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On (Andersen–)Parrinello–Rahman Molecular Dynamics, the Related Metadynamics, and the Use of the Cauchy–Born Rule

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Abstract It is shown that the Parrinello–Rahman Lagrangian is obtained by assuming that (i) the cell inertia tensor is spherical and constant in time, and that (ii) the cell fluctuation motions are irrotational. A slightly different Lagrangian is suggested, arrived at by dropping the sphericity assumption in (i). A related metadynamics is also proposed, based on replacing by (ii) the various no-cell-rotation assumptions that are customarily used. Finally, a zero-temperature, scale-bridging relation is proposed between the intermolecular potential and the macroscopic stored-energy mapping.

Keywords Molecular dynamics · Metadynamics · Cauchy–Born rule · Scale bridging

Mathematics Subject Classification (2000) 82B21 · 82B26 · 74A25

1 Introduction

Current Molecular Dynamics (MD) simulations concern a basic cell $\mathcal{X}$ of attomole size and have a duration $\mathcal{T}$ of nanosecond order. Continuum Mechanics (CM) is a field theory aiming to posit initial/boundary-value problems for such fields as displacement, velocity, and stress. At the CM scale, the space-time regions $\mathcal{X} \times \mathcal{T}$ considered by MD are to be regarded as (point, instant) pairs (x, t).

To establish any link between MD and CM, scale-bridging criteria must be posited: this paper discusses those implicit in the version of MD known as the *Parrinello–Rahman method* [10], a version first proposed by Andersen [1] in 1980 and promptly generalized by Parrinello and Rahman [11, 12].

Continuum theories that aim to go beyond elasticity proceed by lifting some amount of microscopic information up to their own macroscopic level. When seen from the viewpoint of continuum physics, the intriguing novelty of the (Andersen–)P–R method is that

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it proceeds the other way around, in that it mixes macroscopic information—the MD-cell deformation descriptor $\mathbf{F}$—with the microscopic information about the motion of the molecules within the cell, while letting the thermal fluctuations of both molecules and cell be driven by a macroscopic control, the applied stress $\mathbf{S}$. The method's key feature—to allow for fluctuations in volume and shape of the MD cell—is encapsulated into a shrewd specification of the kinetic energy, involving both $\mathbf{F}$ and its time rate $\dot{\mathbf{F}}$ in addition to the molecule velocities $\dot{\mathbf{s}}_I$ $(I = 1, \ldots, N)$. It would seem appropriate to say that the method's success depends crucially on such specification.

As to the Lagrangian associated with the (A–)P–R kinetic energy, here is a quotation from [12]: "Whether such a Lagrangian is derivable from first principles is a question for further study; its validity can be judged, as of now, by the equations of motion and the statistical ensembles that it generates." To the best of my knowledge, the issue raised in this quotation of 1981 still stands, although the reliability of (A–)P–R-based predictions has been demonstrated beyond any doubt. One purpose of this paper is to discuss a set of circumstances under which the kinetic energy—and hence, the Lagrangian—takes exactly the form postulated in [12]. Another purpose is to show how one of the assumptions inducing those circumstances—namely, irrotationality of cell motion—should be incorporated in whatever metadynamics one runs to explore the energy landscape of a crystalline substance [2, 8–10] or of certain chemical reactions [4] along paths connecting local minima. A third and last purpose is to point out a connection between zero-temperature MD and the search via the Cauchy–Born rule for an elastic stored-energy mapping consistent with a given intermolecular potential [3, 5, 15, 16].

2 A Reformulation of (A–)P–R Molecular Dynamics

2.1 Cell Geometry

Let the basic MD cell be observed both in its current shape, where its edges are spanned by the linearly independent vectors $\mathbf{h}_i$ $(i = 1, 2, 3)$ (the *lattice parameters* of [2]), and in its reference shape, where its edges are spanned by the vectors $\mathbf{g}_i$.[1] Then, the cell deformation is described by the tensor

$$\mathbf{F} = \mathbf{h}_i \otimes \mathbf{g}^i. \tag{1}$$

Here $\otimes$ denotes dyadic product and the linearly independent triplets of vectors $\mathbf{g}_i$ and covectors $\mathbf{g}^i$ are such that $\mathbf{g}_i \otimes \mathbf{g}^i = \mathbf{1}_{ref}$, with $\mathbf{1}_{ref}$ the identity tensor in the referential observation space; thus, in particular,

$$\mathbf{h}_i = \mathbf{F}\mathbf{g}_i \quad (i = 1, 2, 3). \tag{2}$$

The MD cell "is allowed to change its shape in order to comply with a new structure" [10] as a consequence of a stress-induced structural phase transition. As anticipated in the Introduction, the case we concentrate on here—the same as in [12]—is when the applied stress is the control parameter.[2]

