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On how to approach the approach to equilibrium

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Abstract

This paper highlights the limitations of typicality accounts of thermodynamic behaviour so as to promote an alternative line of research: understanding and accounting for the success of the techniques and equations physicists use to model the behaviour of systems that begin away from equilibrium. This paper also takes steps in this promising direction. It examines a technique commonly used to model the behaviour of an important kind of system: a Brownian particle that's been introduced to an isolated fluid at equilibrium. It also accounts for the success of the model, by identifying and grounding the technique's key assumptions.

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1 Introduction

A great deal of philosophical literature on statistical mechanics is concerned with underpinning thermodynamic behaviour, i.e. the following qualitative facts: (i) that isolated macroscopic systems that begin away from equilibrium spontaneously approach equilibrium, and (ii) that they remain in equilibrium for incredibly long periods of time. The leading attempts to underpin these facts appeal to phase space considerations and notions of typicality.

This paper ignores the usual concerns with typicality accounts and instead highlights their limitations.[1] Importantly, these accounts do not underpin a large and important set of facts. They do not, for example, underpin facts about the rates in which systems approach equilibrium, or facts about the kinds of states they pass through on their way to equilibrium, or facts about fluctuation phenomena. To remedy these and other shortfalls, this paper promotes an alternative, and arguably more important, line of research: understanding and accounting for the success of the techniques and equations physicists use to model the behaviour of systems that begin away from equilibrium. Accounting for their success would help underpin not just the qualitative facts the literature has focused on, but also many of the important quantitative facts that typicality accounts cannot. This paper also takes steps in this promising direction. It outlines, examines, and grounds the success of a technique commonly used to model the behaviour of an interesting and important kind of system: a Brownian particle that's been introduced to an isolated fluid at equilibrium. The technique generates a collection of quantitatively accurate equations that track important aspects of the system's behaviour. The model is easily generalised, and so is applicable to a wide variety of systems. This paper attempts to account for the success of the model, by identifying and grounding the technique's key assumptions.

This paper is composed of six parts. The next section briefly reviews typicality accounts and highlights their limitations. These limitations motivate pursuing a different line of research. They encourage us to ground the success of the techniques and equations physicists actually use to model the behaviour of systems that begin away from equilibrium. The remaining sections take steps in this promising direction. The third section details an approach to modelling the approach to equilibrium and subsequent behaviour of a Brownian particle that's been immersed in a fluid. It also highlights its success. The fourth section narrows in on, and discusses, the approach's key assumptions. The fifth section attempts to motivate a particular microphysical claim that would ground the success of the technique, justify its key assumptions, and underpin the facts the equations it leads to track. The concluding section includes a summary and a suggestion about future research.

[1] For a discussion of the usual concerns see Frigg (2009) and Frigg (2011).

2 A Review of Typicality Accounts

Thermodynamic systems are characterised by a set of macrovariables: local volume, local temperature, local pressure, etc. When a system contains a Brownian particle, whose motion is macroscopically visible, its position and momentum are usually included among the macrovariables.[2] Macrostates of a system correspond to the macrovariables obtaining certain values, or to some range of values, if we take into consideration our means of distinguishing between them.

Each macrostate $M_i, i = 1, 2, \ldots, m$ (where m is finite) corresponds to a set of macroregions (Γ_{M_i}) that consist of all the microstates in the system's phase space ($x \in \Gamma$) that take the macrovariable values characteristic of M_i. Discussions of thermodynamic behaviour typically focus on classical systems, whose microconstituents are governed by Hamilton's equations, with fixed total energy. In these situations, the system's motion is confined to Γ_E, the system's 6n-1-dimensional energy hypersurface. Together, the Γ_{M_i} form a partition of Γ_E. Hamilton's equations of motion define a measure preserving flow ϕ_t on Γ. This means that for every measurable set A, and every time t, $\mu(\phi_t^{-1}(A)) = \mu(A)$.

Let M_p denote the initial macrostate of the system and M_{eq} denote the equilibrium macrostate. M_{eq} is characterised as the state in which the values of the system's macrovariables are more or less spatially uniform, e.g. the local density is everywhere close to its spatially uniform value. Naturally, this characterisation is slightly widened for systems that contain objects like Brownian particles. For an isolated dilute gas, M_{eq} is identified as the macrostate whose local temperature, pressure, and volume are more or less spatially uniform. For a Brownian particle immersed in a fluid, M_{eq} corresponds to the macrostate in which the values of these same macrovariables are more or less spatially uniform and where the momentum of the Brownian particle fluctuates about zero. Corresponding to these macrostates are, respectively, the macroregions Γ_{M_p} and $\Gamma_{M_{eq}}$.

Ludwig Boltzmann (1877) is thought to have inspired modern typicality accounts. Joel Lebowitz (1993a, b) and Shelly Goldstein (2001) are often credited as having ushered in modern forms of the view.[3] These views have become increasingly popular, since the appearance of their work.

