nature portfolio

Peer Review File

Variance of fluctuations from Noether invariance

Reviewers' comments:

Reviewer #1 (Remarks to the Author):

See attached

Reviewer #2 (Remarks to the Author):

In this manuscript the authors report about an unusual application of Noether's theorem, which (put simply) states that for each symmetry transformation that leaves a functional unchanged there exists a quantity that is conserved. Noether's theorem is well established in several fields of physics, like classical mechanics and quantum mechanics, but it can be applied in other areas. The authors make great use of Noether's theorem in classical equilibrium statistical mechanics, where the starting point is the grand potential as a functional of the external potential.

The authors demonstrate the application in two ways. The first application translates the external potential by a fixed vector. One (trivial) way of looking at the problem is to argue that this translations does not change the value of the grand potential of the system in equilibrium. However, the more sophisticated way of analyzing this translation is to expand the functional in powers of the translation vector. The authors expand up to second order and thereby generate rather complicated zeros: one results in their Eq.(3) and another in Eq.(4). While the meaning of Eq.(3) is rather easy to understand, especially once the authors rewrite it in terms of total external force, Eq.(4) is more difficult to interpret. The authors help the reader with a great visual representation in Fig. 1 and with an example of the harmonic potential.

There is one point that I do not fully understand. The authors write that the Taylor expansion has to vanish identically, independent of the value of the vector epsilon that describes the shift of the external potential. Is this true even if the vector is 'large'? I would assume that in order for the argument to be true the vector has to be small, i.e. sufficiently small that changes in the grand potential due to a shift of the particles relative to the external potential can be neglected, because the grand potential in equilibrium is at a minimum. Am I mistaken, or should this statement rather be that the direction of the small vector epsilon is arbitrary so that the expansion has to vanish term by term?

I also assume that there is no need to truncate the Taylor expansion after the second order and the next term would give a more complicated sum-rule which involves a third order correlation function. Can the authors comment on that?

In the second application of the Noether theorem the authors shift the density profile by a constant vector epsilon. Again the question from above comes to mind: does the vector epsilon have to be small? The question can also be phrased as whether or not it is important that one has a variational principle. For the grand potential functional in the grand ensemble one has it because in equilibrium the grand potential is minimal, but for the intrinsic excess free energy (in the grand ensemble) there is no variational principle. Or is the external potential assumed to vanish?

In my opinion this manuscript makes an important contribution as it demonstrates that even a zero can contain interesting information and tell us about fluctuations in the system. This is potentially the material that will be in text books on statistical physics. Once the authors clarify the minor points in this report, I can highly recommend the publication of this manuscript in Communications Physics.

Reviewer #3 (Remarks to the Author):

This manuscript theoretically derives an exact relation ('sum rule') for the variance of external force in statistical mechanics, using Noether invariance. These results appear from expanding the Grand

Potential under a spatial shift, realizing that the physical properties of the system cannot change. In contrast to earlier work of the same authors, here the second order terms in such shift are considered, which yields the mentioned variances.
The paper is well written and scientifically sound. The topic is very important and relevant, and the new results are intriguing. I think that this manuscript can be a good contribution to communications physics. I would like to pass on the following comments

*) Between Eqs (1) and (2), the authors introduce a spatial displacement. Here, maybe the reader could expect some non-equilibrium situation, where the particles react in some (transient) manner to the shift. If possible, it would be good to state that one compares two equilibrium situations.

*) Eq (5): Maybe some readers would appreciate a sentence that the delta term sitting in H2 has switched sides between (4) and (5). (I think it would also make it easier to read when mentioning the relation between H2 and h before (5), but this is a matter of taste).

*) When the authors discuss Eq (5) for the harmonic trap, it smelled a bit like the equipartition theorem. Maybe, writing the Hamiltonian in terms of relative coordinates and the center of mass coordinate gives some more insights? The Hamiltonian is then quadratic in the center of mass coordinate, and maybe equipartition can be applied to find mean and variance of the external potential and external force?

*) I am a big fan of exact relations like (8), (4), or (5), and I value them strongly. But even I found myself wondering how these relations can be applied. Here, the manuscript gives a lot of suggestions at the end, but stays a bit vague. Could you give one concrete example? (maybe testing the Rosenfeld functional or some other famous candidate?). The text also mentions "validation of simulation data". How could simulation data not obey Noethers theorem?