We work with the collective tensor variable $\mathbf{F}$, rather than with the lattice parameter vectors $\mathbf{h}_i$, because $\mathbf{F}$ admits a well-known direct interpretation as the tensor that rules the local

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[1] Just as in (A–)P–R MD, in CM recourse to a comparison between reference and current shape is expedient to describe solids, while fluid bodies are observed in their current shape.

[2] Other macroscopic controls, like strain or temperature, can and have been chosen.

analysis of deformation in continuum mechanics, and because it enters naturally both the metadynamics simulations and the applications of the Cauchy–Born rule. The representation (1) makes clear that $\mathbf{F}$ maps the reference cell into the current cell; it measures the local *macroscopic deformation*, as seen at the continuum mechanical scale. Due to the limitations in size of the matter chunk considered in any MD simulation, $\mathbf{F}$ cannot depend on space, but it may depend on time. Such time changes account for fluctuations performed by the basic cell while the system evolves toward statistical equilibrium.

2.2 Kinetic Energy

Let

$$\mathbf{r}_I = \zeta_I^i \mathbf{h}_i \quad \text{and} \quad \mathbf{s}_I = \zeta_I^i \mathbf{g}_i \quad (I = 1, \dots, N) \tag{3}$$

be the current and referential position vectors of the I-th molecule of a population occupying the basic cell, the real numbers $\zeta_I^i \in [0, 1]$ being the I-th molecule's convected coordinates. While in a zero-temperature MD calculation the convected coordinates are constant in time, here they are not: in a crystal, their values are to be thought of as changing in time about the coordinates of the lattice positions, with position-velocity fluctuations regarded as a statistical manifestation of a state of nonnull temperature.

In view of (2) and (3), we have that

$$\mathbf{r}_I = \mathbf{F}\mathbf{s}_I, \tag{4}$$

whence, since *both the cell and the particles fluctuate*,

$$\dot{\mathbf{r}}_I = \dot{\mathbf{F}}\mathbf{s}_I + \mathbf{F}\dot{\mathbf{s}}_I, \quad \dot{\mathbf{s}}_I = \dot{\zeta}_I^i \mathbf{g}_i$$

(a superposed dot signifies time differentiation). With this, the *kinetic energy* of the molecule population turns out to be:

$$\begin{aligned} K = \frac{1}{2}\sum_{I=1}^{N} m_I \dot{\mathbf{r}}_I \cdot \dot{\mathbf{r}}_I &= \mathbf{F}^T\mathbf{F} \cdot \frac{1}{2}\sum_{I=1}^{N} m_I \dot{\mathbf{s}}_I \otimes \dot{\mathbf{s}}_I \\ &+ \dot{\mathbf{F}}^T\dot{\mathbf{F}} \cdot \frac{1}{2}\sum_{I=1}^{N} m_I \mathbf{s}_I \otimes \mathbf{s}_I + \dot{\mathbf{F}}^T\mathbf{F} \cdot \sum_{I=1}^{N} m_I \mathbf{s}_I \otimes \dot{\mathbf{s}}_I \end{aligned} \tag{5}$$