Typicality accounts attempt to account for why systems beginning in M_p end up in M_{eq} and why they stay there for incredibly long periods of time. While they typically focus on accounting for the behaviour of dilute gases, most accounts are intended to extend beyond these cases. Intuitively speaking, something is typical if it happens in the "vast majority" of cases. Typical lottery tickets, for example, lose. Typicality accounts attempt to show that thermodynamic behaviour is, in some sense, typical. There are a variety of typicality views. Almost all of them, however, fall into one of the following three categories: dominance views,

[2]There are typically a variety of sets one can use to characterise a thermodynamic system. Physicists often choose sets based on the problems they're dealing with.

[3]See also, Lebowitz (1999) and Goldstein and Lebowitz (2004).

unspecified dynamical views, and ergodic views. All of these views interpret the measure over microstates on the system's phase space energy hypersurface as a typicality measure, and all of them make use of a technical result that applies to dilute gases known as the "dominance of the equilibrium macrostate". It says that under certain circumstances, and for dilute gases, M_{eq} is the largest of all M_i.[4] Typicality measures represent the relative size of sets of states. They are usually understood as a kind of normalised measure. Typical states show a certain property if the measure of the set that corresponds to this property is one or close to one. Dominance views are distinguished from the other views by what they take this property to be.

Dominance views claim that thermodynamic behaviour is accounted for by the fact that equilibrium microstates are typical.[5] This is revealed by the dominance of the equilibrium macrostate. Notice that the dominance view makes no claim about a system's dynamics or initial state. Many authors think this is deeply troubling. Unspecified dynamical views claim that, given any reasonable account of the dynamics, typical initial states are taken by the dynamics into the equilibrium macrostate and that they remain there for incredibly long periods of time.[6] Ergodic views claim that relevant systems possess a dynamical property found towards the bottom of the ergodic hierarchy (usually ergodicity or epsilon-ergodicity), and that typical initial states of these systems approach equilibrium and remain in equilibrium for incredibly long periods of time.[7]

All of these views have serious limitations. They do not provide us with the resources to answer important questions such as: what will this system do in the next five minutes? Ten minutes? Hour? Year? What states will it pass through on its way to equilibrium? If it reaches equilibrium, how long will it stay there before it moves out of equilibrium? How likely is it that we'll see the system fluctuate out of equilibrium in the next few minutes? If it does, how large a fluctuation should we expect? Etc. Importantly, these views do not underpin a large and important set of facts. They do not underpin facts about the rates in which systems approach equilibrium, or about the kinds of states they pass through on their way to equilibrium, or about

[4]See Ehrenfest and Ehrenfest (2002: p.30) for an original statement of this result. See Frigg (2011: pp.89-90) and Uffink (2007: pp.974-983) for discussions of the circumstances in which this result holds. See Werndl and Frigg (2015) for an argument that attempts to generalise this result. See Werndl (2013) for an argument in favour of interpreting the measure over Γ_E as a typicality measure.

[5]See Frigg (2011: Sec.4.3) for a list of authors that endorse this kind of view.

[6]The classic and often cited expression of this view is found in Goldstein (2001: pp.43-44):

> $[\Gamma_E]$ consists almost entirely of phase points in the equilibrium macrostate $[M_{eq}]$, with ridiculously few exceptions whose totality has volume of order $10^{-10^{20}}$ relative to that of $[\Gamma_E]$. For a non-equilibrium phase point $[x]$ of energy E, the Hamiltonian dynamics governing the motion $[x(t)]$ would have to be ridiculously special to avoid reasonably quickly carrying $[x(t)]$ into $[M_{eq}]$ and keeping it there for an extremely long time—unless, of course, $[x]$ itself were ridiculously special.

[7]The expression "ergodic views" is not intended to capture views which maintain that relevant systems are Bernoulli or K-systems. It is, however, intended to capture views which maintain that relevant systems are ergodic, epsilon-ergodic, or mixing. See Berkovitz, Frigg, and Kronz (2006) for a good discussion of these dynamical properties and the ergodic hierarchy.

fluctuation phenomena. Moreover, none of these views help us form expectations about these things or help us justify the expectations we may already have about the behaviour of systems that begin away from equilibrium, having formed them on the basis of experience. They also do not underpin important quantitative relations such as the Einstein-Smoluchowski relation.

