

ACCELERATED SIMULATION OF A HEAVY PARTICLE IN A GAS OF ELASTIC SPHERES*

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Abstract. A new, accelerated algorithm for a system of elastic hard spheres in which one of the particles (a colloid) is significantly heavier than the others is presented. The algorithm follows the framework of the stochastic heterogeneous multiscale method. In the limit in which the ratio between the light and the heavy particles approaches zero, the dynamics of the colloid is given by a stochastic differential equation whose drift and diffusion coefficients are not known explicitly. It is shown that these coefficients can be calculated on the fly using short-time event-driven simulations, thereby allowing us to simulate the stochastic differential equation for the colloid. The efficiency of the resulting scheme is independent of the mass ratio. A few numerical examples, which serve as a proof of principle, are presented. The examples demonstrate that our results are consistent with analytical predictions in the ideal gas limit. A result of a simulation with a dense gas is also presented.

Key words. hard spheres, elastic collisions, stochastic simulation, multiscale algorithm, heterogeneous multiscale methods, colloids, averaging theorem

AMS subject classifications. 37M05, 65C20, 74F20, 70K70

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1. Introduction. Hard-sphere (HS) systems have been the subject of extensive research for over 50 years [3, 5, 14, 23]. Due the simplicity of these systems, they have long been considered as benchmark problems for a wide range of theories and computer simulation techniques. Of particular interest are binary mixtures of spherical species differing in size and mass [8, 28], which are also considered a first approximation to colloidal suspensions.

From a computational point of view, simulating the dynamics of such binary HS mixtures has proven to be highly challenging [1, 6, 15, 26]. Even event-driven molecular dynamics (MD) [18] in which the system is advanced exactly between the discrete and instantaneous elastic collisions tends to be inefficient. The reason is that the lighter of the two HS species is usually also the faster and denser one. This implies that simulations need to resolve a large number of collisions between the small particles in order to observe any significant movement in the heavy particles. A simple estimation shows that the required simulation time is proportional to the mass ratio between the heavy and light particles. Several useful strategies have been proposed for reducing the computational cost of event-driven simulations by clever bookkeeping of possible future collisions [11, 16, 18, 19]. However, all of these methods address the dependence of the simulation efficiency on the number of particles and not on the mass ratio between the two particle species.

In this paper we present a new approach for simulating HS systems. Our method

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follows the framework of the stochastic heterogeneous multiscale method (HMM) [9, 25, 27]. In spirit, the method resembles Brownian dynamics [4] in that one identifies an effective stochastic differential equation (SDE) that approximates the time evolution of the heavy particles in a certain limit. In HMM, however, the coefficients of the effective equation are not approximated a priori. Rather, these coefficients are calculated on the fly using short-time MD simulation, thereby eliminating the need of a closure approximation. We show that the efficiency of the method is independent of the ratio between the masses of the two particle species, which constitutes a considerable improvement over a standard MD simulation.

1.1. Summary of the main results. The main purpose of this manuscript is to present the multiscale computational strategy. Therefore, we restrict the discussion to a simple case, namely a system consisting of a three-dimensional periodic box of volume V containing

- *a colloid*, which is a single hard sphere of mass M and radius R ; and
- *a gas*, which is modeled by N hard spheres of mass m and radius r .

We are interested in situations in which the colloid is much heavier than the particles in the gas, $m \ll M$, and the motion of all the particles (colloid and gas) is ballistic except for collision events. There are two types of such collisions. First, there are elastic collisions between the particles (i.e., gas-gas and gas-colloid collisions). Second, the particles of the gas are also subject to random collisions events with a heat bath which we model via an Andersen thermostat. More precisely, we introduce a sequence of times, $\{\tau_k\}_{k \in \mathbb{Z}}$, such that $\tau_k - \tau_{k-1}$ are independent random variables exponentially distributed with rate ν ; at time τ_k , a particle of the gas is picked at random and its velocity v_g is randomized according to the Gibbs–Maxwell probability density

$$(1.1) \quad \rho(v_g) = Z^{-1} e^{-\beta m |v_g|^2/2},$$

where $1/\beta > 0$ is the temperature and Z is a normalization constant. Initially, we take the colloid at rest, distribute the particles of the gas randomly in the system (subject to the constraint that they do not overlap), and independently pick each of their velocities at random from (1.1).

The role of the heat bath is to compensate for the extremely large difference between physically realistic system sizes (of the order of 10^{23} gas particles) and computationally feasible system sizes, usually of the order of several thousands of particles. In essence, the N gas particles simulate the neighborhood of the colloid. The thermostat is also important for the HMM simulations to be consistent, as discussed at length in section 3.

Because the colloid is so much heavier than the gas particles, each collision has a small effect on the colloid velocity. As a result, noticeable changes in the velocity of the colloid occur only on long time scales due to the collective effect of numerous collisions between colloid and gas, and on these time scales, the velocity performs a diffusion. Heuristically, the origin of diffusion can be explained by a central limit type of argument which goes as follows. Let $\epsilon^2 = m/M$ denote the ratio between the mass of a gas particle, m , and that of the colloid, M , so that the limit $\epsilon \rightarrow 0$ corresponds to a colloid infinitely more massive than a gas particle, and denote by $v(t)$ the velocity of the center of mass of the colloid and by $x(t) = x(0) + \int_0^t v(t') dt'$ its position. The change in the colloid velocity in a single collision is given by