Report for COMMSPHYS-22-0363-T
Variance of fluctuations from Noether invariance
Sophie Hermann and Matthias Schmidt

This work applies Noether's Theorem in order to determine sum rules (exact identities) for the variance in the strength of fluctuations in systems of interacting particles. Such sum rules can be important for assessing and constructing both theoretical and numerical results, as well as directing future theoretical research in the area. The authors go beyond the current state-of-the-art, which tackles averages of quantities such as the internal energy of the system, to deal with the strength of the associated fluctuations. This is done by considering the variance (or autocorrelation) of such quantities when one performs a perturbative expansion up to second order, rather than only to first order as is standard in the literature. In particular, they study the grand potential as a functional of the external potential and the excess free energy in terms of the one-body density. The authors also highlight that whilst, in principal, some of the results presented here could be derived from previous results (such as those in [22]), Noether's theorem provides a *systematic and constructive* way in which to obtain such sum rules.

I find the manuscript to be very clearly written, whilst also being a concise description of the derivation and results. The results themselves are interesting and likely of use to both theoreticians and those developing numerical schemes in areas of statistical mechanics such as (Dynamic) Density Functional Theory.

I have struggled to find anything to criticise in the manuscript, or, indeed, any improvements to suggest. As such, apart from the minor typos listed below, I recommend the manuscript for publication.

Minor points:

- [p1] 'the the asymmetry of quantum states'.
- [p2, Fig 1 caption] should be 'weighted' rather than 'weighed by the local density'.
- [p3] 'up to second *order* in' (rather than 'oder').

Replies to Reviewers' comments:

Reviewer #1 (Remarks to the Author):

We cordially thank the Referee for the efforts in producing the report and we are delighted by the positive assessment. We acknowledge the Referee's depth of understanding of our work. We thank the Referee for pointing out several typos, which we have fixed in the revision.

> This work applies Noether's Theorem in order to determine sum rules (exact identities) for the variance in the strength of fluctuations in systems of interacting particles. Such sum rules can be important for assessing and constructing both theoretical and numerical results, as well as directing future theoretical research in the area. The authors go beyond the current state-of-the-art, which tackles averages of quantities such as the internal energy of the system, to deal with the strength of the associated fluctuations. This is done by considering the variance (or autocorrelation) of such quantities when one performs a perturbative expansion up to second order, rather than only to first order as is standard in the literature. In particular, they study the grand potential as a functional of the external potential and the excess free energy in terms of the one-body density. The authors also highlight that whilst, in principal, some of the results presented here could be derived from previous results (such as those in [22]), Noether's theorem provides a systematic and constructive way in which to obtain such sum rules.

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> *) [p3] 'up to second order in' (rather than 'oder').

Reviewer #2 (Remarks to the Author):

We thank the Referee for a critical reading of our paper, for raising

several relevant and interesting points, and for the positive evaluation of our work. We have performed changes to the manuscript in reaction to the Referee's points and we give a detailed point-by-point response in the following.

> In this manuscript the authors report about an unusual application of Noether's theorem, which (put simply) states that for each symmetry transformation that leaves a functional unchanged there exists a quantity that is conserved. Noether's theorem is well established in several fields of physics, like classical mechanics and quantum mechanics, but it can be applied in other areas. The authors make great use of Noether's theorem in classical equilibrium statistical mechanics, where the starting point is the grand potential as a functional of the external potential.

> The authors demonstrate the application in two ways. The first application translates the external potential by a fixed vector. One (trivial) way of looking at the problem is to argue that this translations does not change the value of the grand potential of the system in equilibrium. However, the more sophisticated way of analyzing this translation is to expand the functional in powers of the translation vector. The authors expand up to second order and thereby generate rather complicated zeros: one results in their Eq.(3) and another in Eq.(4). While the meaning of Eq.(3) is rather easy to understand, especially once the authors rewrite it in terms of total external force, Eq.(4) is more difficult to interpret. The authors help the reader with a great visual representation in Fig. 1 and with an example of the harmonic potential.

