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Exact Solution of a Deterministic Model for Isomerization Kinetics

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Isomerization kinetics is studied on a one-dimensional ideal gas model with deterministic transitions. The concentrations of species are found to satisfy the phenomenological rate laws appropriate for diffusion-controlled kinetics, and the various correlations are determined. In the long-time regime, higher correlations present long tails reflecting a strongly non-Markovian evolution.

KEY WORDS: Chemical kinetics; master equation; ideal gas; molecular dynamics; irreversibility.

1. INTRODUCTION

The justification of kinetic equations for systems involving chemical reactions is a fundamental problem of statistical mechanics. In liquid and in gas phases, most of the approaches proposed so far involve phenomenological elements: the Boltzmann equation or its generalizations, master equations, Fokker–Planck or Langevin stochastic equations, and Smoluchowski equations are the most familiar examples (see Refs. 8 and 11 for recent surveys). A common characteristic of all these *Markovian* descriptions is the introduction of a reaction probability when collisions occur between particles; under appropriate conditions one then obtains a macroscopic rate law which agrees with the requirements imposed on the system by thermodynamics.

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Most of these theories remain poorly justified from first principles. As a matter of fact, the problem here is twofold. First, one has to face the fundamental question of how a Hamiltonian or more generally a conservative flow can reduce to a Markovian process. And second one has to incorporate into the flow dynamical processes capable of describing chemical transformations.

The first question, which constitutes the main subject of nonequilibrium statistical mechanics,(4,8,9,16) has recently been reconsidered in depth for abstract dynamical systems by Prigogine, Misra, and Courbage(12) and, from a different standpoint, by Lebowitz and Spohn (see Ref. 14 for a recent survey). Our principal goal in the present work is to focus on the second problem, postponing to a later communication the discussion of connections with these theories. Specifically, we consider a simple reactive system described by a deterministic mechanical model. This model is reversible, and it so happens that the chemical evolution occurs in a state of thermal equilibrium. In this respect, our procedure can be appropriately referred to as "analytical molecular dynamics."

In Section 2 we define the model and calculate explicitly its microscopic properties. The deterministic dynamics is that of freely moving particles carrying a color η_k changing at each encounter (there are no collisions). Such a crude approach to kinetic theory has provided useful examples, from Kac' lattice ring(2,3,7) to models for one-dimensional diffusion in gas phase.(10)

Given the thermal equilibrium state for the particle velocities and positions, we determine in Section 3 the evolution of particle colors. The number M of the "test" particles involved is finite, but arbitrary; the moment $\langle \eta_k \rangle$ of the family under consideration is rather sensitive to the prescribed state $\{x_k, v_k\}$ of its particles at initial time, but the general behavior (found by averaging also over the test particles' state) is a slow decay to the equilibrium value 0.

The distribution of populations in the color classes (N_+, N_-) can be deduced from the moments $\langle \eta_k \rangle$. They are shown in Section 4 to decay to their binomial equilibrium, but in a manifestly non-Markovian way. An exception to this is the simple equation found for the one-particle state, which turns out to have good decay properties.

Section 5 is devoted to the macroscopic (phenomenological) analog of our dynamical model, and to the comparison with the one-particle color distribution and with the average populations. The final section is devoted to conclusions and prospective remarks.

Appendices A, B, C contain detailed calculations of the moments' evolution.

2. THE MICROSCOPIC MODEL

2.1. The Deterministic Dynamics

Consider N noninteracting point particles on the line, with positions x_k^t and velocities v_k, and with equal masses m. Each of them carries a color $\eta_k \in I = \{-1, 1\}$; we call -1 white (A) and $+1$ black (B). We assume that each time two particles meet, their colors change. In other words, the history of the variable η simply keeps track of the number of encounters.

The dynamical equations of evolution are

$$x_k^t = x_k^0 + v_k t, \qquad v_k^t = v_k \tag{2.1a}$$

$$\eta_k^t = \eta_k^0 s_k^0 s_k^t \tag{2.1b}$$

where

$$s_k^t := \prod_{k'=1}^{N}{}' \operatorname{sgn}\left(x_k^t - x_{k'}^t\right) \tag{2.2}$$

The prime indicates that $k' \neq k$. The color variable η_k, expressing the only "coupling" between particles, is *driven* by the mechanical variables $(\mathbf{x}, \mathbf{v})$. For definiteness, we shall assume that for positive times, η_k is a left-continuous function of time; this amounts to modifying the sign function in (2.2) as

$$\left.\begin{array}{lll} \sigma\left(x_k^t - x_{k'}^t\right) = +1, & \text{if} \quad x_k^t > x_{k'}^t & \\ \sigma\left(x_k^t - x_{k'}^t\right) = -1 & \text{if} \quad x_k^t < x_{k'}^t & \end{array}\right\} \tag{2.3a}$$

$$\left.\begin{array}{lll} \sigma\left(x_k^t - x_{k'}^t\right) = +1 & \text{if} \quad x_k^t = x_{k'}^t & \text{and} \quad v_k \leqslant v_{k'} \\ \sigma\left(x_k^t - x_{k'}^t\right) = -1 & \text{if} \quad x_k^t = x_{k'}^t & \text{and} \quad v_k > v_{k'} \end{array}\right\} \tag{2.3b}$$

The case $(x_k = x_{k'}, v_k = v_{k'})$ may be neglected since it has measure zero in the equilibrium ensemble.

The above specification is necessary to determine the (conservative) flow underlying (2.1):

$$\left.\begin{array}{l} \dot{x}_k^t = v_k \\ \dot{v}_k^t = 0 \end{array}\right\} \tag{2.4a}$$

$$\dot{\eta}_k^t = -2 \sum_{k'=1}^{N}{}' (v_k - v_{k'})\delta\left(x_k^t - x_{k'}^t\right)\eta_k^{t-0} \tag{2.4b}$$

$$= 2 \sum_{k'=1}^{N}{}' (v_k - v_{k'})\delta\left(x_k^t - x_{k'}^t\right)\eta_k^{t+0} \tag{2.4c}$$

The evolution equations (2.1) are obviously invariant under time reversal. So are the differential equations (2.4), but the definition of η_k^t at the very time of an encounter is not: the left-continuity assumption transforms by time reversal into a right-continuity requirement as can be seen from the closed form of (2.3):

$$\sigma(x_k - x_{k'}) = \operatorname{sgn}(x_k - x_{k'}) - 2\bar{\delta}(x_k - x_{k'})\operatorname{sgn}(v_k - v_{k'})\sigma_0 \tag{2.5}$$

where $\sigma_0 := \operatorname{sgn} t$ and $\bar{\delta}$ denotes the Kronecker function. Since collisions are instantaneous, the difference between left- and right-continuity is irrelevant to the evaluation of averages $\langle \eta^0 \eta^t \rangle, \ldots$ at any time $t > 0$; but the initial time $t = 0$ plays a central role in (2.5), which we shall analyze now.