$$(1.2) \quad \Delta v = 2 \frac{m}{M+m} [(v_g - v) \cdot \hat{n}] \hat{n},$$

where \hat{n} is a unit vector pointing from the center of the colloid to the center of the gas particle. Note that Δv is of order ϵ^2 . Suppose that v is small and is of order ϵ —this assumption will turn out to be correct. Assume also that the velocity of gas particles, v_g , is distributed according to (1.1)—this is actually incorrect in general but will give us the right order of magnitude estimate. Then the expectation of Δv is of order $O(\epsilon^2)$, while the variance is $O(\epsilon^4)$. In addition, the number of gas-colloid collisions in a time interval of length T is proportional to $(R+r)^2 \lambda T \langle |(v_g - v) \cdot \hat{n}| \rangle$, where $\lambda = N/V$ is the number density, V is the total volume, and brackets denote expectations with respect to the equilibrium distribution for v_g . Hence, in a time length of order ϵ^{-2} , $\epsilon^{-1}v$ is changed $O(\epsilon^{-2})$ times, where each change is of order ϵ . This suggests that the interesting dynamics of the colloid occurs under the rescaling $u(s) = \epsilon^{-1}v(\epsilon^{-2}s)$. More precisely, it is expected that for any $S \in [0, \infty)$ and any test function ϕ , we have

$$(1.3) \quad \lim_{\epsilon \rightarrow 0} \sup_{0 \leq s \leq S} |\mathbb{E}\phi(\epsilon^{-1}v(\epsilon^{-2}s)) - \mathbb{E}\phi(u(s))| = 0,$$

where $u(s)$ is the solution of the SDE

$$(1.4) \quad du = b(u)ds + \sigma(u)dB_s.$$

Here B_s denotes the Wiener process in \mathbb{R}^3 . In (1.3) the first expectation is over the statistics of the gas particles and the second over that of the Wiener process in (1.4). The drift $b(u)$ and the diffusion $\sigma(u)$ are given in terms of expectations which measure the average effect and the fluctuations above this average that the impact of the gas particles has on the colloid velocity: the form of these expectations is explicit (see section 2), but their value is unknown in general. The statement (1.3) was rigorously proven by Dürr, Goldstein, and Lebowitz [7] for an ideal gas. In the present paper, we will formally extend their argument to nonideal gases and use it to design a numerical scheme to simulate the colloid motion.

To be more specific, the limiting result (1.3) indicates that, for ϵ small but finite, we can still use the limiting SDE (1.4) for computing the evolution of the colloid position. This can be done, for example, using the following numerical scheme:

$$(1.5) \quad \begin{cases} x^{n+1} = x^n + v^n \Delta t, \\ v^{n+1} = v^n + b^\epsilon(v^n) \Delta t + \sigma^\epsilon(v^n) \sqrt{\Delta t} \xi^n, \end{cases}$$

where $b^\epsilon(v) = \epsilon^3 b(\epsilon^{-1}v)$, $\sigma^\epsilon(v) = \epsilon^2 \sigma(\epsilon^{-1}v)$, and ξ^n are independent Gaussian variables with zero mean and unit variance. Equation (1.5) is nothing but a forward Euler scheme for (1.4) to which we have added an equation to update the position of the colloid and which we have rewritten in terms of the original v and t . The scaling of time in (1.3) suggests that Δt can be taken to be of order ϵ^{-2} . Equation (1.5) requires one to evaluate $b^\epsilon(v^n)$ and $\sigma^\epsilon(v^n)$ at every iteration step. The idea behind our proposed algorithm is to do so on the fly by making a short MD simulation of the gas with fixed $v = v^n$. Hence, each Euler step requires three substeps:

1. *Microstep*: Simulate the gas using the full MD event-driven method for a time segment of length t_{micro} keeping the velocity of the colloid fixed at $v = v^n$.
2. *Estimator step*: Use the time series obtained from the microsolver to approximate $b^\epsilon(v^n)$ and $\sigma^\epsilon(v^n)$, e.g., via time averaging.
3. *Macrostep*: Move the colloid according to the forward Euler step (1.5).

This algorithm is advantageous compared to a full MD simulation if the length of the simulation at each microstep, t_{micro} , is shorter than the Euler step size, Δt . One of the main results of this paper is to show that it is possible to take $t_{\text{micro}}/\Delta t$ to be of order ϵ^2 , which represents a significant $O(\epsilon^{-2})$ gain in efficiency over a full MD simulation. This, however, requires using variance reduction techniques to estimate $b^\epsilon(v)$ and $\sigma^\epsilon(v)$, as described in detail in section 3.

1.2. Organization. The layout of the remainder of this paper is as follows. In section 2, the effective dynamics is derived in the limit when the colloid is infinitely more massive than a gas particle. Section 3 presents the HMM scheme for hard spheres, and section 4 describes a few example simulations. Finally, we summarize our results in section 5 and suggest further applications for the method.

2. Limiting dynamics. As explained in the introduction, the HMM scheme relies on the existence of a limiting equation for the colloid when $\epsilon \rightarrow 0$, where $\epsilon^2 = m/M$ measures the ratio between the mass of the gas particles and the mass of the colloid. In this section, we explain how this limiting equation arises. Note that the limit $\epsilon \rightarrow 0$ can be achieved in various equivalent ways. Throughout this paper we will assume that gas particles have unit mass, $m = 1$, while the colloid mass is large, $M = \epsilon^{-2}$.