> There is one point that I do not fully understand. The authors write that the Taylor expansion has to vanish identically, independent of the value of the vector epsilon that describes the shift of the external potential. Is this true even if the vector is 'large'? I would assume that in order for the argument to be true the vector has to be small, i.e. sufficiently small that changes in the grand potential due to a shift of the particles relative to the external potential can be neglected, because the grand potential in equilibrium is at a minimum. Am I mistaken, or should this statement rather be that the direction of the small vector epsilon is arbitrary so that the expansion has to vanish term by term?

This is a good point that addresses the core of our argument and we wish to clarify. Indeed epsilon can be finite ("large") and of arbitrary direction. Let us go into detail why this is the case. The Referee describes correctly that a priori only the external potential is shifted. Taken as a bare operation one could be mislead to think that the system changes substantially, as a given particle location will be associated with a different value of the external potential. (This is true whether one has an infinitesimal effect if epsilon is small or a finite effect if epsilon is finite.) So at first sight, one might think that as a consequence of the change of energy the Boltzmann factor also changes and so does the grand potential. This is

not true though, which one can see by considering that the partition sum is obtained via integration over the entire phase space. Hence the "analog" of a given microstate in the original system is a shifted microstate in the shifted system, where besides the shift of the external potential also all coordinates were shifted. Trivially the value of the Hamiltonian then stays the same, and hence the grand potential is unchanged. As the phase space integral over the coordinates runs over all values (i.e. all real numbers for each coordinate) there is no need to perform an explicit coordinate shift. The shifted state occurs anyway in the phase space integral. We have made this situation clearer in the manuscript by adding the following text (p.2).

> "The invariance with respect to the displacement can be explicitly seen by transforming each position integral in the trace over phase space as \int dr_i = \int d(r_i – epsilon). No boundary terms occur as the integral is over R^3; the effect of system walls is explicitly contained in the form of V_ext(r). This coordinate shift formally "undoes" the spatial system displacement and it renders the form of the partition sum identical to that of the original system. (See reference [24] for the generalization from homogeneous shifting to a position-dependent strain operation.)"

The Referee's further point about the relevance of the orientation of epsilon is also important. The above argument shows that the direction of the shift is arbitrary, as is the magnitude of epsilon. This means that one could displace a nanoscopic system by a macroscopic distance (e.g. move a test vial to a different lab) and not change anything. The shifting operation is constructed in a way that the entirety of the "environment" (as solely represented by V_ext(r) on the present level of description) is moved. As a detail, were one to restrict epsilon along a given fixed orientation, then instead of a vectorial sum rule, one would arrive only at a restricted version of that same sum rule, projected on the given orientation. However, as we have laid out, there is no need for introducing such restrictions.

> I also assume that there is no need to truncate the Taylor
> expansion after the second order and the next term would give a
> more complicated sum-rule which involves a third order correlation
> function. Can the authors comment on that?

This is a good point. Yes, the Referee is entirely correct. Addressing the invariance of the third order term in the same way generates a further (third order) sum rule and the procedure leads naturally to a hierarchy of sum rules. For ease of presentation we had originally omitted to raise this point, but we agree that mentioning such higher-order sum is relevant both as these could be important and also for re-emphasizing that epsilon can be finite (see the previous point), and hence all orders in the Taylor expansion can be analysed to meaningful effect.

We have hence added the following discussion to the end of the

manuscript (p.4).

> "As the displacement vector epsilon is arbitrary both in its
> orientation and its magnitude our reasoning does not stop at
> second order in the Taylor expansion, see Eqs. (2) and
> (6). Assuming that the power series exists, the invariance against
> the displacement rather implies that each order vanishes
> individually, which gives rise to a hierarchy of correlation
> identities of third, fourth, etc. moments that are interrelated
> with third, fourth, etc. derivatives of the external potential
> (when starting from Omega[Vext]) or the one-body direct
> correlation function (when starting from the excess free energy
> density functional F_exc[rho]).

> In the second application of the Noether theorem the authors shift
> the density profile by a constant vector epsilon. Again the
> question from above comes to mind: does the vector epsilon have to
> be small? The question can also be phrased as whether or not it is
> important that one has a variational principle. For the grand
> potential functional in the grand ensemble one has it because in
> equilibrium the grand potential is minimal, but for the intrinsic
> excess free energy (in the grand ensemble) there is no variational
> principle. Or is the external potential assumed to vanish?