(a centered dot signifies the inner product of tensors). Instead, the expression for the kinetic energy postulated in [12] is:

$$\begin{aligned} K_{PR} &= \hat{K}(\dot{\mathbf{s}}_I, I = 1, \dots, N; \mathbf{F}, \dot{\mathbf{F}}) \\ &= \mathbf{F}^T\mathbf{F} \cdot \frac{1}{2}\sum_{I=1}^{N} m_I \dot{\mathbf{s}}_I \otimes \dot{\mathbf{s}}_I + \frac{1}{2} W |\dot{\mathbf{F}}|^2, \end{aligned} \tag{6}$$

with the positive constant W bearing the dimension of mass × length^2. Note that K_{PR} does not depend on the position vectors $\mathbf{s}_I$, whereas K does. Moreover,

$$K - K_{PR} = \frac{1}{2}\dot{\mathbf{F}}^T\dot{\mathbf{F}} \cdot \left(\mathbf{I} - W\mathbf{1}_{ref}\right) + \dot{\mathbf{F}}^T\mathbf{F} \cdot \sum_{I=1}^{N} m_I \mathbf{s}_I \otimes \dot{\mathbf{s}}_I, \tag{7}$$

where

$$\mathbf{I} = \sum_{I=1}^{N} m_I \mathbf{s}_I \otimes \mathbf{s}_I \tag{8}$$

is the referential Euler's *inertia tensor* of the MD cell, a symmetric and (for a nondegenerate cell) positive-definite tensor. One may ask whether necessary and sufficient conditions can be found for $K \equiv K_{PR}$ for all admissible processes of a given molecule population occupying a given MD cell. Sufficient conditions are easily found and interpreted.

Suppose the fluctuation motion of molecules is constrained so as to have

$$\sum_{I=1}^{N} m_I \mathbf{s}_I \otimes \mathbf{s}_I - W\mathbf{1}_{ref} = \mathbf{0} \tag{9}$$

at all times; said differently, suppose that, whatever the cell fluctuations,

(i) *the referential inertia tensor of the molecule population under study are spherical and constant in time*.

Under this assumption, by differentiating (9) with respect to time, we find:

$$\sum_{I=1}^{N} m_I (\dot{\mathbf{s}}_I \otimes \mathbf{s}_I + \mathbf{s}_I \otimes \dot{\mathbf{s}}_I) = \mathbf{0},$$

which is tantamount to the skew-symmetry of the tensor $\sum_{I=1}^{N} m_I \mathbf{s}_I \otimes \dot{\mathbf{s}}_I$. Thus, the second term on the right side of (7) vanishes whenever the tensor $\dot{\mathbf{F}}^T\mathbf{F}$ is symmetric; and this is the case, as is easy to show, iff the tensor $\mathbf{L} = \dot{\mathbf{F}}\mathbf{F}^{-1}$ is symmetric. Now, the tensor $\mathbf{L}$ is nothing but the macroscopic *velocity gradient*; its skew-symmetric part measures vorticity, while its symmetric part measures the rate of strain. Accordingly, our second assumption is that, whatever the molecule fluctuations,

(ii) *the MD-cell's fluctuation motion be irrotational* (have vanishing vorticity).

Remarks 1. To motivate assumption (i), we recall that, for $\mathcal{U}^n$ the n-dimensional unit sphere in the vector space $\mathcal{V}^n$, and for $\mathbf{1}_{\mathcal{V}^n}$ the identity of $\mathcal{V}^n$, we have that

$$\int_{\mathcal{U}^n} \mathbf{e} \otimes \mathbf{e} = \frac{\text{meas}(\mathcal{U}^n)}{n} \mathbf{1}_{\mathcal{V}^n}.$$

Assuming (i) seems appropriate for fluids (the materials for which conventional pre-Andersen MD was devised); it does not seem unreasonable for certain classes of crystalline solids either, for N large and a suitably uniform molecule distribution within the cell.

2. The essential content of assumption (i) is that the cell inertia tensor $\mathbf{I}$ be independent of time: dropping the assumption that $\mathbf{I}$ be spherical, and replacing (i) by

(i)′ *the referential inertia tensor of the molecule population under study be constant in time*,

the path to assumption (ii) would not change. With (i)′ and (ii), the kinetic energy would reduce to:

$$K = \frac{1}{2}\mathbf{F}^T\mathbf{F} \cdot \sum_{I=1}^{N} m_I \dot{\mathbf{s}}_I \otimes \dot{\mathbf{s}}_I + \frac{1}{2}\dot{\mathbf{F}}^T\dot{\mathbf{F}} \cdot \sum_{I=1}^{N} m_I \mathbf{s}_I \otimes \mathbf{s}_I,$$

a choice that should preserve all the relevant simplifications inherent to the (A–)P–R kinetic energy without enforcing too special an assumption on the crystalline structure of the computational cell. Needless to say, such an assumption may modify the phase space sampling of the resulting system, an issue that deserves attention.