To begin, recall that the only force acting on the colloid is due to elastic collisions with gas particles. In other words, if we concentrate on the velocity $v(t)$ of the colloid, its equation of motion can be written as

$$(2.1) \quad \dot{v}(t) = \sum_{j \in \mathbb{N}} \Delta v_j \delta(t - t_j),$$

where t_j denote the collision times between the colloid and a particle of the gas, and Δv_j is the change in velocity in a collision occurring at time t_j . Denoting by $\{v_g^k\}_{k=1, \dots, N}$ the velocities of the N particles of the gas, Δv_j is explicitly

$$(2.2) \quad \Delta v_j = 2 \frac{\epsilon^2}{1 + \epsilon^2} [(v_g^{k(j)}(t_j) - v(t_j)) \cdot \hat{n}_j] \hat{n}_j,$$

where $v_g^{k(j)}(t_j)$ is the velocity of the $k(j) \in \{1, \dots, N\}$ gas particle hitting the colloid at time t_j and \hat{n}_j is the unit vector pointing from the center of the colloid to the center of the gas particle. In terms of the scaled velocity $u(s) = \epsilon^{-1}v(\epsilon^{-2}s)$, (2.1) can be written in integral form as

$$(2.3) \quad u(s + \Delta s) = u(s) + Q_{\epsilon, \epsilon^{-2}\Delta s}(s).$$

Here we defined

$$(2.4) \quad Q_{\epsilon, T}(s) = \frac{2\epsilon}{1 + \epsilon^2} \sum_{j \in \mathbb{N}} [(v_g^{k(j)}(t_j) - \epsilon u(t_j)) \cdot \hat{n}_j] \hat{n}_j \mathbf{1}_{[\epsilon^{-2}s, \epsilon^{-2}s+T]}(t_j),$$

where $\mathbf{1}_A(t)$ is the indicator function of the set A ; i.e., $\mathbf{1}_A(t) = 1$ if $t \in A$ and $\mathbf{1}_A(t) = 0$ otherwise.

Since the change in the colloid velocity is significant only as a cumulative effect of many collisions, it is convenient to introduce a virtual fast process in which the colloid velocity is fixed. This is the essence of the argument made by Dürr, Goldstein, and Lebowitz for the case of an ideal gas [7]. In the limit of $\epsilon \rightarrow 0$, $\Delta s \rightarrow 0$ with

$\Delta s/\epsilon^2 \rightarrow \infty$, the virtual fast process approximates the change in scaled velocity in the original system, $Q_{\epsilon,\epsilon^{-2}\Delta s}(s)$. To be more precise, consider a system in which the colloid is anchored to a pivot that is moving with a fixed velocity $v = \epsilon u$. All aspects of the virtual model are the same as in the original one, except that the colloid is assumed to have an infinite mass and hence does not change its velocity even after colliding with gas particles. Gas initial conditions and their interaction with the heat bath are the same. For $j \in \mathbb{N}$, denote by $\tilde{v}_g^{\tilde{k}(j)}(\tilde{t}_j)$ the velocity of the $\tilde{k}(j) \in \{1, \dots, N\}$ gas particle hitting the colloid at time \tilde{t}_j and by \tilde{n}_j the unit vector pointing from the center of the colloid to the center of the gas particle. While in the virtual fast process the velocity of the colloid is unchanged at each collision, the velocity of the gas particle is updated as

$$(2.5) \quad \tilde{v}_g^{\tilde{k}(j)}(\tilde{t}_j+) = \tilde{v}_g^{\tilde{k}(j)}(\tilde{t}_j) - \Delta \tilde{w}_j(u),$$

where

$$(2.6) \quad \Delta \tilde{w}_j = 2[(\tilde{v}_g^{\tilde{k}(j)}(\tilde{t}_j) - \epsilon u) \cdot \tilde{n}_j] \tilde{n}_j.$$

Approximating $Q_{\epsilon,\epsilon^{-2}\Delta s}(s)$ by $\tilde{Q}_{\epsilon,\epsilon^{-2}\Delta s}(u(s))$ in (2.3), we arrive at

$$(2.7) \quad u(s + \Delta s) = u(s) + \tilde{Q}_{\epsilon,\epsilon^{-2}\Delta s}(u(s)),$$

where

$$(2.8) \quad \tilde{Q}_{\epsilon,T}(u) = \epsilon \sum_{j \in \mathbb{N}} \Delta \tilde{w}_j \mathbf{1}_{[0,T]}(\tilde{t}_j).$$

Note that, at equilibrium, the statistics of $\tilde{Q}_{\epsilon,T}(u)$ does not depend on the initial time s but only on u and the time length T . Note also that the interaction of the gas with the heat bath guarantees the existence of an equilibrium measure for the gas. This measure may be different from the initial Gibbs–Maxwell distribution because collisions with the colloid increase the energy in the system. Here we will assume that these effects are small and that the rate of convergence of the gas system to its equilibrium measure is fast on a time scale that is ϵ independent. This assumption is justified in section 3.

Then, in the limit as $\epsilon \rightarrow 0$, it can be proved using a central limit argument that $\tilde{Q}_{\epsilon,\epsilon^{-2}\Delta s}(u)$ converges to a Gaussian process with mean and variance given by

$$(2.9) \quad \begin{aligned} m_{\Delta s}(u) &= \lim_{\epsilon \rightarrow 0} \mathbb{E} \tilde{Q}_{\epsilon,\epsilon^{-2}\Delta s}(u), \\ c_{\Delta s}(u) &= \lim_{\epsilon \rightarrow 0} \mathbb{E} \left[(\tilde{Q}_{\epsilon,\epsilon^{-2}\Delta s}(u) - m_{\Delta s}(u)) \otimes (\tilde{Q}_{\epsilon,\epsilon^{-2}\Delta s}(u) - m_{\Delta s}(u)) \right], \end{aligned}$$

where \mathbb{E} denotes expectation with respect to the virtual process. The virtual process converges to equilibrium on the fast time scale. Therefore, for fixed Δs , one can replace the time segment $\epsilon^{-2}\Delta s$ with any long enough segment T with proper rescaling of the mean and variance. This becomes exact in the limit $T \rightarrow \infty$. This yields

$$(2.10) \quad \begin{aligned} m_{\Delta s}(u) &= \Delta s \lim_{\substack{\epsilon \rightarrow 0 \\ T \rightarrow \infty}} \mathbb{E} \left[\frac{1}{T} \sum_{j \in \mathbb{N}} \epsilon^{-1} \Delta \tilde{w}_j \mathbf{1}_{[0,T]}(\tilde{t}_j) \right], \\ c_{\Delta s}(u) &= \Delta s \lim_{\substack{\epsilon \rightarrow 0 \\ T \rightarrow \infty}} \mathbb{E} \left[\frac{1}{T} \sum_{i \in \mathbb{N}} \sum_{j \in \mathbb{N}} \Delta \tilde{w}_i \tilde{w}_j^T \mathbf{1}_{[0,T]}(\tilde{t}_i) \mathbf{1}_{[0,T]}(\tilde{t}_j) \right], \end{aligned}$$

where we neglected lower-order corrections coming from centering. Due to the ϵ^{-1} factor in the expression for $m_{\Delta s}(u)$ it is not clear a priori that the sum converges. However, there are additional cancellations due to the isotropy of the system when the colloid is moving slowly. This is discussed in section 2.1 for the ideal gas case and confirmed for the general case numerically in section 3.