These are all very good points and we acknowledge once more the Referee's depth of critical thinking in going through our arguments. The core of the argument that clarifies all these points is the recognition of the functional dependence of the relevant functional. In the point discussed above it is Omega[V_ext] and hence the only and complete way to change the system is by displacing the function V_ext(r). The coordinates will follow "automatically" according to the corresponding shifted thermal distribution. In this case the density profile "responds" to the shift of the external potential by a corresponding shift. This effect is "automatic" as the shifted V_ext(r) will generate the shifted density profile.

The Referee's present point addresses the free energy functional. Here the situation is different, as the excess contribution F_exc[rho] is according to the Mermin-Evans map of classical DFT a functional solely of the density profile, and is hence independent of the external potential. Thus the density functional F_exc[rho] carries knowledge of absolute position only via the dependence of the density profile on the position coordinate, rho(r). Hence displacing the density profile is all that one needs to do (and indeed all that one can do) in order to shift the entire system. There is no need (and no possibility) to actively also shift the external potential. This is in full analogy to the above case of Omega[V_ext], where the conjugate field is shifted "automatically", hence the displacement of the corresponding V_ext(r) that is associated with the shifted density profile is an outcome rather than an input to the argument and indeed to the calculation. On a formal level, seeing this is straightforward by considering the Euler-Lagrange minimization equation of classical DFT. We lay this out in the revised manuscript as follows.

"As a conceptual point concerning the derivations of Eqs. (7) and (8), we point out that the excess free energy density functional F_exc[rho] is an intrinsic quantity, which does not explicitly depend on the external potential V_ext(r). Hence there is no need to explicitly take into account a corresponding shift of V_ext(r). This is true despite the fact that in an equilibrium situation one would consider the external potential (and the correspondingly generated external force field) as the physical reason for the (inhomogeneous) density profile to be stable. Both one-body fields are connected via the (Euler-Lagrange) minimization equation of density functional theory [26–28]: kT ln rho(r) = kT c_1(r) – V_ext(r) + mu, where we have set the thermal de Broglie wavelength to unity. For given density profile, we can hence trivially obtain the corresponding external potential as V_ext(r) = –kT ln rho(r)+kT c_1(r) + mu, which makes the fundamental Mermin-Evans [26–29] map rho(r) \to V_ext(r) explicit."

This text also clarifies the Referee's further points. We make explicit that we do not assume the external potential to vanish. Rather considering the external potential explicitly is not required in the argument that we present. (The above explanation "only" serves to guide physical intuition.) Importantly, while the above explanation indeed requires the variational principle, this is not true for the bare Noether argument. Exploiting the symmetry of the functional itself "only" requires the identification of the symmetry of the given functional. This analysis is indeed independent of whether or not there is a variational principle. Of course in terms of practical use, the functionals in physics typically come with a corresponding variational principle, so in order to not confuse general and maybe also casual readers we have shied away from adding this discussion.

> In my opinion this manuscript makes an important contribution as
> it demonstrates that even a zero can contain interesting
> information and tell us about fluctuations in the system. This is
> potentially the material that will be in text books on statistical
> physics. Once the authors clarify the minor points in this report,
> I can highly recommend the publication of this manuscript in
> Communications Physics.

We are grateful for the positive recommendation and once more thank the Referee for their very constructive role in raising all the above interesting points.

Reviewer #3 (Remarks to the Author):

We thank the Referee for a critical reading of our paper, for raising several relevant and interesting points, as well as for the positive

assessment of our work. We respond in detail to all points below.

> This manuscript theoretically derives an exact relation ('sum
> rule') for the variance of external force in statistical
> mechanics, using Noether invariance. These results appear from
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> the following comments

> *) Between Eqs (1) and (2), the authors introduce a spatial
> displacement. Here, maybe the reader could expect some
> non-equilibrium situation, where the particles react in some
> (transient) manner to the shift. If possible, it would be good
> to state that one compares two equilibrium situations.

Yes, we agree that we should avoid any confusion about the nature of the shift, which is here -as the Referee correctly points out- entirely static, without addressing any real dynamics. We have hence added the following statement to the manuscript.

"Throughout we do not consider the dynamics of the shifting and rather only compare statically the original with the displaced system, with both being in equilibrium. (Ref. [22] presents dynamical Noether sum rules that arise from invariance of the power functional [29] at first order in a time-dependent shifting protocol epsilon(t).)"