2.2. Liouville Formalism and Time Reversal

In a conservative dynamical system, the evolution of any variable q^t may be written as[13]

$$\partial_t q = iLq \tag{2.6}$$

$$q^t = e^{iLt} q^0 \tag{2.7}$$

where L is the Liouville operator.

For the ideal gas,

$$L_0 = -i \sum_{k=1}^{N} v_k \frac{\partial}{\partial x_k} \tag{2.8a}$$

whereas for our model,

$$L_c = -i \sum_{k=1}^{N} \left(\dot{x}_k \frac{\partial}{\partial x_k} + \dot{\eta}_k \frac{\partial}{\partial \eta_k} \right) \tag{2.8b}$$

These expressions can be used to express the time evolution of any correlation function $\langle q^0 q^t \rangle$ as a formal series in time:

$$\langle q^0 q^t \rangle = \sum_{n=0}^{\infty} \frac{(it)^n}{n!} \langle q^0 L^n q^0 \rangle \tag{2.9}$$

where all coefficients $\langle q^0 L^n q^0 \rangle$ are evaluated in the initial statistical ensemble. In the ideal gas, the observables are functions of $(\mathbf{x}, \mathbf{v})$, and the velocity distribution is stationary (chosen initially to be Maxwellian). For any function q of the positions x_k, we thus have

$$\langle q^0 L q^0 \rangle = -i \sum_{k=1}^{N} \langle v_k \rangle_h \left\langle q^0 \frac{\partial q^0}{\partial x_k} \right\rangle_\varphi \tag{2.10}$$

where h is the Maxwellian and φ is the spatial distribution. Because of the parity of the Maxwellian with respect to velocity reversal, this first coefficient vanishes (as does any odd power of L). There remains

$$\langle q^0 q^t\rangle = \sum_{n=0}^{\infty} \frac{(-t^2)^n}{(2n)!} \langle q^0 L^{2n} q^0\rangle \tag{2.11}$$

which is an even function of time. The equivalence between time reversal and velocity reversal operators for the ideal gas, and the parity of the initial state thus imply parity of the correlation functions under time reversal. For analytic functions, this also means that the short-time deviation from $\langle q^0 q^0\rangle$ is quadratic in t—as it can be verified in many examples of gas dynamics.(5,6)

In our model, the continuity convention (2.4) renders the prescriptions for time reversal different from a simple velocity reversal. Specifically, if we consider the color as a function of positions (as q), we simply apply the ideal gas Liouvillian to η_k ($k = 1$ for simplicity):

$$s_1 iLs_1 = s_1 \sum_{k=1}^{N} v_k \frac{\partial}{\partial x_k} \prod_{k'=2}^{N} \sigma(x_1 - x_{k'}) \tag{2.12}$$

$$= -2s_1 \sum_{k=2}^{N} (v_k - v_1)\delta(x_1 - x_k) \prod_{l=2}^{N}{}' \sigma(x_1 - x_l)$$

$$= -2 \sum_{k=2}^{N} (v_k - v_1)\delta(x_k - x_1)\sigma(x_1 - x_k) \tag{2.13}$$

$$= -2\sigma_0 \sum_{k=2}^{N} |v_k - v_1|\delta(x_k - x_1) \tag{2.14}$$

where use was made of (2.5) to resolve the ambiguity arising from the product in (2.13). The same conclusion can also be reached by using the full operator L_c and considering the η_k's as independent variables. The violation of velocity-reversal parity allows the coefficient $\langle \eta^0 L \eta^0\rangle$ to be nonzero, but the sign factor restores the parity under time reversal *at initial time*:

$$\langle \eta^0 \eta^t\rangle = \langle \eta^0 \eta^0\rangle - 2|t| \sum_{k=2}^{N} \langle |v_k - v_1| \delta(x_k - x_1)\rangle + \cdots \tag{2.15}$$

A similar expansion in $|t|$ (rather than in t^2) describes the initial decay in correlation functions for hard spheres(13); it also follows from the instantaneous jumps of velocity due to collisions, and it can also be derived from a pseudo-Liouville operator like (2.8b). Though hard-sphere dynamics are not solved exactly, the Enskog approximation and computer experiments yield enough evidence for this steep behavior close to $t = 0$. Our model can also be thought as still another illustration of pseudo-Liouville formalism but the possibility to find an exact solution dispenses us with the need to apply this formalism.

2.3. The Role of Initial Conditions

For most (mechanical) models, time reversal and velocity reversal really are equivalent (TP invariance!), so that asymmetric evolution in time, and eventually irreversible behavior, can only be derived by violating some other Liouvillian premises. One possibility is to select asymmetric initial conditions, as in Lanford's derivation of the Boltzmann hierarchy(9) or in the time-operator formalism for K systems(12); the simplest such prescription is to retain only those initial states in which the test particles have not interacted in the past. It should be pointed out, however, that in one dimension (as in the present model) the requirement for one (or more) test particle(s) to have never interacted with any other particle can only be satisfied on an ensemble of measure zero: it amounts to requiring that all particles to the left of a test particle k at initial time have velocities larger than v_k (and the ones to the right, smaller)!

3. EVOLUTION AT THE LEVEL OF PARTICLES

Though the system is explicitly integrable, we cannot write the evolution of the one-particle distribution $f(x, v, \eta, t)$ in closed form, for s_k obviously depends on the position of all other particles. But if we assume initially a state of equilibrium for the mechanical variables, we are left with only $f(\eta, t)$ or $f(\eta_1 \ldots \eta_M, t)$ for any M particles considered. A useful intermediate quantity will be the conditional distribution $f(\eta_1 \ldots \eta_M, t \mid x_1, v_1, \eta_1; \ldots; x_M, v_M, \eta_M)$. Since a discrete distribution $f(\{\eta_k\}, t)$ is completely determined by its moments $\langle \prod_{k \in \mathbf{k}} \eta_k \rangle$ for all $\mathbf{k} \subset [1, M]$, we shall first determine the latter.