The argument above suggests that if (2.10) converges, then (2.3) converges to the forward Euler scheme for an SDE with drift and diffusion terms given by

$$(2.11) \quad \begin{aligned} b(u) &= \Delta s^{-1} m_{\Delta s}(u), \\ a(u) &= \Delta s^{-1} c_{\Delta s}(u). \end{aligned}$$

How to prove all the assumptions stated above and compute b and a is explained in section 2.1 in the case of an ideal gas when the size of the gas particle is zero ($r = 0$); these results are formally generalized in section 2.2 to the nonideal case, which is our prime interest. The general framework is developed in [12, 13, 17, 20, 21, 22, 25, 27].

2.1. The ideal gas situation. When $r = 0$, (2.3) can be analyzed by following Dürr, Goldstein, and Lebowitz [7]. The main difficulty that had to be overcome in this analysis is that successive gas-colloid collisions are not statistically independent, even in the ideal gas situation. For instance, a gas particle can hit the colloid twice if, after collision, the colloid is pushed back by a second gas particle with enough momentum, so that the colloid catches up with the first. Such correlated events, however, become increasingly unlikely as $\epsilon \rightarrow 0$ because in this limit more and more collisions are necessary to change the colloid velocity by a noticeable amount. The main result in [7] was to show that, in the ideal gas case, gas-colloid collisions become statistically independent as $\epsilon \rightarrow 0$ and the velocities of the gas particles hitting the colloid are distributed according to the equilibrium distribution (1.1). In particular, the probability that a gas particle with velocity $|v_g| \in [v_1, v_1 + dv_1]$ hits the colloid from direction \hat{n} during the interval $[s, s + ds]$ is

$$(2.12) \quad d\mu(v_1, \hat{n}, s) = \lambda R^2 (v_1 - \epsilon u(s) \cdot \hat{n})_+ \sqrt{\frac{\beta}{2\pi}} e^{-\beta v_1^2/2} dv_1 d\nu(\hat{n}) ds,$$

where $\lambda = N/V$ is gas density, $(\cdot)_+ = \max\{\cdot, 0\}$, and $\nu(\hat{n})$ is the uniform measure on S^2 . The probability distribution (2.12) allows one to analyze the statistical properties of $\tilde{Q}_{\epsilon, \epsilon^{-2}\Delta s}(s)$ and the residue $\tilde{Q}_{\epsilon, \epsilon^{-2}\Delta s}(s) - Q_{\epsilon, \epsilon^{-2}\Delta s}(s)$. Dürr, Goldstein, and Lebowitz find that

$$(2.13) \quad \begin{aligned} b_{\text{id}} &= -2\sqrt{\frac{2\pi}{\beta}} \lambda R^2 u, \\ a_{\text{id}} &= 4\sqrt{\frac{2\pi}{\beta^3}} \lambda R^2 \text{Id}, \end{aligned}$$

where Id is the identity matrix. Hence, $u(s)$ is an Ornstein–Uhlenbeck process. It remains to show that the error introduced by replacing Q by the virtual process \tilde{Q} has a variance which is $o(\Delta s)$ when $\epsilon \rightarrow 0$. This last statement can be proven by a bootstrap argument based on $u(\epsilon^2 t_j) = u(s) + O(\sqrt{\Delta s})$ for $t_j \in [\epsilon^{-2}s, \epsilon^{-2}(s + \Delta s)]$.

This is the essence of the statement that was proven in [7]. In fact, the authors show a stronger statement than (1.3):

$$(2.14) \quad \lim_{\epsilon \rightarrow 0} \mathbb{P} \left(\sup_{0 \leq s \leq S} |\epsilon^{-1} v(\epsilon^{-2}s) - u(s)| \right) = 0,$$

where v is the velocity of the colloid in the original model and u is the solution of (1.4) with drift and diffusion coefficients given by (2.13), respectively. Note that the strong convergence result (2.14) (unlike the weak one (1.3)) requires one to relate the probability space of the Wiener process in (1.4) to that of the gas in the original system. For details see [7].

2.2. The nonideal case. The nonideal gas situation ($r > 0$) is more complicated than the ideal gas one because gas particles collide amongst themselves. While expression (2.1) remains valid, gas-gas collisions increase correlation effects in the second term at the right-hand side of (2.1). In addition, the velocities of gas particles hitting the colloid are no longer distributed according to (1.1). *In this paper, we will assume that the assumptions outlined at the beginning of section 2 remain valid in this case and hence that the motion of the colloid can be approximated by the limiting equation (1.4) with the drift and diffusion coefficient given by (2.11).* Although this assumption seems intuitively correct, we shall not attempt to prove it (in essence, it would amount to proving that gas-colloid collisions become uncorrelated before the velocity of the colloid changes noticeably). We will, however, verify its validity numerically in section 3.

3. The numerical algorithm. In this section we describe the numerical algorithm used to approximate $u(s)$ in a time segment $[0, S]$ for some $S < \infty$ independent of ϵ . Since only the virtual process \tilde{Q} is involved, all tilde notations are dropped for the rest of the paper in order to simplify notation.