Each view fails to underpin these facts, and fails to answer these questions, for the same reason: they do not incorporate enough dynamical information. The dominance view is unable to underpin these facts and answer these questions because it does not incorporate *any* dynamical information. We have no way of accounting for what a system will do without *some* account of its dynamics. The unspecified dynamical view is unable to underpin these facts, and answer these questions, because it, as its name suggests, leaves a system's dynamics, for the most part, unspecified. And ergodic views fail because they are tied to dynamical properties that only hold in the long term time limit. Consequently, these properties cannot be used to validly conclude anything about a system's state at a particular time, or about its behaviour over finite time intervals.[8]

Of course, none of this should come as much of a surprise once we remember what typicality views directly aim at recovering: thermodynamic behaviour. As it's understood, this behaviour is attributed to isolated macroscopic systems that spontaneously approach equilibrium, when they begin away from equilibrium, and that remain in equilibrium for incredibly long periods of time. This property does not make any reference to the rates in which systems approach equilibrium, or about the states they pass through on their way to equilibrium, or about fluctuation phenomena.

In light of all of these concerns, it seems natural to turn some of our attention towards understanding and accounting for the success of the techniques physicists use to model the behaviour of systems that begin away from equilibrium. These techniques lead to equations that track a large and important set of facts that concern a system's behaviour. These equations also appear to answer the kinds of questions we're often most interested in. The hope is that by understanding and accounting for the success of these techniques and equations, we will underpin the large and important set of quantitative facts that typicality accounts cannot. Accounting for their success will also provide us, hopefully, with an underpinning, albeit a mosaic one, of the general qualitative facts that are presently at the center of foundational discussions.

3 Modelling a Brownian Particle's Behaviour

The theory of Brownian motion is quite possibly the simplest approximate way to treat the dynamics of nonequilibrium systems. The theory arose from investigations into the irregular behaviour of objects such as pollen grains and dust particles when they are placed into various

[8]In fact, these criticisms also apply to views which hold that relevant systems are mixing. Some of these criticisms, however, do not apply to views which hold that relevant systems are K-systems or Bernoulli. Again, for more on the ergodic hierarchy, see Berkovitz et al. (2006) and Frigg, Berkovitz, and Kronz (2014).

kinds of fluids. What's particularly interesting about the theory is that it can be successfully applied to many other phenomena (e.g. the motions of ions in water and the reorientation of dipolar molecules). In fact, the theory has been extended to situations in which the "Brownian particle" is not really a particle at all, but is instead some collective property of a macroscopic system.[9]

The *Langevin equation* is the theory's fundamental dynamical equation. It contains both frictional forces and random forces. It's a linear, first-order, inhomogeneous differential equation. It's often used to construct expressions that track interesting macroscopic variables. We often have detailed quantitative information about these variables and they capture what we're often most interested in tracking. This section examines the evolution of a system in which a Brownian particle is introduced to an isolated fluid at equilibrium. It also highlights the Langevin equation's use in the construction of equations that track the behaviour of two interesting macroscopic variables—the Brownian particle's mean squared displacement and its mean squared velocity. The theory also possesses an instance of the fluctuation-dissipation theorem: the Einstein-Smoluchowski relation. It relates the forces that appear in the Langevin equation to each other.

As one may have already noticed from this brief introduction, and from the description of the paradigm system it is used to model, the Langevin approach to equilibration abandons much of the machinery that is central to typicality based approaches. The system's phase space, for example, does not enter into the story. As the astute reader will more vividly notice shortly, the Langevin approach helps itself to aspects of equilibrium statistical mechanics. For example, the approach makes use of the equipartition theorem, a concept that belongs to equilibrium statistical mechanics. It is also important for the approach that the fluid surrounding the equilibrating Brownian particle is in equilibrium. While these concepts would not appear in a typicality based analysis of the system, one of the benefits of the Langevin approach, as we'll see, is that we arrive at equations that accurately track interesting and important quantitative aspects of this system (and ones like it) that typicality accounts cannot.

When a single Brownian particle is immersed in an isolated fluid at equilibrium it typically does one of three things, depending on its initial velocity. If the Brownian particle enters the fluid with a mean squared velocity (an expectation value around which the actual value fluctuates) that's greater than the value given by the equipartition theorem, then it typically slows down to that value. If the Brownian particle enters the fluid with a mean squared velocity that's less than the value given by the equipartition theorem, then it typically speeds up. The particle's speeding up and slowing down is the result of collisions with the molecules that comprise the fluid. If the Brownian particle enters the fluid with a mean squared velocity that's close to the value given by the equipartition theorem, then it typically remains at this value. When the

[9] An example is the instantaneous concentration of any component of a chemically reacting system near thermal equilibrium. In this situation, the irregular fluctuations of the concentration in time correspond to the irregular motion of the Brownian particle.

Brownian particle reaches equilibrium, it jostles about, on macroscopic time scales, with a mean displacement of zero. Slight deviations from this behaviour can occur, but large deviations are extremely rare. From the standpoint of an ordinary observer, the Brownian particle's short-term behaviour seems to be random, both as it approaches equilibrium and once it has reached equilibrium. As such, there isn't much more an unaided observer can say about its motion.

While the motion of a Brownian particle appears to be random, it's nonetheless describable by the same equations of motion that model the behaviour of other classical systems.