3.1. The Specific Moments

For a family $\mathbf{k} \subset [1, M]$ of particles, let

$$\eta_{\mathbf{k}} = \prod_{k \in \mathbf{k}} \eta_k \tag{3.1}$$

and the relevant sign function:

$$s_{\mathbf{k}} = \prod_{k \in \mathbf{k}} \prod_{i \notin \mathbf{k}} \sigma(x_k - x_i) \tag{3.2}$$

The particles i, whose colors are not specified here, are in complete (x, v) equilibrium. They thus play the role of a bath driving the colors of the "test" particles (η_k) to equilibrium:

$$\langle\eta_h\rangle\left(\left\{x_k^0, v_k, \eta_k^0\right\}, t\right) = \int_{\mathbb{R}^{2(N-M)}} \eta_{\mathbf{k}}^0 s_{\mathbf{k}}^0 s_{\mathbf{k}}^t \prod_{i \notin \mathbf{k}} h(v_i)\, dv_i\, \varphi(x_i)\, dx_i \tag{3.3}$$

where for simplicity the velocity distribution

$$h(v) = \left(\frac{m}{2\pi k_B T}\right)^{1/2} \exp\left(-\frac{mv^2}{2k_B T}\right) \tag{3.4}$$

is chosen to be the Maxwell–Boltzmann distribution at temperature T. The spatial distribution $\varphi(x)$ is uniform since the particles are Poisson-distributed on the line:

$$\varphi(x) = \lim_{L\to\infty} \frac{1}{2L} \chi_{[-L,L]}(x) \tag{3.5}$$

and χ_Δ is the characteristic function of the subset $\Delta \subset \mathbb{R}$. The convenient scaled variables:

$$w = \left(\frac{m}{2k_B T}\right)^{1/2} v \tag{3.6a}$$

$$\tau = \left(\frac{2k_B T}{m}\right)^{1/2} |t| \tag{3.6b}$$

will directly incorporate the effect of temperature and the time-reversal parity discussed in Section 2.2. Since the bath particles have independent, identical distributions,

$$\langle\eta_{\mathbf{k}}\rangle\left(\left\{x_k^0, v_k, \eta_k^0\right\}, t\right) = \eta_{\mathbf{k}}^0 B^{N-M} \tag{3.7}$$

where

$$B\left(\left\{x_k^0, v_k\right\}, t\right) = \int_{\mathbb{R}} \prod_{k \in \mathbf{k}} \operatorname{sgn}\left(x_k^0 - x_i^0\right) A\left(\left\{x_k^0 - x_i^0 + v_k t\right\}, t\right) \varphi\left(x_i^0\right) dx_i^0 \tag{3.8a}$$

$$A\left(\left\{\xi_k\right\}, t\right) = \int_{\mathbb{R}} \prod_{k \in \mathbf{k}} \operatorname{sgn}(\xi_k - v_i t)\, h(v_i)\, dv_i \tag{3.8b}$$

These integrals are performed in Appendix A. The second physical assumption is now the thermodynamic limit $N \to \infty$, $L \to \infty$:

$$\rho = \frac{N}{L} = \lim_{L\to\infty} \frac{N-M}{L} \tag{3.9}$$

which converts the binomial expression (3.7) into the exponential:

$$\langle\eta_{\mathbf{k}}^t \eta_{\mathbf{k}}^0\rangle = \exp\left[-\rho D\left(\left\{x_k^0, v_k\right\}, t\right)\right] \tag{3.10}$$

where the function D is given by (A12). Since this function does not depend on the background particles' distribution, the only role of their large number is to allow for the thermodynamic limit (3.9) and to scale as the density in the exponent of (3.10). One can check that $D \geqslant 0$.

For one (test) particle, the decay function D is linear in time

$$D(x^0, v, t) = \tau\mu(w) \tag{3.11}$$

with

$$\mu(w) = \int_0^w \operatorname{erf} x \, dx + \frac{1}{\sqrt{\pi}} = w \operatorname{erf} w + \frac{e^{-w^2}}{\sqrt{\pi}} \tag{3.12}$$

The even function μ is convex, with its minimum at $w = 0$:

$$\mu(w) = \frac{1}{\sqrt{\pi}}(1 + w^2 + \cdots) \tag{3.13a}$$

and it increases monotonically as $w \to \pm\infty$:

$$\mu(w) = |w| + \frac{e^{-w^2}}{\sqrt{\pi}}\left(-\frac{1}{2w^2} + \cdots\right) \tag{3.13b}$$

Since the decay of the one-particle state is just determined by its mean free path, this result is in no way surprising. The angular point at $t = 0$ implied by (3.11) has been justified in Section 2.2.

The Mth degree moment $\langle \eta_{\mathbf{k}}^t \eta_{\mathbf{k}}^0 \rangle$ also starts its decay exponentially, for $|t| \ll \min_{k \neq l} |(x_k^0 - x_l^0)/(v_k - v_l)|$, the test particles are in uncorrelated parts of the "bath":

$$D\left(\left\{x_k^0, v_k\right\}, t\right) = \tau \sum_{k=1}^{M} \mu(w_k) + \mathscr{O}(\tau^2) \tag{3.14a}$$

$$\langle \eta_{\mathbf{k}}^t \eta_{\mathbf{k}}^0 \rangle = \prod_{k \in \mathbf{k}} \langle \eta_k^t \eta_k^0 \rangle e^{\mathscr{O}(\tau^2)} \tag{3.14b}$$

but with increasing time they have an increasing chance to meet some of the same background particles, and the final decay is dominated by

$$D\left(\left\{x_k^0, v_k\right\}, t\right) = \tau D_1^\infty + D_0^\infty + \mathscr{O}\left(\frac{1}{\tau}\right) \tag{3.15}$$

$$D_1^\infty = \frac{1 + (-1)^M}{2} \sum_{k=1}^{M} w_k s_k^\infty + \frac{1 - (-1)^M}{2} \sum_{k=1}^{M} \mu(w_k) s_k^\infty \tag{3.16a}$$

$$D_0^\infty = \frac{1 + (-1)^M}{2} \sum_{k=1}^{M} x_k^0 (s_k^0 + s_k^\infty) + \frac{1 - (-1)^M}{2} \sum_{k=1}^{M} x_k^0 s_k^\infty \operatorname{erf} w_k$$
$$- \sum_{k=1}^{M} s_k^0 x_k^0 \sum_{l=1}^{M} s_l^0 \operatorname{erf} w_l \tag{3.16b}$$

and

$$s_k^\infty = \prod_{k' \neq k} \operatorname{sgn}(w_k - w_{k'})$$

If we decide to release all our test particles (at the same time) from the same point, in finite number M, the moments are always in this asymptotic regime, since $D_0^\infty = 0$ as one can check directly using Eq. (3.16b).

3.2. The Average Moments

All moments decay exponentially as $|t| \to \infty$, but the damping rate depends upon the initial conditions on the test particles. Since all particles are distributed according to the equilibrium measure $h\varphi\, dv\, dx$, we have to superpose the decay laws (3.10) for all initial conditions; this will destroy the general exponential-like character of the decays.