The essence of the algorithm is to approximate (3.1) by a large, but finite T . This leads to the following approximations for the drift $b(u)$ and diffusion coefficient $a(u)$ in (2.11):

$$(3.1) \quad \begin{aligned} b_{\epsilon,T}(u) &= \epsilon^{-1} \frac{1}{T} \sum_{j \in \mathbb{N}} \Delta w_j \mathbf{1}_{[0,T]}(t_j), \\ a_{\epsilon,T}(u) &= \frac{1}{T} \sum_{i \in \mathbb{N}} \sum_{j \in \mathbb{N}} \Delta w_i \Delta w_j^T \mathbf{1}_{[0,T]}(t_i) \mathbf{1}_{[0,T]}(t_j). \end{aligned}$$

We can then use these coefficients in a forward Euler scheme as macrosolver with step size $\Delta t = \epsilon^{-2} \Delta s$ for evolving the colloid (compare with (1.5)):

$$(3.2) \quad \begin{cases} x^{n+1} = x^n + v^n \epsilon^{-2} \Delta s, \\ v^{n+1} = v^n + b_{\epsilon,T}(\epsilon^{-1} v^n) \epsilon \Delta s + \sigma_{\epsilon,T}(\epsilon^{-1} v^n) \epsilon \sqrt{\Delta s} \xi^n, \end{cases}$$

where $\sigma_{\epsilon,T} \sigma_{\epsilon,T}^T(u) = a_{\epsilon,T}(u)$. The rest of the section gives more details about the algorithm, in particular the evaluation of $b_{\epsilon,T}(u)$ and $a_{\epsilon,T}(u)$.

3.1. Estimating the drift $b_{\epsilon,T}(u)$. From (2.6), the velocity transfer to the colloid at each collision, Δw_j , is of order one. Hence, the sum in $b_{\epsilon,T}$ changes in jumps of order one as well. At first glance, it may seem like $b_{\epsilon,T}$ diverges in the limit $\epsilon \rightarrow 0$. However, there are additional cancellations due to the isotropy of the system at $u = 0$. To see this, we separate Δw_j into two distinct terms: $2v_g^{k(j)}(t_j) \cdot \hat{n}_j$ and $2\epsilon(u(t_j) \cdot \hat{n}_j) \hat{n}_j$. Accordingly, $b_{\epsilon,T}(u)$ can also be separated into two contributions:

$$(3.3) \quad b_{\epsilon,T}(u) = X_{\epsilon,T}(u) + Y_{\epsilon,T}(u),$$

where

$$(3.4) \quad \begin{aligned} X_{\epsilon,T}(u) &= 2\epsilon^{-1} \frac{1}{T} \sum_{i \in \mathbb{N}} v_g^{k(j)}(t_j) \cdot \hat{n}_j \mathbf{1}_{[0,T]}(t_j), \\ Y_{\epsilon,T}(u) &= 2 \frac{1}{T} \sum_{i \in \mathbb{N}} (u \cdot \hat{n}_j) \hat{n}_j \mathbf{1}_{[0,T]}(t_j). \end{aligned}$$

Note that $X_{\epsilon,T}(u)$ depends on u through the details of the collision process such as t_j and $v_g^{k(j)}(t_j)$.

We begin with the second term $Y_{\epsilon,T}(u)$. Let $R(T) = \lim_{T \rightarrow \infty} Y_{\epsilon,T}(u) - Y_{\epsilon,T}(u) = \mathbb{E}[Y_{\epsilon,T}(u)] - Y_{\epsilon,T}(u)$ denote the error in approximating the average by a finite time segment of length T . It is a random variable whose variance depends on the rate of decay of correlations in the gas, $1/\tau_{\text{cor}}$. For dilute gases, correlations decay exponentially [2, 10]. However, even at higher densities the gas evolves on a time scale that is independent of ϵ . Hence, $\mathbb{E}[R^2(T)]$ is of the order of τ_{cor}/T . This means that $Y_{\epsilon,T}(u)$ can be evaluated directly from the virtual fast process.

The term $X_{\epsilon,T}(u)$ presents additional difficulties due to the ϵ^{-1} prefactor. For a colloid at rest we have that $\mathbb{E}X_{\epsilon,T}(0) = 0$. Formally expanding in u yields $\mathbb{E}X_{\epsilon,T}(0) = O(\epsilon)$, which suggests that the limit $\epsilon \rightarrow 0$ exists. Our goal is to reduce the variance of $X_{\epsilon,T}(u)$ by eliminating the leading-order term in the sum that averages out to zero. Using the same gas initial conditions, we simulate the system twice up to time T independent of ϵ . In the first run, we take $u = 0$; i.e., the position of the colloid is fixed in the virtual fast process. In the second simulation, we move the colloid with a constant velocity $v = \epsilon u$. The difference in velocity transfer between the two simulations comes from the fact that collisions do not take place at exactly the same place on the colloid surface because the colloid moves in the second simulation and not in the first. However, since the colloid does not move by more than $\epsilon u T$, which is $O(\epsilon)$, the angle φ between u and the point of collision is also different by order ϵ . The velocity transfer, which is proportional to $\cos \varphi$, changes by order ϵ at worst. Note that this analysis also includes the case in which a collision is completely missed or added since in this case $\varphi = \pi/2$. Instead of estimating $X_{\epsilon,T}(u)$ directly, we then estimate $\epsilon^{-1} [X_{\epsilon,T}(u) - X_{\epsilon,T}(0)]$: the expectation of these two quantities is the same, but the variance of the second is $O(1)$ instead of $O(\epsilon^{-2})$ for the first.