We'll consider the one-dimensional motion of a spherical particle with radius a, mass M, position x, and velocity V, in a fluid medium with viscosity η.

Newton's equation of motion for the particle is

$$M\frac{dV}{dt} = F_{total}(t). \tag{1}$$

$F_{total}(t)$ is the total instantaneous force on the particle at time t. This force is the result of the particle's interaction with the fluid molecules. If the positions of the molecules are known as functions of time, then, in principle, this force is a known function of time. In this sense, the particle is not subject to a "random force" at all.

It's usually not practical or even desirable to look for an exact expression of $F_{total}(t)$. Experience teaches us that in ordinary cases this force is dominated by a frictional force, $-\zeta V$, that is proportional to the velocity of the Brownian particle. The friction coefficient is given by Stokes' law, $\zeta = 6\pi\eta a$. If this were the whole story, the equation of motion for the Brownian particle would be

$$M\frac{dV}{dt} \cong -\zeta V, \tag{2}$$

whose solution is

$$V(t) = e^{-\zeta t/M}V(0). \tag{3}$$

According to (3), the velocity of the Brownian particle decays, over time, to zero. This result, however, cannot be quite right. It follows from the equipartition theorem that the mean squared velocity of the particle at thermal equilibrium is $\langle V^2\rangle_{eq} = k_{\mathrm{B}}T/M$. Obviously, the assumption that $F_{total}(t)$ is dominated by the frictional force has to be modified. Standardly, an additional force $\delta F(t)$ is added to the frictional force. For reasons that will become clear shortly, this force is referred to as the fluctuating force. The equation of motion then becomes

$$M\frac{dV}{dt} = -\zeta V + \delta F(t). \tag{4}$$

This is the Langevin equation for a Brownian particle. It partitions the total force in two. Because both parts are the result of the Brownian particle's interaction with the fluid, it's

reasonable to think that a fundamental relation exists between them.

The additional force, $\delta F(t)$, is the result of occasional collisions between the Brownian particle and molecules in the fluid. It's typically assumed, given the observed randomness of an individual trajectory, that this force has the following properties.

$$\langle \delta F(t) \rangle = 0, \tag{5}$$

and

$$\langle \delta F(t) \delta F(t') \rangle = 2B\delta(t - t'). \tag{6}$$

Because of these properties, $\delta F(t)$ is standardly referred to as the fluctuating force. B is a measure of the strength of the fluctuating force. The delta function in time indicates that there is no correlation between collisions in distinct time intervals dt and dt'.

The Langevin equation can be solved to give

$$V(t) = e^{-\zeta t/M} V(0) + \int_0^t dt' e^{-\zeta(t-t')/M} \delta F(t')/M. \tag{7}$$

The first term describes the exponential decay of the particle's initial velocity. The second term describes the extra velocity produced by the fluctuating force.

This expression can be used, in conjunction with (5) and (6), to model the equilibration of the Brownian particle's mean squared velocity.

$$\langle V(t)^2 \rangle = e^{-2\zeta t/M} V(0)^2 + \frac{B}{\zeta M}(1 - e^{-2\zeta t/M}). \tag{8}$$

In the long time limit, the exponentials fall out, and this quantity approaches $B/\zeta M$. But at long times the mean squared velocity obtains the value $k_{\mathrm{B}}T/M$. As a consequence, we find that

$$B = \zeta k_{\mathrm{B}} T. \tag{9}$$

This result is known as the *Einstein-Smoluchowski relation.* It relates the strength B of the fluctuating force to the magnitude ζ of the friction.

The evolution of one of the system's macrovariables is described by (8). It models the Brownian particle's spontaneous approach to equilibrium. It provides qualitative and quantitative information. It tells us to expect the system to approach equilibrium reasonably quickly and for it then to remain in equilibrium for incredibly long periods of time. It helps us form expectations about the kinds of macrostates the system will be in at various stages of its evolution and it helps us form expectations about how quickly the system will reach equilibrium. It also helps us form expectations about fluctuation phenomena. What's more, as the Einstein-Smoluchowski

relation reveals, (8) also leads to quantitative information about the strength of the fluctuating force.

The Langevin equation can also be used, again with the help of (5) and (6), to derive an expression for the mean squared displacement of a Brownian particle that's been in the fluid for a long time.

$$\langle x^2 \rangle = \frac{2k_{\mathrm{B}}T}{\zeta}[t - \frac{1}{\tau}(1 - e^{-\tau t})], \tag{10}$$

where $\tau \equiv \frac{\zeta}{M}$, so that τ^{-1} is a characteristic time constant of the system.

