids in contact with curved substrates [64]. These authors derive a contact sum rule of the hard sphere fluid against a hard curved wall. Their argumentation rests on the observation that the force that is necessary to move the wall by an amount ϵ is balanced by the presence of the fluid. The authors then succeed in relating this force to the value of the density profile close to the wall. Closely related work was carried out for the shape dependence of free energies [65]. Further studies that are related to Noether's theorem were aimed at broken symmetries [66] and emerging Goldstone modes [67–69].

The general form of Noether's theorem applies to variational calculus, and statistical mechanics falls well into this realm. We have spelled out the connections explicitly, such as the canonical free energy being viewed as a functional of the external potential [13]. Notably only elementary statistical objects such as the partition sum are required. We have also described two more advanced variational theories. Classical density functional theory [11–13] allows to view the grand potential as a functional of the one-body density distribution. A formally exact minimization principle then reformulates the physics of system in thermal (and chemical) equilibrium. The dynamic variational principle of power functional theory [30, 31] consists of instantaneous minimization with respect to the time- and position-resolved current distribution. Together with the continuity equation, a formally closed one-body reformulation of the dynamics of the underlying many-body system is achieved.

Both density functional theory and power functional theory can be viewed as systematic approaches to coarse-graining the many-body problem to the level of one-body correlation functions. In the static case, the correlation functions hence depend on position alone, in the dynamics case the dependence is on position and on time. Crucially, a microscopically sharp description is formally retained, which is important for the description of correlations on the particle (i.e. molecular or colloidal) level. One of the most important features of these theories is the identification of a universal intrinsic functional that contains the coupled effects of the interparticle interac-

tions, but is independent of the external forces that act on the system.

A wealth of productive research has been devoted to constructing powerful approximations for free energy functionals for specific model systems. In the context of liquids the important case of the hard sphere fluid is treated with excellent accuracy within Rosenfeld's fundamental measure theory [17, 18], see e.g. reference [61] for a quantitative assessment of the quality of theoretical density profiles against simulation data. Notable recent progress to incorporate short-ranged attraction into density functional theory is due to Tschopp, Brader and their co-workers [62, 63], who systematically addressed and exploited two-body correlations.

Despite power functional theory [30, 31] being significantly younger than density functional theory, its usefulness has been amply demonstrated, both for formal work as well as for practical solution of physical problems and the discovery of novel fundamental mechanisms. The reformulation on the basis of the velocity gradient [39], instead of the current distribution, allowed to identify and to study structural forces [40, 41] in driven systems that are governed by overdamped Brownian dynamics. The splitting of the total internal force field into flow and structural contributions is fundamental to understanding the emerging effects in microscopically inhomogeneous flows [41]. Active Brownian particles, as a model for self-propelled colloids (see e.g. [46–48]), are well suited for the application of power functional theory. The general framework [33, 34] for active systems was shown to physically explain and quantitatively predict the motility-induced phase separation that occurs in such systems at high enough levels of driving [35–37]. Interfacial properties such as polarization [38] and surface tension [35] were systematically studied.

The dynamical sum rules for forces and correlation functions presented in reference [14] offer great potential for systematic progress in the description of complex temporal behaviour, including memory [44, 45]. The nonequilibrium rules play a similar role than fundamental equilibrium sum rules such e.g. the Lovett–Mou–Buff–Wertheim equation [70, 71]. The section on 'methods' in reference [14] gives a detailed description of the relationship of the equilibrium Noether sum rules to such classical results from the liquid state literature. Together with the nonequilibrium Ornstein–Zernike relations [42, 43] the dynamical sum rules provide fertile ground for making progress in nonequilibrium many-body physics; see also the recent study of the relevance of invariance in inhomogeneous dense liquids [72] and of the role of fluctuations when going to effects that are higher than linear in the displacement [73]. Hence the fundamental character of Emmy Noether's work will surely continue to prove its worth in the future.

Acknowledgments

We thank Daniel de las Heras, Roland Roth, Gerhard Kahl, and Bob Evans for useful comments and discussions. This work is supported by the German Research Foundation (DFG) via Project Number 436306241.

Data availability statement

All data that support the findings of this study are included within the article.

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