Summarizing, $b_{\epsilon,T}(u)$ is approximated by

$$(3.5) \quad b_{\epsilon,T}(u) = \epsilon^{-1} [X_{\epsilon,T}(u) - X_{\epsilon,T}(0)] + Y_{\epsilon,T}(u).$$

This expression is, to leading order, ϵ independent and can therefore be evaluated by a time segment of length $T = O(1)$.

3.2. Estimating the diffusion coefficient $a_{\epsilon,T}(u)$. Recall the definition of $a_{\epsilon,T}(u)$ given by (3.1). Following the discussion on the evaluation of $Y_{\epsilon,T}$, $a_{\epsilon,T}(u)$ can be evaluated similarly using a short simulation with length T , which is several times larger than τ_{cor} , i.e., independent of ϵ .

Alternatively, the random variable $\sigma_{\epsilon,T}(u) \sqrt{\Delta s} \xi_i$ can be generated directly from the simulation itself since it can be checked by direct calculation that

$$(3.6) \quad \sqrt{\frac{\Delta s}{T}} \sum_{i \in N} \Delta w_i \mathbf{1}_{t_i \in [0,T]}$$

has the correct distribution to order ϵ .

3.3. Efficiency gain. The numerical scheme presented above approximates both $b(u)$ and $a(u)$ at each macrotime step. Suppose we wish to simulate the colloid dynamics with a prescribed accuracy Δ . The Euler method used for the macrosolver requires that $S\Delta s$ is of order Δ . In addition, the rate of decay of correlations of colloid-gas collisions requires that $\Delta t/\tau_{\text{cor}}$ is also of order Δ . The overall complexity of the method is $S\Delta t/(\Delta s\tau_{\text{col}})$. Hence, recalling that Δt and τ_{col} are $O(1)$ and that S and Δs are $O(\epsilon^{-2})$, we find that the complexity is independent of ϵ . This is a considerable improvement over previous methods that run in $O(\epsilon^{-2})$ time.

3.4. Details of the MD simulation. The method used for the event-driven MD simulation has a large impact on the actual running time of the simulation. However, the gain in computational time due to the multiscale scheme we suggested is independent of the MD scheme.

In the simulations described in the following section, the simulated volume is divided into cubic cells, as suggested in [3]. Denoting the length of the cells' side by l , simulation time is divided into long cycles in which none of the particles moves by more than $l/2 - r$. This guarantees that within a single long cycle a particle can collide only with others that are in one of its neighboring cells. Then we calculate the first collision time for every particle. The information on prospected collisions that may occur before the end of the long cycle are kept in a heap, arranged according to collision time. The system is then advanced, collision by collision, until the end of the long cycle. Note that at each collision there is no need to update the position of all particles but only of the particles participating in the collision. This method is described in [18].

The number of cells is chosen to maximize performance. We found that the optimal number of cells is such that the time length of long cycles is a little longer than T . Most of the computational time is spent at processing the beginning of long cycles.

Initially, gas particles are placed on a cubic lattice and velocities are chosen randomly from the Gibbs distribution with inverse temperature β . The system is equilibrated by running the MD simulation until on average all gas particles collide once. We have found that longer equilibration times do not affect the results.

3.5. The thermostat. The implementation of the thermostat is a delicate issue in our algorithm. Since we employ an Andersen thermostat, the main parameter that controls the influence of the bath on the system is the rate of randomization, ν . On one hand, this rate needs to be high enough, so that the velocity distribution of a "fresh" gas particle, which did not previously hit the colloid, is as expected at equilibrium. On the other hand, the rate cannot be too high to ruin correlation effects, at least up to several times the correlation decay time.

The reason why it is possible to adjust the heat bath to fulfill both requirements is the short time, $T = O(1)$, for which the full MD simulation is performed at each macrostep. During the MD simulation, the coupling with the bath is taken to be small. In addition, particles that recently hit the colloid, or are suspected to do so within T , are not randomized. However, after the colloid is advanced by the macrosolver, the velocity of a large fraction (or even all) of the gas particles is randomized. Using this approach, the movement of the colloid does not "heat up" the gas, while the bath does not interfere with gas-colloid collisions in the vicinity of the colloid. In practice, these requirements are checked a posteriori by testing the dependence of the results on the coupling constant and by monitoring the average and variance of the velocity of gas particles.

3.6. Some technical aspects. Our numerical scheme depends on a self-consistent assumption that the scaled velocity u is of order one. However, these assumptions may be temporarily violated due to large fluctuations, which are not only inevitable but constitute an integral part of the dynamics.

In particular, the method for calculating the drift term $b_{\epsilon,T}(u)$ depends on a fine canceling of the velocity transfer between two different simulations. An uncharacteristic velocity can result in an unrealistic value for $b_{\epsilon,T}(u)$, and the whole scheme may become unstable. In order to deal with these occurrences, the consistency of the above assumptions needs to be monitored. To this end, if the value of v is larger than a given threshold (around several times ϵ), then we do not perform any macrosteps. Instead, we advance the system using MD alone until the colloid is slowed down due to collisions with the gas. We also check to see that, at each step, the total velocity transfer to the colloid is also of order ϵ . As before, if it is larger than several times ϵ , then the macrostep is not performed. The two mechanisms described above do not change the accuracy estimate of the previous sections. However, they do reduce the efficiency since some of the macrosteps are discarded. In section 4 we show that in practice this mechanism is not applied too frequently. Nonetheless, it is important for the stability of the algorithm.

4. Example experiments. To illustrate our method, we conducted a few numerical experiments. These examples serve as a proof of principle and demonstrate that our results are consistent with analytical predictions in the infinitely dilute limit. We also describe the results of a simulation we performed with a dense gas.

The compatibility of our simulations with the expected limiting behavior is evaluated through two dynamical properties: the average fluctuation of the scaled velocity and the colloid diffusion coefficient. At equilibrium, it is expected that if collisions with gas particles are independent, then the average square velocity should be given by the equipartition theorem

$$(4.1) \quad \frac{1}{2}\epsilon^{-2}\langle v^2 \rangle = \frac{3}{2}\beta^{-1},$$

or $E_k = \beta\langle u^2 \rangle/3 = 1$.