2.3 Molecular Potential

The molecules in the basic cell interact as specified by a positional *potential* $V(\mathbf{r}_1, \dots, \mathbf{r}_N)$, whose simplest additive pairwise form is:

$$V = \frac{1}{2}\sum_I \sum_J \Phi(r_{IJ}) = \sum_{I=1}^{N}\sum_{J>I}^{N} \Phi(r_{IJ}), \quad r_{IJ} := |\mathbf{r}_I - \mathbf{r}_J|.$$

In view of (4),

$$r_{IJ} = |\mathbf{F}(\mathbf{s}_I - \mathbf{s}_J)|; \tag{10}$$

consequently, we set

$$V = \hat{V}(\mathbf{s}_I, I = 1, \dots, N; \mathbf{F}) = \sum_{I=1}^{N}\sum_{J>I}^{N} \Phi(|\mathbf{F}(\mathbf{s}_I - \mathbf{s}_J)|). \tag{11}$$

2.4 Lagrangian Equations of Motion

Collecting (6) and (11), we consider the *Lagrangian*

$$\begin{aligned} L &= \hat{L}(\mathbf{s}_I, \dot{\mathbf{s}}_I; \mathbf{F}, \dot{\mathbf{F}}) \\ &= \hat{K}_{PR}(\dot{\mathbf{s}}_I; \mathbf{F}, \dot{\mathbf{F}}) - \hat{V}(\mathbf{s}_I; \mathbf{F}) + \Omega_{ref}\mathbf{S}\cdot\mathbf{F}, \end{aligned} \tag{12}$$

where $\mathbf{S}$ is the *external stress*, that is, the observable applied stress (for simplicity, the specification of the range of index I has been omitted) and Ω_{ref} is the cell's referential volume. The associated *Lagrangian equations of motion* are:

$$\begin{cases} \dfrac{d}{dt}\left(\dfrac{\partial L}{\partial \dot{\mathbf{s}}_I}\right) - \dfrac{\partial L}{\partial \mathbf{s}_I} = \mathbf{0}, \\ \dfrac{d}{dt}\left(\dfrac{\partial L}{\partial \dot{\mathbf{F}}}\right) - \dfrac{\partial L}{\partial \mathbf{F}} = \Omega_{ref}\mathbf{S}. \end{cases} \tag{13}$$

Thus, the first N vectorial equations (13) read:

$$\ddot{\mathbf{s}}_I + \mathbf{C}^{-1}\dot{\mathbf{C}}\dot{\mathbf{s}}_I + \frac{1}{m_I}\sum_{J\neq I}\frac{1}{r_{IJ}}\Phi'(r_{IJ})(\mathbf{s}_I - \mathbf{s}_J) = \mathbf{0}, \tag{14}$$

where $\mathbf{C} = \mathbf{F}^T\mathbf{F}$ (cf. (2.9) of [12]). As to the $(N+1)$-th tensorial equation, we get:

$$W\ddot{\mathbf{F}} = \Omega_{ref}(\mathbf{Q} + \mathbf{S}), \tag{15}$$

where $\mathbf{Q} = \mathbf{F}\widetilde{\mathbf{P}}$ and

$$\Omega_{ref}\widetilde{\mathbf{P}} = \sum_{I=1}^{N} m_I \dot{\mathbf{s}}_I \otimes \dot{\mathbf{s}}_I - \sum_{I=1}^{N}\sum_{J>I}^{N}\frac{1}{r_{IJ}}\Phi'(r_{IJ})(\mathbf{s}_I - \mathbf{s}_J)\otimes(\mathbf{s}_I - \mathbf{s}_J) \tag{16}$$

is the *internal stress*. Differences in notation apart, (15) coincides with (2.25) of [12], a generalization of (2.10) of [12] which is arrived at with considerable unnecessary effort.