> *) Eq (5): Maybe some readers would appreciate a sentence that the
> delta term sitting in H2 has switched sides between (4) and
> (5). (I think it would also make it easier to read when
> mentioning the relation between H2 and h before (5), but this is
> a matter of taste).

This is a good point and we share the Referee's taste in this matter. We have hence moved the definition of the relationship between H_2 and h up in the flow of arguments and also point out the switching of sides of the delta term. These additions (p.2, above Eq.(5)) read as follows.

"It is standard practice [26–29] to split off the trivial density covariance of the ideal gas and define the total correlation function h(r, r’) via the identity H_2(r, r’) = rho(r)rho(r’)h(r, r’) + rho(r)delta(r – r’). Insertion of this relation into Eq. (4) and then moving the term with the delta function to the right hand side yields the following alternative form of the second order

Noether sum rule: [Eq.(5) as before]"

> *) When the authors discuss Eq (5) for the harmonic trap, it
> smelled a bit like the equipartition theorem. Maybe, writing the
> Hamiltonian in terms of relative coordinates and the center of
> mass coordinate gives some more insights? The Hamiltonian is
> then quadratic in the center of mass coordinate, and maybe
> equipartition can be applied to find mean and variance of the
> external potential and external force?

This is an intriguing thought and we agree with the Referee's premises. We have tried to make this more explicit, but failed to cleanly do so in the present context. We are quite certain though that having such a shortcut (or alternative derivation) should be restricted to the harmonic trap. -For a general form of the external potential, the effect on the center-of-mass position should not be simple, as far as we can see. Triggered by the Referee's comment we have though expanded our discussion of the harmonic trap. The added text reads as follows.

"The remaining (second) term on the right hand side of Eq. (5) turns into −kappa^2 \int dr rho(r)rr, where the integral is the matrix of second spatial moments of the density profile. The alternative form −κappa^2<sum_i r_i r_i> is obtained upon expressing the density profile as the average of the density operator and carrying out the integral over r. Collecting all terms and dividing by kappa^2 we obtain the sum rule (5) for the case of an interacting system inside of a harmonic trap as: \int dr dr' rho(r)rho(r')h(r,r) rr' = \int dr rho(r)(kT kappa 1 − rr)."

> *) I am a big fan of exact relations like (8), (4), or (5), and I
> value them strongly. But even I found myself wondering how these
> relations can be applied. Here, the manuscript gives a lot of
> suggestions at the end, but stays a bit vague. Could you give
> one concrete example? (maybe testing the Rosenfeld functional or
> some other famous candidate?). The text also mentions
> "validation of simulation data". How could simulation data not
> obey Noethers theorem?

To give a blunt answer: If the simulation code has bugs, then the output can surely violate sum rules. Hence as a concrete check for internal self-consistency of data generation, data accumulation, and data post-processing, we deem the sum rules to be a highly useful resource. Furthermore the present sum rules hold in thermal equilibrium. In practice, judging whether a given simulation run or dataset represents thermal equilibrium in a satisfactory way can be an intricate task and can require much experience for making correct judgements. Although we have not yet tested this, we can well imagine that insufficient sampling could raise warning flags via numerical sum rule violation. Recall that the sum rules do not hold per individual

microstate and hence they require accurate numerical representation (importance sampling) of the thermal ensemble.

We have hence added the following explanation (in parentheses) to the conclusions (p.4).

> "Future use of the sum rules can be manifold, ranging [...] to validation of simulation data (to ascertain both correct implementation and sufficient equilibration and sampling) and numerical theoretical results."

Furthermore, altough we do not carry out such work in the present paper, we conclude the outlook with a concrete suggestion along the Referee's line as follows.

> "To give a concrete example, in systems like the confined hard sphere liquid considered in reference [24] on the basis of fundamental measure theory, one could apply and test the sum rule (5) explicitly, as the inhomogeneous total pair correlation function h(r,r′) is directly accessible in the therein proposed force-DFT approach."

REVIEWERS' COMMENTS:

Reviewer #2 (Remarks to the Author):

The authors have addressed all the points of my referee report to my full satisfaction. I think by addressing these points the manuscript is clearly improved. I can now recommend the publication of the manuscript in its present form.

Reviewer #3 (Remarks to the Author):

I thank the authors for their thoughtful response.
I am happy to recommend the manuscript in its current form for publication.

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