The diffusion constant of the colloid is defined as

$$(4.2) \quad D = \lim_{T \rightarrow \infty} \frac{\langle x^2(T) \rangle}{T}.$$

In the ideal gas case we have that

$$(4.3) \quad D = \frac{1}{\sqrt{2\pi}\beta\lambda(r+R)^2},$$

where (4.3) takes into account the contribution of the radius of gas particles to the cross section of colloid-gas collisions.

As an example, we performed two different experiments. The first tests the dependence of the colloid dynamics on the mass ratio between the colloid and gas particles, ϵ^{-2} . Table 1 details our results for a dilute gas with two different values of ϵ : 0.1 and 0.02. We find that the dynamics of the colloid is well approximated by the limiting Ornstein–Uhlenbeck process even for relatively large values of ϵ . The number of particles in both simulations is $N = 40000$, and the inverse temperature is $\beta = 1$. The radius of gas particles is $r = 0.001$ and that of the colloid $R = 0.1$. The density

TABLE 1

Simulation results for a system of $N = 40000$ gas particles and $\beta = 1$. The table compares the average kinetic energy and diffusivity of the colloid as obtained using our accelerated method, with values predicted by the limiting Ornstein-Uhlenbeck process.

ϵ	E_k	D
0 (limiting)	1	0.003
0.02	0.98 ± 0.08	0.003 ± 0.0004
0.1	1.1 ± 0.1	0.0029 ± 0.0003

TABLE 2

Simulation results for a system of approximately $N = 20000$ gas particles and $\beta = 1$. The table compares the average kinetic energy and diffusivity of the colloid as obtained using our accelerated method, with values predicted by the limiting Ornstein-Uhlenbeck process.

ϕ	Analytic E_k	Analytic D	Simulation E_k	Simulation D
$1.5 \cdot 10^{-4}$	1	0.0031	0.95 ± 0.1	0.003 ± 0.0006
0.3	1	0.0015	0.9 ± 0.1	0.0009 ± 0.0002

of the gas, measured by the ratio between the volume occupied by the gas particles and the close packing volume, is approximately $\phi = 2.5 \cdot 10^{-4}$. Hence, the gas can be considered to be dilute. The length of the MD simulation, T , is taken to include, on average, about 2.5–3.5 collisions between the colloid and gas particles. The size of the macrosolver steps, Δt , is taken to be about $\Delta t = \epsilon^{-2}T/5$. Statistical errors were obtained using block averaging.

A second pair of experiments was intended to check the dependence of the colloid dynamics on the gas density. Table 2 presents our results for two additional simulations. In the first, the number of particles is $N = 25000$ and $r = 0.001$, i.e., $\phi = 1.5 \cdot 10^{-4}$. Hence, the gas is dilute. Additional simulation parameters are $\epsilon = 0.01$, $R = 0.07$, and $\beta = 1$. Once again, T was chosen to include three colloid-gas collisions on average, and the acceleration is $\Delta t/T = \epsilon^{-2}/4$. In the second simulation, the number of gas particles is $N = 20000$ and $r = 0.014$. Hence, the density of the gas is $\phi = 0.3$, which implies that it is no longer dilute. Note that this concentration is still below the liquid-solid phase transition for hard spheres, which is expected at a ratio of approximately $\phi = 0.65$. Additional simulation parameters are $R = 0.1$ and $\beta = 1$. To the best of our knowledge, there are no previous results in the literature for this system in the above parameter range.

5. Conclusions. The different schemes available for simulations of binary mixture of hard spheres can be roughly divided into two categories. The first type of method attempts to follow the evolution of all particles according to Newton's equations of motion. Included in this category are the multiscale methods proposed by Tuckerman, Berne, and Rossi [24] and similar ones. Although these methods save considerable computing time by evaluating slowly changing forces less frequently than fast changing ones, the time step taken by their innermost loops is always on the same scale as the fastest dynamics. The integrator they suggest does not include any stochastic elements. The second type of method uses Brownian dynamics [4] to simulate the limiting equations of motion without resolving any details of the gas. In this approach dynamical parameters such as b and σ have to be calculated beforehand. HMM lies in between these two types of approaches. It uses the existence of a limiting equation for the colloid but does not make a priori assumptions about the form of the coefficients in this equation. Rather, these parameters are calculated on the fly. In particular, the drift and diffusion coefficients do not necessarily have to be given by

(2.13), and this greatly increases the range of validity of the algorithm. This allows us to run the simulation in a regime which is quite different from the dilute, ideal gas case. Our results show that with dilute gases, the dynamics of the colloid is well described by an Ornstein–Uhlenbeck process with parameters b and σ given by (2.13). However, when the density of gas particles is high, correlations between successive collisions become important. Our simulations show that in this case the dynamics of the colloid deviates significantly from the analytic solution of the infinitely dilute, ideal gas limit. This, together with the fact that the efficiency of the method does not depend on the mass ratio between the colloid and gas particles, makes our HMM-based algorithm a very promising alternative to existing schemes for simulating the dynamics of binary mixtures of hard spheres.

The simulation method presented here suggests numerous applications and generalizations to systems in which the colloid dynamics is more complicated, and the limiting equation is more difficult to obtain or may not be known. For example, the case in which the colloid is not a sphere but an ellipsoid poses an enormous computational challenge. The angular momentum of the colloid has to be taken into account, and calculating collision times is more complicated. Another interesting generalization is to the case of two or more colloids. When the separation between two colloids is a few times the diameter of gas particles, the collective effect of colloid-gas collisions is to push the colloids closer together [6, 28]. We expect to find that under appropriate scaling, the two colloids become effectively trapped in a metastable state keeping them close for a long time. Hence, the limiting rate for the dynamics may be the escape rate out of this state. Simulating this system is more complicated since due to the effective force on each colloid, the system is expected to show nontrivial dynamics on the ϵ^{-1} time scale.