Note two interesting limiting cases. *Case 1*: $t << \tau^{-1}$. If $t < \tau^{-1}$, then $e^{-\tau t} = 1 - \tau t + \frac{1}{2}\tau^2 t^2 - \ldots$. So for $t << \tau^{-1}$ and $O(t^3) = 0$,

$$\langle x^2 \rangle = \frac{k_{\mathrm{B}}T}{M}t^2. \tag{11}$$

This means that on very short time scales the particle behaves as if it were a free particle moving along with constant velocity $V = (k_{\mathrm{B}}T/M)^{\frac{1}{2}}$.

Case 2: $t >> \tau^{-1}$. If $t >> \tau^{-1}$, then $e^{-\tau t} \to 0$. So (10) simply becomes

$$\langle x^2 \rangle = \frac{2k_{\mathrm{B}}T}{\zeta}t. \tag{12}$$

(10) provides both interesting qualitative information and interesting quantitative information about one of the system's macrovariables. It models another aspect of the Brownian particle's behaviour. The Brownian particle jostles about with a mean displacement of zero and with a mean squared displacement given by (10). It tells us to expect it to behave as if it were a free particle moving along with constant velocity on very short time scales, and for it to behave like a diffusing particle executing a random walk on longer time scales. It helps us form expectations about the kinds of macrostates the system will be in at various stages of its evolution, and it helps us form expectations about fluctuations. And this does not exhaust the quantitative information that can be extracted from the model. Since we're able to measure $\langle x^2 \rangle$ experimentally, then, if we know the size and density of the particles, as well as the viscosity of the medium, we can deduce from these observations a good approximation of k_B, Boltzmann's constant. Moreover, if we have knowledge of the gas constant, then we can also calculate the value of Avogadro's number. As a final point, it's worth noting that observations confirm many of these expressions.

4 Comments on the Approach

The purpose of this section is to narrow in on the approach's key assumptions and to set aside aspects of the approach that may appear mysterious. Justifying these assumptions is central to

underpinning the qualitative and quantitative facts the technique tracks.

4.1 Constructing a Langevin Equation

First, it may seem as though the Langevin equation came out of nowhere. Its form was motivated by aspects of ordinary experience. The discussion began by noting that experience teaches us that in ordinary cases the total force acting on the particle is dominated by a frictional force, $-\zeta V$, proportional to the velocity of the Brownian particle. It was then indicated that this couldn't be the whole story, since it's at odds with what we expect over longer periods of time. This led to adding a force to the frictional force that would account for the difference. We were thus led to (4), the Langevin equation for a Brownian particle. This kind of motivation is common.[10] It is, however, "top down". Since it's motivated by phenomenal considerations, one may worry about whether and how it connects to the microphysics. Happily, it can be constructed from a combination of physical and mathematical considerations.

Consider a similar but simpler system than the one discussed in the previous section, a one-dimensional system that's comprised of a relatively large Brownian particle with mass M, which is hit from both sides by molecules of mass m.[11] We'll also assume that $M \gg m$ and that collisions are elastic. The velocity of the Brownian particle before and after a single collision will be denoted by V and V', respectively, and the velocity of a molecule before and after a collision will be denoted by v and v', respectively. If we combine the equations for conservation of momentum and energy, then we can write the velocities after the collision in terms of the velocities before the collision. That is,

$$V' = \frac{M-m}{M+m}V + \frac{2m}{M+m}v, \tag{13}$$

$$v' = \frac{m-M}{M+m}v + \frac{2M}{M+m}V. \tag{14}$$

Using the assumption that $M \gg m$, and the following approximations,

$$\frac{M-m}{M+m} \approx 1 - 2\frac{m}{M} + O\left(\left(\frac{m}{M}\right)^2\right), \tag{15}$$

$$\frac{M}{M+m} \approx 1 - \frac{m}{M} + O\left(\left(\frac{m}{M}\right)^2\right), \text{ and} \tag{16}$$

$$\frac{m}{M+m} \approx \frac{m}{M} + O\left(\left(\frac{m}{M}\right)^2\right), \tag{17}$$

[10] See Reif (1965: Sec.15.5), Zwanzig (2001: Ch.1), Mazenko (2006: Ch.1), and Pathria and Beale (2011: Ch.15), for example.

[11] This system is also discussed by de Grooth (1999).

(13) can be written as

$$V' = \left(1 - \frac{2m}{M}\right)V + \frac{2m}{M}v. \tag{18}$$

So the change in momentum of the Brownian particle due to a single collision is

$$\Delta P = 2mv - 2mV. \tag{19}$$

And the momentum change of the Brownian particle due to N collisions is

$$\Delta P_N = 2m \sum_{i=0}^{N-1} v_i - 2m \sum_{i=0}^{N-1} V_i. \tag{20}$$

If we consider a time interval Δt that's small enough that the velocity of the Brownian particle does not change appreciably, but because $M >> m$, we still have a large number of collisions, then the second sum in (20) can be approximated by $2mNV = 2mnV(t)\Delta t$, where $V(t)$ is the velocity of the Brownian particle at time t, and n is the mean number of collisions per second so that $N = n\Delta t$. So, we have,