Remark To see that our (15) and (16) describe the same physics as (2.25) and (2.11) of [12], it is convenient to introduce some terminology and concepts from CM. As is standard in that discipline, we refer to **F** and **C** as, respectively, the *deformation gradient* and the *Cauchy–Green strain tensor*; and we refer to **S** as the *Piola stress*. Other stress measures of common use are the symmetric *Cauchy stress* **T** and *Cosserat stress* $\widetilde{\mathbf{S}}$, with

$$\mathbf{S} = \mathbf{T}\mathbf{F}^*, \quad \mathbf{F}^* = (\det\mathbf{F})\mathbf{F}^{-T}, \quad \text{and} \quad \widetilde{\mathbf{S}} = \mathbf{F}^{-1}\mathbf{S}; \tag{17}$$

note that

$$\mathbf{T} = (\det\mathbf{F})^{-1}\mathbf{F}\widetilde{\mathbf{S}}\mathbf{F}^T. \tag{18}$$

The stress is a *pressure* if $\mathbf{T} = -\pi\mathbf{1}_{cur}$, $\pi > 0$ (here $\mathbf{1}_{cur} = \mathbf{h}_i \otimes \mathbf{h}^i$ denotes the identity tensor in the current observation space); or, alternatively, if

$$\mathbf{S} = -\pi\mathbf{F}^* \quad \text{or} \quad \widetilde{\mathbf{S}} = -\pi(\det\mathbf{F})\mathbf{C}^{-1}. \tag{19}$$

It follows from the first two of (17) that

$$\mathbf{S}\cdot\mathbf{F} = (\det\mathbf{F})\,\mathrm{tr}\,\mathbf{T};$$

therefore, when the stress is a pressure,

$$\mathbf{S}\cdot\mathbf{F} = -3\pi\,\det\mathbf{F},$$

and, on setting $p = 3\pi$ and $\Omega_{cur} = (\det\mathbf{F})\Omega_{ref}$ for the cell's current volume, our expression (12) for the Lagrangian coincides with (2.8) of [12].

It is convenient to parallel the above definitions of external-stress measures with three corresponding definitions for the internal stress:

$$\mathbf{S} \leftrightarrow \mathbf{Q}, \qquad \widetilde{\mathbf{S}} \leftrightarrow \widetilde{\mathbf{P}}, \qquad \mathbf{T} \leftrightarrow \mathbf{P} = (\det\mathbf{F})^{-1}\mathbf{F}\widetilde{\mathbf{P}}\mathbf{F}^T. \tag{20}$$

It follows from relations (20) that (15) can be rewritten as both

$$W\ddot{\mathbf{F}} = \Omega_{ref}\mathbf{F}(\widetilde{\mathbf{P}} + \widetilde{\mathbf{S}}) \tag{21}$$

and

$$W\ddot{\mathbf{F}} = \Omega_{cur}(\mathbf{P} + \mathbf{T})\mathbf{F}^{-T}, \tag{22}$$

a form of (15) that reduces to (2.10) in [12] when the stress is a pressure.

3 Consistent Metadynamics

Metadynamics is [10] "…a powerful molecular dynamics method for the study of pressure-induced structural transformations. We use the edges of the simulation cell as collective variables and define a metadynamics that drives the system away from the local minimum towards a new crystal structure."

Now, almost invariably if under different forms, an assumption of the type of (ii) in Sect. 2.2 is made whatever metadynamics one uses to charter an energy landscape. Here is a couple of relevant quotations, one from [9]: "We freeze the box rotations by assuming the matrix **h** [**F**, in our notation] to be upper triangular ...", the other from [10]: "We assume, following Nosé and Klein, that the matrix **h** is symmetric in order to eliminate rotations of the supercell ...".[3]

Neither upper-triangularity nor symmetry of **F** guarantee that the simulation box does not rotate. As is well-known, a matrix **F** with positive determinant is uniquely decomposable in the composition product $\mathbf{F} = \mathbf{R}\mathbf{U}$ of a positive-definite symmetric matrix **U** and a rotation matrix **R**. Thus, to prevent box rotations, one should assume that, in addition to being symmetric, **F** is positive-definite. But, it would seem that a successful metadynamics might simply require that the velocity gradient **L** is symmetric-valued, consistently with our discussion of the (A–)P–R kinetic energy.[4]

4 Zero-Temperature Molecular Dynamics and the Cauchy–Born Rule

The Cauchy–Born rule is the standard recipe for computing a continuum mechanical stored-energy mapping corresponding to a given atomistic potential. There are various ways to do so, recently reviewed by Ericksen in [5]. From the Introduction of [3]: "We study the connection between atomistic and continuum models for the elastic deformation of crystalline solids at zero temperature. We prove, under certain sharp stability conditions, that the correct nonlinear elasticity model is given by the classical Cauchy–Born rule in the sense that the elastically deformed states of the atomistic model are closely approximated by solutions of the continuum model with stored energy functionals obtained from the Cauchy–Born rule."