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REFERENCES

- [1] B. J. ALDER, *Studies in molecular dynamics. III. A mixture of hard spheres*, J. Chem. Phys., 40 (1963), pp. 2724–2730.
- [2] B. J. ALDER, D. M. GASS, AND T. E. WAINWRIGHT, *Studies in molecular dynamics. VIII. Transport coefficients for a hard-sphere fluid*, J. Chem. Phys., 53 (1970), pp. 3813–3826.
- [3] B. J. ALDER AND T. E. WAINWRIGHT, *Studies in molecular dynamics. I. General method*, J. Chem. Phys., 31 (1959), pp. 459–466.
- [4] M. P. ALLEN, *Algorithms for Brownian dynamics*, Mol. Phys., 47 (1982), pp. 599–601.
- [5] S. ASAKURE AND F. OOSAWA, *On interaction between two bodies immersed in a solution of macromolecules*, J. Chem. Phys., 22 (1954), pp. 1255–1256.
- [6] T. BIBEN, P. BLADON, AND D. FRENKEL, *Depletion effects in binary hard-sphere fluids*, J. Phys.: Condens. Matter, 8 (1996), pp. 10799–10821.
- [7] D. DÜRR, S. GOLDSTEIN, AND J. L. LEBOWITZ, *A mechanical model of Brownian motion*, Comm. Math. Phys., 78 (1981), pp. 507–530.
- [8] R. DICKMAN, P. ATTARD, AND V. SIMONIAN, *Entropic forces in binary hard sphere mixtures: Theory and simulation*, J. Chem. Phys., 107 (1997), pp. 205–213.
- [9] W. E AND B. ENGQUIST, *The heterogeneous multiscale methods*, Commun. Math. Sci., 1 (2003), pp. 87–132.
- [10] J. P. HANSEN AND I. R. McDONALD, *Theory of Simple Liquids*, Academic Press, London, 1986.
- [11] M. ISOBE, *Simple and efficient algorithm for large scale molecular dynamics simulation in hard disk system*, Internat. J. Modern Phys. C, 10 (1999), pp. 1281–1293.
- [12] R. Z. KHAS’MINSKII, *Principle of averaging for parabolic and elliptic differential equations and for Markov processes with small diffusion*, Theory Probab. Appl., 8 (1963), pp. 1–21.

- [13] R. Z. KHAS'MINSKII, *A limit theorem for solutions of differential equations with random right-hand sides*, Theory Probab. Appl., 11 (1966), pp. 390–406.
- [14] J. G. KIRKWOOD, E. K. MAUN, AND B. J. ALDER, *Radial distribution functions and the equation of state of a fluid composed of rigid spherical molecules*, J. Chem. Phys., 18 (1950), pp. 1040–1047.
- [15] W. G. KRANENDONK AND D. FRENKEL, *Thermodynamic properties of binary hard sphere mixtures*, Molec. Phys., 72 (1991), pp. 715–733.
- [16] A. T. KRANTZ, *Analysis of an efficient algorithm for the hard-sphere problem*, ACM Trans. Mod. Comp. Sim., 6 (1996), pp. 185–209.
- [17] T. G. KURTZ, *A limit theorem for perturbed operator semigroups with applications to random evolution*, J. Functional Analysis, 12 (1973), pp. 55–67.
- [18] B. D. LUBACHEVSKY, *How to simulate billiards and similar systems*, J. Comput. Phys., 94 (1991), pp. 255–283.
- [19] M. MARIN, D. RISSO, AND P. CORDERO, *Efficient algorithms for many-body hard particle molecular dynamics*, J. Comput. Phys., 109 (1993), pp. 306–317.
- [20] G. C. PAPANICOLAOU, *Some probabilistic problems and methods in singular perturbations*, Rocky Mountain J. Math., 6 (1976), pp. 653–674.
- [21] G. C. PAPANICOLAOU, *Introduction to the asymptotics analysis of stochastic equations*, in Modern Modeling of Continuum Phenomena, Lectures in Appl. Math. 16, R. C. DiPrima, ed., AMS, Providence, RI, 1977, pp. 109–147.
- [22] G. C. PAPANICOLAOU AND W. KOHLER, *Asymptotic theory of mixing stochastic ordinary differential equations*, Comm. Pure Appl. Math., 27 (1974), pp. 641–668.
- [23] H. REISS, H. L. FRISCH, AND J. L. LEBOWITZ, *Statistical mechanics of rigid spheres*, J. Chem. Phys., 31 (1959), pp. 369–380.
- [24] M. E. TUCKERMAN, B. J. BERNE, AND A. ROSSI, *Molecular dynamics algorithm for multiple time scales: Systems with disparate masses*, J. Chem. Phys., 94 (1991), pp. 1465–1469.
- [25] E. VANDEN-ELJNDEN, *Numerical techniques for multi-scale dynamical systems with stochastic effects*, Commun. Math. Sci., 1 (2003), pp. 385–391.
- [26] A. VRABECZ AND G. TÓTH, *Simulation of binary hard-sphere systems with 1:5 and 1:10 size ratios*, Mol. Phys., 104 (2006), pp. 1843–1853.
- [27] D. LIU, W. E, AND E. VANDEN-ELJNDEN, *Analysis of multiscale methods for stochastic differential equations*, Comm. Pure Appl. Math., 58 (2005), pp. 1544–1585.
- [28] Y. MAO, M. E. CATES, AND H. N. W. LEKKERKERKER, *Depletion effects in colloidal systems*, Phys. A, 222 (1995), pp. 10–24.