$$\Delta P_N = 2m \sum_{i=0}^{n\Delta t-1} v_i - 2mnV(t)\Delta t. \tag{21}$$

This gives

$$M\frac{dV}{dt} = -\gamma V + F_s, \tag{22}$$

where the damping constant $\gamma = 2mn$ and

$$F_s = \frac{1}{\Delta t} \sum_{i=0}^{n\Delta t-1} 2mv_i. \tag{23}$$

F_s is a fluctuating force, if, as before, it's assumed to have the following properties:

$$\langle F_s(t)\rangle = 0, \tag{24}$$

and

$$\langle F_s(t)F_s(t')\rangle = 2B\delta(t - t'). \tag{25}$$

(24) entails that the incoming velocities of colliding molecules have an expectation value of zero. (25) entails that the incoming velocities of colliding molecules at distinct times are uncorrelated.

(22) has the same form as the Langevin equation. It, however, contains explicit expressions for both the damping force and the fluctuating force. Much like (4), (22) can be used together with (24), (25), and the equipartition theorem, to arrive at important results such as (12).

4.2 The Time Reversal Non-Invariance of the Langevin Equation

Something else that may have seemed mysterious about the approach is the time-reversal non-invariance of the Langevin equation. The one-dimensional version, (22), is also asymmetric under time-reversal. This too may seem mysterious. Each equation describes the evolution of a system whose underlying dynamics are symmetric under time-reversal.

To see that (22) is asymmetric under time-reversal, first note that the expectation value of the fluctuating force is zero. Then, taking the expectation values of both sides of (22), we get the conclusion that the expectation value of V decays exponentially to zero. The temporal reverse of this would have an exponentially increasing expectation value of V. This reasoning also applies to the Langevin equation. Again, the expectation value of the fluctuating force is taken to be zero. Since the frictional force term is temporally asymmetric, we are led, when we take the expectation values of both sides of (4), to the conclusion that the expectation value of V decays exponentially to zero. And similarly, the temporal reverse would have an exponentially increasing expectation value of V.

The time-reversal non-invariance of the Langevin equation is the result of the temporal asymmetry of its frictional force term and the properties attributed to its second, fluctuating force term. The same is true of (22). Interestingly, both equations, understood simply as equations that divide the total force acting on the Brownian particle in two, are compatible with time-reversal invariance. What's more, this compatibility holds even after the choice is made to split the total force into a frictional force and what is left over. What ensures the time-reversal non-invariance of these equations, given the time-reversal non-invariance of their respective frictional force terms, are the properties attributed to their second terms.

The time-reversal non-invariance of the Langevin equation prompts further questions. First, why do physicists standardly assume that the Langevin equation's second term has the properties identified in (5) and (6)? And second, what does their rationale reveal about the microphysics of those systems whose behaviour is accurately modelled by the Langevin equation, and the equations derived from it (e.g. (8) and (10))? Otherwise said, what would have to be true, or at least be approximately true, at the microlevel to account for the success of equations such as (4), (8), and (10), given that the underlying dynamics is symmetric under time-reversal?

First, it's standardly assumed that the second force term has an expectation value of zero because the Brownian particle, observed at ordinary scales, seems just as likely to move in any direction at any moment as any other. In the one-dimensional model, the analogous thought is that the Brownian particle seems just as likely to move, at any moment, to the left as it is to the right. What's more, if observation provided us with reason to think that the Brownian

particle was more likely to move in one direction than another—say, because we thought it was more likely to be struck from one side rather than another—then we would describe this thought using some force expression and extract it from the second term.

Interestingly, (5) is standardly presented alongside an assumption analogous to (6).[12] Notice too that (24) was presented along with (25). Both (6) and its analogue, (25), say that no correlation exists between the forces acting on the Brownian particle at any two distinct times.[13]

Importantly, what standardly underlies and motivates both (5) and (6), or, analogously, (24) and (25), is something that closely resembles the following microphysical assumption.

Collision Assumption: That v is, at any time, independent of V.

Spelled out, the underlying claim is that the velocity of any incoming colliding fluid molecule (drawn from the distribution of velocities of molecules of the fluid), is, at any time, probabilistically independent of the incoming velocity of the Brownian particle.

Interestingly, the collision assumption is itself temporally asymmetric. To see this, consider the one-dimensional model. Next, note that the collision assumption has to do with the probability distribution of the velocities of molecules that are about to hit the Brownian particle. Now consider (14). That is, the probability distribution of the velocities of molecules that have just collided with the Brownian particle. If the expectation value of v is zero, as (24) entails, then the expectation value of v' is proportional to V. So, if V is greater than its equilibrium value, then colliding molecules in the path of the Brownian particle will have a greater velocity after the collision than before. Meanwhile, colliding molecules that are travelling on the Brownian particle's path will have a post-collision velocity that's less than their pre-collision velocity. When we velocity-reverse the situation, we get a state of affairs in which the distribution of velocities of incoming colliding molecules are, contrary to the assumption, not independent of the Brownian particle's velocity. The velocities of the incoming colliding molecules are distributed so that their combined force increases the Brownian particle's velocity along its path.