For one test particle, the above averaging amounts to a Laplace transform:

$$\langle \eta' \eta^0 \rangle = \int_{\mathbb{R}} e^{-\tau\rho\mu(w)} h(v)\, dv \tag{3.17}$$

$$= \int_{1/\sqrt{\pi}}^{\infty} e^{-\tau\rho g} H(g)\, dg \tag{3.18}$$

with the substitution

$$g = \mu(w) \tag{3.19a}$$

$$H(g) = \frac{d \operatorname{erf} w}{d\mu(w)} = \frac{2e^{-w^2}}{\sqrt{\pi} \operatorname{erf} w} \tag{3.19b}$$

The divergence of H at $g = \pi^{-1/2}$ as

$$H\left(\frac{1+\lambda}{\sqrt{\pi}} \right) = \frac{2}{(\pi\lambda)^{1/2}} + \mathscr{O}(1) \tag{3.20}$$

determines the long-time behavior of $\langle \eta' \eta^0 \rangle$:

$$\langle \eta^0 \eta' \rangle \simeq e^{-\tau\rho/\sqrt{\pi}} \left[\frac{2\pi^{1/4}}{\sqrt{\rho\tau}} + \mathscr{O}\left(\frac{1}{\rho\tau} \right) \right] \tag{3.21}$$

The asymptotically dominant contribution in $\langle \eta^0 \eta' \rangle$ comes from the slowly moving particles (those having the largest waiting times $(\rho g)^{-1}$ between collisions). On the contrary, the short-time evolution of $\langle \eta^0 \eta' \rangle$ is sensitive mainly to the case of an intermediate test-particle velocity, implying frequent collisions:

$$gH(g) = \frac{2}{\sqrt{\pi}} \kappa(w) e^{-w^2} \frac{dw}{dg}$$
$$\langle \eta^0 \eta^t \rangle = 1 - \left(\frac{2}{\pi} \right)^{1/2} \rho\tau + \mathscr{O}(\rho^2\tau^2) \tag{3.22}$$

The decay law (3.21) is not exactly exponential because of the thermal distribution of the particle velocity smoothing the decay (3.10) (compare with the more macroscopic interpretation of Section 5), but it exhibits a definite relaxation time of order

$$t_r = \frac{1}{\rho} \left(\frac{\pi m}{2 k_B T} \right)^{1/2} \tag{3.23}$$

for both positive and negative times [cf. (3.6)]. A striking result is the validity of such an exponential approximation even in the short-time limit, Eq. (3.22):

$$\langle \eta^0 \eta^t \rangle = \langle \eta^0 \eta^{-t} \rangle = e^{-\sqrt{2}|t|/t_r} + \mathscr{O}\left(\frac{t^2}{t_r^2} \right) \tag{3.24}$$

implying nondifferentiable behavior at $t = 0$, in contrast with usual kinetic theory as discussed in Section 2.2.

A similar evaluation is possible for higher moments. For $M = 2$, $D_1^\infty = |w_2 - w_1|$:

$$\int_{\mathbb{R}^2} e^{-\rho\tau D_1^\infty} h(v_1) h(v_2)\, dv_1\, dv_2 = e^{\rho^2\tau^2/2} \operatorname{erfc} \frac{\rho\tau}{\sqrt{2}} \simeq \left(\frac{2}{\pi} \right)^{1/2} \frac{1}{\rho\tau} + \mathscr{O}\left(\frac{1}{\rho^3\tau^3} \right) \tag{3.25}$$

so that the two-particle correlation has a long-time tail

$$\langle \eta_{12}^t \rangle \sim \frac{1}{\sqrt{\pi}\, \rho\tau} = \left(\frac{m}{2\pi k_B T} \right)^{1/2} \frac{1}{\rho |t|} \tag{3.26}$$

We show in Appendix B that higher moments behave the same way: their slow decay appropriately reflects the slowly increasing ($\sim t$) separation between the test particles. Their short-time behavior, on the other hand, directly follows from (3.14) as long as they are not released from the same initial position.

The trivial character of the equation for x_i and v_i makes the spatial correlations quite irrelevant, and the evolution laws for the color lead to the following factorization of the n-time functions:

$$\langle \eta^0(x^0)\eta^{t_1}(x^1)\eta^{t_2}(x^2)\rangle \div \delta\left(x^2 - \frac{x^1 - x^0}{t_1} t_2\right) \tag{3.27}$$

$$\begin{aligned} \left\langle \prod_{l=0}^{2n} \eta^{t_l} \right\rangle &= \prod_{l=1}^{n} \langle \eta^{t_{2l}} \eta^{t_{2l-1}} \rangle \langle \eta^0 \rangle \\ \left\langle \prod_{l=0}^{2n+1} \eta^{t_l} \right\rangle &= \prod_{l=0}^{n} \langle \eta^{t_{2l}} \eta^{t_{2l+1}} \rangle \end{aligned} \tag{3.28}$$

with complete ordering of the times t_l.

3.3. Periodic Boundary Conditions

The absence of collisions enabling particles to forget their past motion makes the ideal gas very sensitive to boundary conditions. On a ring of length L (or in a box of size $L/2$), the particles encounter periodically, and the color evolution changes dramatically:

$$\tilde{s}_k = \prod_{l=1}^{N}{}' \operatorname{sgn} \sin \frac{\pi(x_k - x_l)}{L} \tag{3.29}$$

With this periodic operator, the one-particle moment exhibits a Gaussian decay (Appendix C):

$$\langle \eta^0 \eta^t \rangle \simeq \frac{N!}{((N/2)!)^2} \left(\frac{2}{\pi}\right)^{2N} e^{-N\pi\theta^2} + \mathcal{O}(e^{-(N+8)\pi\theta^2}) \tag{3.30}$$

with a scaled time

$$\theta = \frac{\sqrt{\pi}}{2L} \tau \tag{3.31}$$

Here recollisions smooth out the effect of high velocities on the decay laws of the moments. Moreover, the time-reversal operation is here equivalent to velocity reversal, and the moments are entire functions of t^2 rather than of $|t|$.

4. THE DISTRIBUTIONS OF COLORS AND POPULATIONS

The moments $\langle \eta_{\mathbf{k}} \rangle$ (for all $\mathbf{k} \subset [1, M] \cap \mathbb{N}$) also determine the probability distribution

$$f(\eta_1 = \xi_1, \ldots, \eta_M = \xi_M, t) = 2^{-M} \sum_{\mathbf{k} \subset [1,M]} \left\langle \prod_{i \in \mathbf{k}} \eta_i \xi_i \right\rangle \tag{4.1}$$

The asymptotic evaluations (Appendix B) imply the same slow decay for the probabilities

$$f(\{\xi_i\},t)-2^{-M}\sim\frac{1}{\rho\tau}+\mathscr{O}(\rho^{-2}\tau^{-2}) \tag{4.2}$$

towards the microcanonical equilibrium state:

$$\begin{aligned}\langle\eta_{\mathbf{k}}\rangle&=0, &&\forall\mathbf{k}\neq\phi\\ f(\{\xi_i\},t)&=2^{-M}, &&\forall\{\xi_i\}\in I^M\end{aligned} \tag{4.3}$$