At zero temperature, what prescription for kinetic energy is made does not matter. The first N of (14) reduce to a statement of force balance for each molecule:

$$\sum_{J\neq I} \frac{1}{r_{IJ}} \Phi'(r_{IJ})(\mathbf{s}_I - \mathbf{s}_J) = \mathbf{0} \tag{23}$$

(collectively, these equations can be seen as a discrete equivalent of the point-wise microforce balance that enters the Allen–Cahn equation for solid/solid phase transitions in the absence of diffusion [6, 7, 14]); the tensorial o.d.e. (21) reduces to

$$\sum_{I=1}^{N}\sum_{J>I}^{N} \frac{1}{r_{IJ}} \Phi'(r_{IJ})(\mathbf{s}_I - \mathbf{s}_J) \otimes (\mathbf{s}_I - \mathbf{s}_J) = \widetilde{\mathbf{S}}. \tag{24}$$

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[3] The paper by S. Nosé and M.L. Klein referred to in this quotation is found in *Mol. Phys.*, 50:1055, 1983. To see that, strictly speaking, assuming that the mapping that delivers **F** be symmetric-valued all along a metadynamics process does not serve the indicated purpose, it is enough to recall that symmetric rotations do exist: all those of the form $\mathbf{R} = 2\mathbf{w}\otimes\mathbf{w} - \mathbf{1}$, $|\mathbf{w}| = 1$ (these are rotations of π radians about an axis parallel to **w**). Moreover, for **U** a symmetric positive matrix with **w** a proper direction, it is easy to check that $\mathbf{F} = \mathbf{R}\mathbf{U}$ is a symmetric matrix whose polar decomposition entails a nontrivial rotation factor.

[4] A well-known formula from continuum kinematics:

$$\mathbf{L} = \dot{\mathbf{R}}\mathbf{R}^T + \mathbf{R}(\dot{\mathbf{U}}\mathbf{U}^{-1})\mathbf{R}^T,$$

shows that neither $\mathbf{R} \equiv \mathbf{I}$ implies that **L** is identically symmetric-valued nor the converse is true.

Interestingly, the constitutive equation for an elastic material can be given the form

$$\widetilde{\mathbf{S}} = \partial_{\mathbf{C}}\Psi(\mathbf{C}).$$

On recalling the definition of $\mathbf{C}$ and keeping in mind that any evaluation of Φ does depend on $\mathbf{F}$, we deduce the following *consistency condition* between the 'microscopic' intermolecular potential Φ and the 'macroscopic' stored-energy mapping Ψ: for all $\mathbf{F}$,

$$\partial_{\mathbf{C}}\Psi(\mathbf{F}^T\mathbf{F}) = \sum_{I=1}^{N}\sum_{J>I}^{N} \frac{1}{r_{IJ}}\Phi'(r_{IJ})(\mathbf{s}_I - \mathbf{s}_J) \otimes (\mathbf{s}_I - \mathbf{s}_J). \tag{25}$$

It would not seem that this condition has been recognized and its many implications scrutinized so far: for one, with the use of (25) the elasticity tensor

$$\mathbb{A} := \partial_{\mathbf{F}}\big(\mathbf{F}\partial_{\mathbf{C}}\Psi(\mathbf{C})\big)$$

is expressible (and computable, at any instant of an MD run) as follows in terms of the intermolecular potential:

$$\mathbb{A} = \sum_{I=1}^{N}\sum_{J>I}^{N}(\mathbf{s}_I - \mathbf{s}_J) \otimes (\mathbf{s}_I - \mathbf{s}_J) \otimes \partial_{\mathbf{F}}\left(\frac{1}{r_{IJ}}\Phi'(r_{IJ})\right).$$

It would be interesting to see whether the predictions of this general formula agree with those made in [13] on the basis of a completely different argument.

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