4.3 Why Does the Langevin Equation Work?

Since (4), (8), and, in particular, (10) have consequences that are confirmed by experiment, it's worth considering what would have to be true, or be at least approximately true, at the microlevel, to justify the use of the collision assumption, and to ensure that its consequences—(5) and (6)—are at least approximately true. Answering this helps explain the success of equations such as (4), (8), and (10). It also helps to underpin the quantitative and qualitative facts these equations track. As one might have expected, the answer is suggested by the assumption itself.

[12] See Zwanzig (2001: p.5), Kadanoff (2000: p.120), and Mazenko (2006: p.8), for example.

[13] It's worth noting that concerns about the conflict between the time-reversal non-invariance of the Langevin equation and the time-reversal invariance of the underlying dynamics do not standardly play a role in the determination of the properties that are attributed to the Langevin equation's second term.

The natural suggestion is that it's a convenient approximation of the following microphysical fact.

> **Microphysical Fact:** That v is at most independent of V at some initial time and that at any other time v is *effectively* independent of V.

The claim here is that, at all times (except, perhaps, initially), the velocity of any incoming colliding fluid molecule and the incoming velocity of the Brownian particle are approximately probabilistically independent.[14]

Notice that we don't claim that the velocities of incoming colliding molecules are, at all times, *in fact* independent of the incoming velocity of the Brownian particle, as the collision assumption has it. The reason for this more modest claim is that these velocities are at least correlated for very short times after collision. This can be seen by reflecting on what we think's going on at the microlevel. Once the Brownian particle is introduced to the fluid, it begins to collide with fluid molecules. The subsequent positions and momenta of the molecules, like the Brownian particle, are the result of collisions. Because the forces acting on the particle can be expressed by smooth functions—at least to a good approximation—the forces resulting from these collisions will be correlated.

But it should be remembered that the motion of the Brownian particle appears to be random on macroscopic time scales. So it seems reasonable to think, as the microphysical fact intends to suggest, that any correlations that form between the velocities of colliding particles wash out incredibly quickly. Happily, weakening (6) (or (25)) to accommodate these considerations—say by instead assuming that correlations between fluctuating forces at distinct times exponentially decay on scales that are incredibly short compared to the system's relaxation to equilibrium—yields results that closely approximate (10) and (9). Similar results also hold if we assume that correlations between fluctuating forces at distinct times are Gaussian on scales that are extremely short compared to the system's relaxation to equilibrium.

Having identified the approach's crucial assumption, the collision assumption, it's important to ask whether its use is justified. Or, more crucially, what reason do we have to think that the microphysical fact is, in fact, true? This question is important, since we can hardly ground the success of the technique, or the facts its resulting equations track, on an unsupported microphysical claim.

5 Motivating the Collision Assumption

The microphysical fact, if true, provides reason to utilise the collision assumption. Support for the microphysical fact comes from at least two sources: from a scientifically informed reflection

[14]The idea then is that, for practical purposes, one can treat the velocities of these colliding particles *as if* they are probabilistically independent. That is, one may be justified in using the collision assumption.

on the microphysical behaviour of relevant systems, and from results that emerge from the study of an idealised system, a hard sphere gas.

First, when thinking about the behaviour of a Brownian particle that's just been placed into an isolated fluid at equilibrium, it seems reasonable to have the following picture in mind. Once the Brownian particle is placed into the fluid, it begins to collide with fluid molecules as it approaches equilibrium. Since the fluid is composed of a very large number of molecules, which are involved in very many collisions, it's reasonable to think that whenever two of them collide it's overwhelmingly likely that a very large number of collisions will occur before they collide again—if, in fact, they ever collide again. This suggests that by the time the Brownian particle were to collide with some molecule it had already encountered neither would, in effect, carry a memory of their past collision. That is, any correlation that resulted from their previous interaction would have effectively been washed out. Because these collisions happen incredibly quickly, so too would the washing out of correlations. So then, we can reasonably expect the forces acting on the Brownian particle to be, at any moment, effectively random, and we can expect the velocities of incoming colliding molecules to be, at any moment, effectively independent of the velocity of the Brownian particle. The reasonableness of this picture supports the truth of the microphysical fact.

Notice too how bizarre the temporal reverse of a situation in which a Brownian particle slowed to equilibrium would be. That is, a situation in which the microphysical fact does not hold. If we reversed the velocities of all of the molecules that comprise the system, then we would witness a conspiratorial situation similar to the one mentioned at the end of the last section. The Brownian particle would miraculously speed up and the velocities of the incoming colliding molecules would be correlated with it. They would be distributed so that their combined force increased the Brownian particle's velocity along its path.