The number of test particles of each color is

$$N_{\pm}=\sum_{k=1}^{M}\frac{1\pm\eta_k}{2}=\frac{M\pm Y}{2} \tag{4.4}$$

where $Y=\sum\eta_k$. It is distributed according to

$$\begin{aligned}P(Y,t)&=\sum_{\{\xi_k\}}\bar{\delta}\Big(Y-\sum\xi_k\Big)f(\xi_1\ldots\xi_M,t)\\ &=2^{-M}C_M^{N_-}\sum_{\mathbf{k},\mathbf{l}}(-1)^{|\mathbf{l}|}\Big\langle\prod_{k\in\mathbf{k}}\eta_k\prod_{l\in\mathbf{l}}\eta_l\Big\rangle\end{aligned} \tag{4.5}$$

where $\{\xi_k\}$ ranges over I^M, $\mathbf{k}$ over the subsets of $[1,N_+]$, and $\mathbf{l}$ over the subsets of $[1+N_+,M]$. Its moments are even easier to obtain:

$$\langle Y\rangle=2\langle N_+\rangle-M=Y(0)\langle\eta_1^t\rangle \tag{4.6a}$$

$$\langle Y^2\rangle=4\langle N_+^2\rangle-4M\langle N_+\rangle+M^2=M+\big(Y(0)^2-M\big)\langle\eta_{12}^t\rangle \tag{4.6b}$$

and the equilibrium state is the binomial

$$P(Y)=2^{-M}C_M^{(M+Y)/2} \tag{4.7}$$

While the expected populations $\langle N_{\pm}\rangle$ decay to equilibrium nearly exponentially, their variances only decay algebraically. Since analogous relations can be shown for higher moments, we see that the odd part of $P(Y)$ relaxes much faster than its even part. Such a decay is not compatible with a Markovian master equation.

5. THE MACROSCOPIC THEORY

The macroscopic analog of the dynamical system (2.1) is a mixture of two species A (or $+$) and B (or $-$) undergoing isomerization reactions:

$$\begin{aligned}A+A&\rightleftharpoons B+B\\ A+B&\rightleftharpoons B+A\end{aligned} \tag{5.1}$$

In the traditional phenomenological description, the motion of the particles between reactions would be described by diffusion. Let us introduce the variables

$$\rho = n_+ + n_- \tag{5.2a}$$

$$n = n_+ - n_- \tag{5.2b}$$

The total density ρ satisfies the conservation equation:

$$\partial_t \rho + \partial_x J = 0 \tag{5.3}$$

J being the associated current. We assume as in Section 3 that the "mechanical" variables are at equilibrium; hence

$$\rho = \rho_0, \qquad J = 0 \tag{5.4}$$

On the other hand, the color density n satisfies a phenomenological equation of the reaction-diffusion type:

$$\partial_t n = D \partial_x^2 n - 2Q\rho n \tag{5.5}$$

$$n(\pm \infty, t) = 0 \tag{5.6a}$$

$$n(x,0) = \delta(x) \tag{5.6b}$$

displaying, respectively, the diffusion coefficient D and reaction constant Q. The Green function for this system is

$$n(x,t) = \frac{Y(t)}{(4\pi D t)^{1/2}} e^{-x^2/4Dt} \tag{5.7}$$

with the global chemical population

$$Y(t) = e^{-2Q\rho t} \tag{5.8}$$

$$\frac{d}{dt} Y = -2Q\rho t \tag{5.9a}$$

$$Y(0) = 1 \tag{5.9b}$$

If our model is to bear some relevance to macroscopic chemical dynamics, it must at least exhibit the same asymptotic decay. Now, evaluating (5.7) in the long-time limit yields locally

$$n(x,t) = \frac{e^{-2Q\rho t}}{(4\pi D t)^{1/2}} \left[1 + \mathcal{O}\left(\frac{x^2}{4Dt} \right) \right] \tag{5.10}$$

which has the same form as (3.21) provided that we identify

$$Q = \left(\frac{k_B T}{2\pi m} \right)^{1/2} \tag{5.11a}$$

$$D = \frac{Q}{2\sqrt{\pi}\, \rho} \tag{5.11b}$$

Despite our very crude microdynamics, the solution of the phenomenological reaction-diffusion equation (5.5) is thus recovered as a limit of (3.21), if we focus on a spatial interval $|x| \ll (Dt)^{1/2}$. The connection between D and Q implies that diffusion of species A (and B) is governed by the free motion of the particles between reactions: one could speak of *reaction-controlled diffusion*!

In this context, it is worth noting that in the long-time limit the average color satisfies the equation [cf. (3.26)]

$$\partial_t \langle \eta \rangle = -2\mathcal{Q}\rho\langle \eta \rangle \tag{5.12}$$

with a time-dependent "rate coefficient"

$$\mathcal{Q} = \left(\frac{k_B T}{2\pi m} \right)^{1/2} + \frac{1}{8\rho t} \tag{5.13}$$

The finite limit of $\mathcal{Q}$ as $t \to \infty$ corresponds to the dominance of the exponential in (3.21) and justifies the comparison with (5.8)–(5.11).

Unfortunately, no similar equation can be written for $f(\xi_1 \ldots \xi_M, t)$, owing to the nonfactorization of correlations. It is also well known$^{(5)}$ that no diffusion equation

$$\partial_t f = \mathcal{D}\,\partial_x^2 f \tag{5.14}$$

can be derived in general for the ideal gas; at best (with a Maxwellian velocity distribution) the "diffusion coefficient" $\mathcal{D}$ would be proportional to time! For these reasons, the diffusive behavior of $\langle \eta \rangle$ in our model is really induced by reactions.

6. CONCLUSIONS

The model studied in this paper is a very crude approximation of chemical reactions. The basic element that it tries to capture is that an uncorrelated sequence of encounters between the particles leads to a chemical equilibrium in a way very similar to classical phenomenology, without resorting to a stochastic approximation in the reaction scheme. Knowing the very unphysical behavior of the density ρ of the ideal gas, the proper decay of the one-particle function $\langle \eta \rangle$ in the long-time approximation is rather satisfactory. The limitations of the free particle dynamics are nevertheless reflected by the poor decay of correlation functions, which do not factorize asymptotically into one-body functions and preclude the derivation of a closed-form master equation. In this sense of factorization, the basic elements for the evolution are not the particles, but the pairs, as is seen clearly from Eq. (3.28).

In view of the realistic behavior of our model insofar as the macroscopic evolution of concentrations is concerned, it is of interest to generalize it to the more common case of reactions involving an activation energy and to more complicated reaction kinetics.(17) Besides, since the chemical variables behave better than the mechanical ones, a further improvement would come from a more realistic dynamics such as hard-sphere interactions in one or more dimensions. Differentiable potentials can also be envisaged if one resorts to a Boltzmann–Grad limit. Such interactions lead to a stronger divergence of trajectories and so enhance the loss of correlations between pairs of particles. Yet in one dimension, the stringent ordering constraints (see Ref. 10) do not allow for a many-body reactive-diffusive behavior; Markovian reaction kinetics can, however, be derived in the hydrodynamic scaling limit.(18)

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APPENDIX A: EVALUATION OF THE PARTICLES' MOMENTS

The integrals (3.8) are expectation values of the "color factor" $s_k^t s_k^0$ for one background particle with initial position x_i^0 and velocity v_i given by the equilibrium distributions (3.4)–(3.5)

$$A(\xi_1 \ldots \xi_M, t) = \int_{\mathbb{R}} \prod_{k=1}^{M} \operatorname{sgn}(\xi_k + w_i \tau) \frac{e^{-w_i^2}}{\sqrt{\pi}}\, dw_i \tag{A1}$$

But:

$$\lim_{\xi_M \to \infty} A(\xi_1 \ldots \xi_M, t) = A(\xi_1 \ldots \xi_{M-1}, t) \tag{A2a}$$

$$\lim_{\xi_1 \to \infty} A(\xi_1, t) = 1 \tag{A2b}$$

and

$$\partial_{\xi_M} A(\xi_1 \ldots \xi_M, t) = \frac{2}{\tau} \frac{\exp(-\xi_M^2 \tau^{-2})}{\sqrt{\pi}} \prod_{k=1}^{M-1} \operatorname{sgn}(\xi_k - \xi_M) \tag{A3}$$

by direct differentiation of the sign functions. Straightforward integration of (A3) with the boundary condition (A2), and summation of the resulting series for A yields:

$$A(\xi_1 \ldots \xi_M, t) = 1 - \sum_{l=1}^{M} \operatorname{erfc}\left(\frac{\xi_l}{\tau}\right) \prod_{k=1}^{M}{}' \operatorname{sgn}(\xi_k - \xi_l) \tag{A4}$$

with the error function complement erfc defined in Ref. 1a.

The spatial integral (3.8) can also be written as

$$B\left(\left\{x_k^0, v_k\right\}, t\right) = \int_{\mathbb{R}} A\left(\left\{x - x_k^0\right\}, 0\right) A\left(\left\{x - x_k^0 - v_k t\right\}, t\right) \varphi(x)\, dx \qquad \text{(A5)}$$

with the initial sign factor:

$$A\left(\left\{x - x_k^0\right\}, 0\right) = 1 - \sum_{l=1}^{M} \left[1 - \operatorname{sgn}\left(x - x_l^0\right)\right] \prod_{k=1}^{M}{}' \operatorname{sgn}\left(x_l - x_k^0\right) \qquad \text{(A6)}$$

According to the definition (3.5) of the spatial distribution φ, B is given by the limit of

$$B_L = \frac{1}{2L} \int_{-L}^{L} A(0) A(t)\, dx \qquad \text{(A7)}$$

$$= 1 - \sum_{l=1}^{M} s_l^0 C_0^L\left(x_l^0\right) - \sum_{l=1}^{M} s_l^t C_1^L\left(x_l^t\right) + \sum_{l=1}^{M} \sum_{k=1}^{M} s_l^0 s_k^t C_2^L\left(x_l^0, x_k^t\right) \qquad \text{(A8)}$$

where each term is found explicitly:

$$C_0^L(u) = \frac{1}{2L} \int_{-L}^{L} \left[1 - \operatorname{sgn}(x - u)\right] dx = 1 + \frac{u}{L} \qquad \text{(A9a)}$$

$$\begin{aligned} C_1^L(r) &= \frac{1}{2L} \int_{-L}^{L} \operatorname{erfc} \frac{x - r}{\tau}\, dx \\ &= 1 + \frac{r}{L} + \frac{\tau}{2L}\left(\operatorname{ierfc} \frac{L + r}{\tau} - \operatorname{ierfc} \frac{L - r}{\tau}\right) \\ &= 1 + \frac{r}{L} + o\left(\frac{\tau}{L}\right) \end{aligned} \qquad \text{(A9b)}$$

$$\begin{aligned} C_2^L(u, r) &= \frac{1}{2L} \int_{-L}^{L} \left[1 - \operatorname{sgn}(x - u)\right] \operatorname{erfc} \frac{x - r}{\tau}\, dx \\ &= 2 + \frac{u + r}{L} + \frac{\tau}{L}\left(\operatorname{ierfc} \frac{L + r}{\tau} - \operatorname{ierfc} \frac{r - u}{\tau}\right) \\ &= 2 + \frac{u + r}{L} - \frac{\tau}{L} \operatorname{ierfc} \frac{r - u}{\tau} + o\left(\frac{\tau}{L}\right) \end{aligned} \qquad \text{(A9c)}$$

It seems appropriate to define

$$D_1(\{x_k\}) = \sum_{k=1}^{M} x_k s_k \qquad \text{(A10a)}$$

$$D_2\left(\left\{x_k^0, x_k^t\right\}, \tau\right) = \tau \sum_{k=1}^{M} \sum_{l=1}^{M} s_l^0 s_k^t \operatorname{ierfc} \frac{x_l^0 - x_k^t}{\tau} \qquad \text{(A10b)}$$

$$D\left(\left\{x_k^0, v_k\right\}, t\right) = D_1\left(\left\{x_1^0\right\}\right) + (-1)^M D_1\left(\left\{x_l^t\right\}\right) - D_2\left(\left\{x_k^0, x_k^t\right\}, \tau\right) \qquad \text{(A11)}$$

to obtain the dominant contribution to B_L:

$$B_L = 1 - \frac{1}{L} D + o\left(\frac{1}{L}\right) \qquad \text{(A12)}$$

A remarkable feature of the exponential factor D is its fundamental distinction between the even and odd cases of M; this property may be traced back to the summations of sign factors:

$$\sum_{l=1}^{M} s_l = \frac{1-(-1)^M}{2} \tag{A13}$$

APPENDIX B: ASYMPTOTIC BEHAVIOR OF AVERAGE MOMENTS

The moments

$$I_M(t) = \left\langle \prod_{k=1}^{M} \eta_k^t \eta_k^0 \right\rangle \tag{B1}$$

are the averages of $\langle \eta_{\mathbf{k}}^t \eta_{\mathbf{k}}^0 \rangle(\{x_k^0, v_k\}, t)$ for an equilibrium distribution of initial conditions $\{x_k^0, v_k\}$. To evaluate them from (3.17) in the limit $t \to \infty$, we define the ordered subspace of $\mathbb{R}^n$:

$$\mathrm{Or}(\mathbb{R}^n) = \{(w_k) \in \mathbb{R}^n \mid k < k' \Rightarrow w_k < w_{k'}\} \tag{B2}$$

It is well known that

$$\lim_{t\to\infty} \int_0^t t e^{-tD(x)} f(x)\, dx = \frac{f(0)}{D'(0)} \tag{B3}$$

where D is a positive function vanishing at $x = 0$, and f is continuous and bounded.