What makes the first picture reasonable and the second situation bizarre is that only in the second situation are the velocities of incoming colliding molecules correlated *before* they interact. What's peculiar about this is that in the absence of some earlier event that would account for this correlation, their correlation is to be explained by some event that lies in their future. And this flies in the face of the fundamental idea that causes precede their effects.[15]

If we assume that the microphysical fact holds (or that something close to it holds), then we are led to equations that accurately model and predict the behaviour of systems we can and do observe. The models outlined in earlier sections attest to this fact. So we have support for the truth of the microphysical fact. As the temporal reversals of the ordinary behaviour of these systems suggest, deviations from such an assumption lead us to expect systems to behave in ways

[15]This claim might be controversial to some. Huw Price (1996), for example, disputes its truth at the microphysical level. The following things, however, are not controversial. First, we take this idea for granted in our ordinary dealings with the world. That it's universally true is the default position. Second, even on reflection, it's not disputed at the macroscopic level. Third, scientists standardly develop successful physical models on the basis that causes precede their effects.

we simply do not ever witness. So we have further support for the truth of the microphysical fact.

The study of idealised models also supports the truth of the microphysical fact. Oscar Lanford III has shown that an instance of the microphysical fact is true, under certain conditions, for a hard sphere gas model.[16] Lanford has shown that when the initial state of the gas satisfies a certain condition—that, in effect, amounts to there being a lack of correlation between the momenta and positions of gas molecules—the system effectively sustains this property, as it approaches equilibrium.[17] The result, which follows from Lanford's theorem, applies to systems whose behaviour is described by Boltzmann's equation. These systems also have an underlying dynamics that is invariant under time-reversal. While the result holds only for a short period of time, there are good reasons to think that it can be extended.[18]

On the basis of these considerations, it seems reasonable to think that the microphysical fact is true. Its truth would support the use of the collision assumption and its consequences, (5) and (6) ((24) and (25)). In particular, it would justify the use of (5) and (6) in the derivations of (8) and (10). Its truth would also help explain the success of these equations, and help underpin the quantitative and qualitative facts these equations track.

6 Conclusion

This paper highlighted the limitations of typicality accounts and suggested pursuing an alternative line of research: understanding and grounding the success of the techniques and equations physicists use to model the behaviour of systems that begin away from equilibrium. It also took steps in this direction by outlining, examining, and attempting to ground the success of a technique and equation that's used to model the behaviour of a Brownian particle that's been immersed in an isolated fluid. The technique generates a collection of interesting and quantitatively accurate equations whose predictions are confirmed by experiment. This paper attempted to account for the success of the model, by identifying and motivating the technique's key assumptions. It noted that support for them can be traced back to an endorsement of the collision assumption, which is a convenient approximation of the microphysical fact. The body of the paper ended with several reasons to think that the microphysical fact is, in fact, true.

Of course, the technique and equation discussed in this paper are but the first in a collection of more elaborate and predictively accurate techniques and equations.[19] There are also limitations on its applicability—despite its generality. Naturally, it would be good for future investigations to consider and examine more elaborate techniques and equations, and for them to also examine more complicated systems (e.g. systems that are influenced by external forces). It would be

[16] See Lanford III (1975, 1976, & 1981).
[17] See Uffink (2007: Sec.6.4), Uffink and Valente (2015), and Valente (2014) for discussions of Lanford's results.
[18] For a discussion of its extension, see Valente (2014: Sec.7.2) and Lanford III (1976: p.14).
[19] See, for example, Zwanzig (2001) and Mazenko (2006).

good for these investigations to uncover and discuss the presuppositions these techniques and equations trade on (if any), and, where possible, to discuss the grounds we have for believing that these conditions are satisfied.

A more concrete suggestion is to examine and motivate the steps that lead to the Fokker-Planck equation. The Fokker-Planck equation is the starting point for many useful calculations in nonequilibrium statistical mechanics. For example, it's used to determine the rate at which a Brownian particle crosses a potential barrier (Zwanzig 2001: p.40). The Fokker-Planck equation is often called upon in situations in which it's suitable to model a system's behaviour using a *non-linear* Langevin equation. Linear Langevin equations are easy to solve analytically, non-linear Langevin equations are not. Physicists standardly side-step this difficulty by constructing a Fokker-Planck equation that corresponds to a given Langevin equation. It would be good to highlight whatever presuppositions are required to make these steps legitimate, and to discuss the grounds we have for believing that these conditions are met.

The hope is that the successful grounding of these, and other techniques and equations, would underpin many of the important and interesting quantitative facts that typicality accounts cannot. Accounting for the success of these techniques and equations will also lead, in a mosaic fashion, hopefully, to an underpinning of the very concept that is currently at the center of foundational discussions of statistical mechanics: thermodynamic behaviour.

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