For $M = 2n$ ($n \in \mathbb{N}$)

$$D_1^\infty = \sum_{k=1}^{\infty} w_k s_k^\infty \tag{B4}$$

is the symmetric function of $\{w_k\}$ equal to

$$D_1^{\infty *} = \sum_{k=1}^{n} (w_{2k} - w_{2k-1}) \tag{B5}$$

on the ordered subspace. This positive function is minimal when $w_{2k} = w_{2k-1}$, for which case

$$\begin{gathered} D_1^\infty = 0, \qquad s_k^\infty = 0 \\ D_0^\infty = \sum_{k=1}^{M} x_k^0 s_k^0 \end{gathered} \tag{B6}$$

Hence

$$I_{2n}(t) \simeq \gamma_{2n} G_{2n}$$

with

$$\gamma_{2n} = \int_{\mathbb{R}^{2n}} \exp(-\rho \textstyle\sum x_k^0 s_k^0) \prod \varphi(x_k^0)\, dx_k^0 \tag{B7}$$

and

$$\begin{aligned} G_{2n} &= (2n)!\int_{\mathrm{Or}(\mathbb{R}^{2n})} \exp\left[-\rho\tau\sum_{k=1}^{n}(w_{2k}-w_{2k-1})\right]\prod_{k=1}^{2n}\frac{\exp(-w_k^2)}{\sqrt{\pi}}\,dw_k \\ &= (2n)!\int_{\mathrm{Or}(\mathbb{R}^{2n-2})} \exp\left[-\rho\tau\sum_{k=1}^{n-1}(w_{2k}-w_{2k-1})\right] g(w_{2n-1}) \\ &\quad\times\prod_{k=1}^{2n-2}\frac{\exp(-w_k^2)}{\sqrt{\pi}}\,dw_k \end{aligned} \tag{B8}$$

$$\begin{aligned} g(w) &= \frac{1}{\pi}\int_w^\infty\int_0^\infty \exp(-\rho\tau w'' - 2w'^2 - 2w'w'' - w''^2)\,dw''\,dw' \\ &\simeq \frac{1}{\pi}\int_w^\infty \frac{1}{\rho\tau}\exp(-2w'^2)\,dw' + \mathcal{O}\left(\frac{1}{\rho^2\tau^2}\right) \\ &\simeq \frac{1}{2(2\pi)^{1/2}\rho\tau}\operatorname{erfc}(\sqrt{2}\,w) + \mathcal{O}\left(\frac{1}{\rho^2\tau^2}\right) \end{aligned} \tag{B9}$$

Iterating this procedure, we find

$$I_{2n}(t) = \left(\frac{1}{\sqrt{\pi}\,\rho\tau}\right)^n G_{2n}^{*}\gamma_{2n} \tag{B10a}$$

where

$$G_{2n}^{*} = (2n)!\int_{\mathrm{Or}(\mathbb{R}^{n})}\exp\left(-\sum_{k=1}^{n} w_k^2\right)\prod\frac{\exp(-w_k^2)}{\sqrt{\pi}}\,dw_k = \frac{(2n)!}{n!}2^{-n/2} \tag{B10b}$$

The spatial integral γ_{2n} is spurious, as we shall not release the test particles arbitrarily far from each other (if we did, γ_{2n} would vanish). We thus find

$$I_{2n}(t) \sim \left(\frac{1}{\sqrt{\pi}\,\rho\tau}\right)^n \tag{B11}$$

The odd case $M = 2n + 1$ is evaluated similarly

$$D_1^\infty = \sum_{k=1}^{2n+1}\mu(w_k)s_k^\infty \tag{B12}$$

D_1^∞ is minimum as $w_{2l+1} = 0$ for some l, and

$$\begin{aligned} w_{2k+1} &= w_{2k} \geqslant 0, &&\text{for}\quad k > l \\ w_{2k-1} &= w_{2k} \leqslant 0, &&\text{for}\quad k \leqslant l \end{aligned} \tag{B13}$$

on the ordered subspace. For these values

$$\begin{aligned} D_1^{\infty} &= \frac{1}{\sqrt{\pi}} \\ s_k^{\infty} &= \delta_{kl} \\ D_0^{\infty} &= 0 \end{aligned} \tag{B14}$$

so that the spatial integral over $\{x_k^0\}$ disappears, but

$$\left(\frac{\partial D_1^{\infty}}{\partial w_k} \right)^{-1} = s_k^{\infty} (\operatorname{erf} w_k)^{-1} \tag{B15}$$

diverges as $w_k \to 0$. We can, however, proceed by induction over n; for $M \geqslant 5$ $(n \geqslant 2)$

$$\begin{aligned} I_{2n+1}(r) &\simeq (2n+1)! \int_{\mathrm{Or}(\mathbb{R}^{2n+1})} \exp\left[-\rho\tau \sum_{k=1}^{2n+1} \mu(w_k)(-1)^k \right] \\ &\quad \times \prod_{k=1}^{2n+1} \frac{\exp(-w_k^2)}{\sqrt{\pi}} \, dw_k \\ &= (2n+1)! \int_{\mathrm{Or}(\mathbb{R}^{2n-1})} \exp\left[-\rho\tau \sum_{k=1}^{2n-1} \mu(w_k)(-1)^k \right] \\ &\quad \times F\left(w_{2n-1}, \frac{\rho\tau}{\sqrt{\pi}} \right) \prod_{k=1}^{2n-1} \frac{\exp(-w_k^2)}{\sqrt{\pi}} \, dw_k \end{aligned} \tag{B16a}$$

where

$$F(w, \alpha) = \int_w^{\infty} \int_{w'}^{\infty} \exp\left\{ \sqrt{\pi}\, \alpha [\mu(w') - \mu(w'')] - w'^2 - w''^2 \right\} \frac{dw'\, dw''}{\pi} \tag{B16b}$$

We first assume $w > 0$ and let

$$y = \sqrt{\alpha}\, w \tag{B17}$$

Then, expanding the function μ by (3.13) up to y'^4 and y''^2, we get

$$\begin{aligned} F(w, \alpha) &\simeq \int_y^{\infty} \exp\left[y'^2 - \frac{1}{6\alpha} (y'^4 + 6y'^2) \right] \operatorname{erfc} y' \, \frac{dy'}{2\sqrt{\pi}\, \alpha} \\ &\simeq \int_y^{\infty} \exp\left[-\frac{1}{6\alpha} (y'^4 + 6y'^2) \right] \frac{1}{\sqrt{\pi}\, y'} \frac{dy'}{2\sqrt{\pi}\, \alpha} \end{aligned} \tag{B18}$$

In terms of the variable

$$r = y'^2 \alpha^{-1/2} \tag{B19}$$

F reduces to an exponential integral$^{(1b)}$:

$$F(w, \alpha) \simeq \frac{1}{8\pi\alpha} \int_{y^4/6\alpha}^{\infty} e^{-r} \frac{dr}{r} \tag{B20}$$

$$= \frac{1}{8\pi\alpha} E_1\left(\frac{y^4}{6\alpha} \right)$$

$$\simeq \frac{1}{8\pi\alpha} \left[\ln\alpha + \mathscr{O}(\ln y) \right] \tag{B21}$$

The $\mathscr{O}(\ln y)$ term is integrable even when $y \to 0$, and its contribution to $\langle \eta_{\mathbf{k}} \rangle$ may here be neglected. For negative values of y, we have

$$l_3 \leqslant y = l_{2n-1} < 0 \tag{B22}$$

and the parity of the integrand in (B16) is used to reverse all w's. Thus

$$I_{2n+1} \simeq \frac{(2n+1)!}{(2n-1)!} \frac{\ln \rho\tau}{8\sqrt{\pi}\, \rho\tau} I_{2n-1} \tag{B23}$$

On the other hand,

$$I_3 = \frac{3!}{\pi^{3/2}} \int_{-\infty}^{\infty} \exp\left[\mu(w)\rho\tau - w^2 \right] \cdot \int_{-\infty}^{w} \exp\left[-\mu(w_1)\rho\tau - w_1^2 \right] dw_1$$

$$\times \int_{w}^{\infty} \exp\left[-\mu(w_3)\rho\tau - w_3^2 \right] dw_3 \cdot dw \tag{B24}$$

$$\simeq \frac{3! \exp(-\rho\tau/\sqrt{\pi})}{\left(\sqrt{\pi}\, \rho\tau\right)^{3/2}} \int_{-\infty}^{\infty} \exp\left[y^2 - \frac{1}{6\alpha}(y^4 + 6y^2) \right]$$

$$\times \int_{-\infty}^{y} \exp(-y_1^2)\, dy_1 \int_{y}^{\infty} \exp(-y_3^2)\, dy_3\, dy$$

$$\simeq \frac{3I_1}{4\rho\tau} \int_{-\infty}^{\infty} \exp\left[y^2 - \frac{1}{6\alpha}(y^4 + 6y^2) \right] (1 - \mathrm{erf}^2 y)\, dy$$

$$\simeq \frac{3I_1}{2\rho\tau} \left(\int_{c}^{\infty} \exp\left[y^2 - \frac{1}{6\alpha}(y^4 + 6y^2) \right] \frac{2e^{-y^2}}{\sqrt{\pi}\, y}\, dy \right.$$

$$\left. + \int_{0}^{c} \exp\left[y^2 - \frac{1}{6\alpha}(y^4 + 6y^2) \right] dy \right) \tag{B25}$$

where c is an arbitrary (small) number. Since the second term is finite, we find again

$$I_3 \simeq \frac{3I_1}{4\sqrt{\pi}\,\rho\tau}\ln\rho\tau$$
$$I_{2n+1}(t) = (2n+1)!\left(\frac{\ln\rho\tau}{8\sqrt{\pi}\,\rho\tau}\right)^n I_1(t) \tag{B26}$$

The recurrent factor here decays a little more slowly than for the even case (B11), but the exponential-like decay of I_1 implies a much faster decay for I_{2n+1} than for any even moment I_{2n}.

APPENDIX C: MOMENTS ON THE RING

The moment $\langle\eta\rangle(x^0, v, t)$ for one test particle on the ring is obtained as on the line by (3.7)

$$\langle\eta^t\rangle = \eta^0 B^{N-1} \tag{C1}$$

$$B(x^0, v, t) = \frac{1}{L}\int_0^L \operatorname{sgn}\left(\sin\pi\frac{x^0 - x}{L}\right) A\left(\frac{x^0 - x}{2L}, v, t\right) dx \tag{C2}$$

$$A(\xi, v, t) = \int_{\mathbb{R}} \operatorname{sgn}\sin 2\pi\left[\xi + (\omega - \omega')\theta\right]\exp(-\pi\omega'^2)\,d\omega$$
$$= 1 - 2\sum_{h\in\mathbb{Z}}\int_0^{1/2}\exp\left[-\pi(\omega\theta + \xi + h + r)^2\theta^{-2}\right]\frac{dr}{\theta} \tag{C3}$$

where

$$\theta = \left(\frac{\pi k_B T}{2m}\right)^{1/2}\frac{t}{L} = \sqrt{\pi}\,\frac{\tau}{2L}\operatorname{sgn} t \tag{C4a}$$

$$\omega = \left(\frac{m}{2\pi k_B T}\right)^{1/2} v \tag{C4b}$$

The summation is simplified by means of Poisson's identity$^{(15)}$:

$$A(\xi, v, t) = 1 - 2\int_0^{1/2}\sum_{n\in\mathbb{Z}}\exp\left[-\pi n^2\theta^2 + 2\pi i n(\omega\theta + \xi + r)\right]dr \tag{C5}$$

$$= \sum_{n\in\mathbb{Z}_0}\exp(-\pi n^2\theta^2)\frac{1 - (-1)^n}{\pi n}\sin 2\pi n(\omega\theta + \xi) \tag{C6}$$

$$B(x^0, v, t) = \sum_{n\in\mathbb{Z}_0}\exp(-\pi n^2\theta^2)\left[\frac{1 - (-1)^n}{\pi n}\right]^2\cos 2\pi n\theta\omega \tag{C7}$$

The average decay law of $\langle\eta\rangle$ is thus:

$$\begin{aligned}\langle\eta\rangle(t) &= \int_{\mathbb{R}} B^{N-1}(x^0, v, t)\exp(-\pi\omega^2)\,d\omega \\ &= \sum_{(n_k)\in\mathbb{Z}^{N-1}} \exp\left[-\pi\theta^2 K(\mathbf{n})\right] \prod_{k=1}^{N} \left[\frac{1-(-1)^{n_k}}{\pi n_k}\right]^2 \end{aligned} \tag{C8}$$

with

$$\begin{aligned} n_N &= -\sum_{k=1}^{N-1} n_k \\ K(\mathbf{n}) &= \sum_{k=1}^{N} n_k^2 \end{aligned} \tag{C9}$$

The factor $1-(-1)^n$ actually restricts the summation to only the odd values of n_k. Higher-order correlation functions are evaluated similarly: the r integral is then split into more complicated parts, but the Gaussian decay law will remain valid:

$$B\left(\left\{x_k^0, v_k\right\}, t\right) = \sum_{n\in\mathbb{Z}} \exp(-\pi n^2\theta^2)\, b\left(n, \left\{x_k^0, v_k\right\}, t\right) \tag{C10}$$

with a coefficient b given by two integrals over $[0, 1]$ or $[0, L]$. Since this coefficient need not vanish for even indices n, the dominant contribution $K_{\mathbf{k}}(\mathbf{n})$ to the long-time decay may be slower than in the one-particle states, as we found on the line.

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