Modified Stokes-Einstein Relation for Small Brownian Particles

Hanqing Zhao\textsuperscript{1,2} and Hong Zhao\textsuperscript{1}

\textsuperscript{1}Department of Modern Physics, University of Science and Technology of China, Hefei 230026, China
\textsuperscript{2}Department of Modern Physics, University of Science and Technology of China, Hefei 230026, China

The validity of the Stokes-Einstein relation is well acknowledged for simple fluid and widely applied to quantitatively characterize the particle diffusion. In this Letter, we show that indeed it is not a precise law. Deviations exist for Brownian particles even at the micron level, and increases with the decrease of the Brownian particle radius. By decomposing the diffusion coefficient into the kinetic and hydrodynamic parts, we reveal that the kinetic part is inversely proportional to the square of the Brownian particle radius, and thus violates the relation. By excluding the kinetic part, we present a modified version of the Stokes-Einstein relation, and verify that it works for the Brownian particle down to several times of the fluid particle size over entire fluid region.

The Stokes-Einstein (SE) relation,

\begin{equation}
DR = \frac{k_BT}{c\eta},
\end{equation}

establishes a connection between the diffusion coefficient $D$ of a Brownian particle and the shear viscosity $\eta$ of the fluid, where $R$ is the radius of the Brownian particle, $k_B$ is the Boltzmann constant, $T$ is the temperature, and $c$ is a boundary condition dependent constant. It makes the Einstein relation \textsuperscript{11} \langle r(t)^2 \rangle = 2Dt, i.e., the mean-squared displacement is proportional to the time $t$, be a quantitative law. The validations have been concreted in certain extreme situations, such as in supercooled and glass-forming liquids \textsuperscript{216}. In dense complex media, intensive efforts have been focused on finding alternative formulas \textsuperscript{711}. However, in usual fluid or so-called Newtonian fluid, the SE relation is well acknowledged and widely applied as a general tool to estimate the size of diffusing particles \textsuperscript{1214}.

However, a fine verification of the SE relation remains insufficient even in simple fluid. Previous examinations, either experimentally \textsuperscript{2661517} or numerically \textsuperscript{151823}, focus on examining this relation for fluid particles. These studies check whether the diffusion coefficient $D$ of fluid particles and the viscosity $\eta$ of fluid satisfy the SE relation with the change of $T$ or with the change of the fluid density. The validity of the SE relation is shown for liquids, as a result that the constant $c$ drawing from these studies lies in an interval of $c \approx (\pi/6, \pi/4)$, i.e., between the predictions of slipping and stick boundary conditions. Meanwhile, the relation fails in gas region since $c$ diverges rapidly with the decrease of the fluid density \textsuperscript{1523}.

In principle, the SE relation is exacted for sufficiently large Brownian particles since it is established on the basis of the macroscopic Stokes law. For real applications, the spectrum of the Brownian particle size across several orders of magnitude, ranging from millimeter to nanometer. The open problems respective to previous examinations are as follows. First, above what a radius threshold the SE relation is applicable also for Brownian particles in gas? This is a problem of practical importance. For example, particulate matters such as aerosols and PM2.5 in atmosphere have various sizes. They are a kind of major health hazards since they can carry viruses and can go directly to the alveoli of the lungs, and also play important role in climate\textsuperscript{2425}. Second, can we really confirm the SE relation precise at molecular level in liquids? The previous positive answer implies the SE relation applies for Brownian particles of various sizes. Together with various technique difficulties, whether the SE relation really depends on sizes, has been always ignored.

The present work performs a direct size and mass dependent examination of the SE relation. Note that the right-hand side of Eq. (1) does not include any intrinsic properties of the Brownian particle. Therefore, at a given fluid density, the violation can be confirmed if $DR$ changes with $R$ or $M$. We employ the hard-sphere fluid model to perform our task. This model is the simplest nontrivial fluid model for studying fluid theories \textsuperscript{2628}. Especially to our purpose, the radius of a hard sphere is definitely defined. In such a case, only the diffusion coefficient needs to be calculated, and thus reducing dramatically the ambiguous interpretation of results. While in previous examinations, both $D$ and $\eta$ need to be obtained simultaneously.

The key step is to decompose $D$ into the kinetic and hydrodynamic parts, $D_K$ and $D_H$, respectively. In doing so, we find that $D_K \sim R^{-2}$ while $D_H \sim R^{-1}$ with the increase of $R$. The scaling behavior of $D_K$ indicates that $DR$ cannot remain a $R$-independent constant when $D_K$ cannot be ignored. In other words, the SE relation is not a precise law. Meanwhile, the behavior of $D_H$ inspires us to modify the SE relation as

\begin{equation}
D_H R = \frac{k_BT}{c\eta},
\end{equation}

We apply large-scale numerical simulation to examine Eqs. (1) and (2). The results indicate the original SE relation is approximately correct for Brownian particles in micron sizes, while significant deviations may be observed for smaller Brownian particles. On the other hand, the modified relation is accurate till Brownian particles in nanometer sizes. Meanwhile, we clarify that both relations fail significantly at the molecular level in liquids.
The SE relation is established basing on the hydrodynamic Stokes law. The successes of the modified SE relation excluding the kinetic effect obey this principle straightforwardly. We also report another example to confirm the necessity of the decomposition. The Chapman-Enskog theory of diffusion coefficient is a pure kinetic theory accounts for only the binary collisions mutually uncorrelated \[9, 28\]. Previous studies have declared the validity without performing the decomposition. In this way, the simulated diffusion coefficient may show large deviations to the theoretical prediction in higher fluid densities. \[18, 27–31\]. Excluding the hydrodynamic effect, we show that this equation is perfectly accurate over the entire fluid region.

The model. The model consists of \(N\) spheres of unit mass as fluid particles. They move in a cubic box of size \(L\) with the periodic boundary conditions. We divide the space cubic geometry into cubic boxes of side \(l = 10\), and put a sphere of radius \(b\) in each box. So, the parameter \(b\) characterizes the fluid packing density. Under these settings, the particle number density is fixed at \(n = 0.001\). The fluid particles have random velocities with unit average kinetic energy corresponding to the system temperature of \(T = 1\) (\(k_B\) is set to be unit). The Brownian particle of radius \(R\) and mass \(M\) of a sphere is set at the center of the cubic initially, and the fluid particles being overlapped are removed. The velocities are adjusted so that the total momentum vanishes. The event-driven molecular dynamics algorithm is used to evolve the system. We let the system evolve for a sufficiently long time so it has fully relaxed to the equilibrium state, then the velocity autocorrelation function (VACF), defined as \(C(t) = \langle v(t) \cdot v(0) \rangle / 3\), is calculated, where \(v(t)\) is the velocity of the Brownian particle at time \(t\). The results are averaged over multiple runs with different initial conditions.

To speed up the simulation we employ some computer tricks such as dividing the system into \(k\) subsystems and using the heap structure to sort the collision events. With these strategies, we develop an algorithm with time complexity \(\sim O(\log(N/k))\) for each collision event. When the system only involves fluid particles and we want to calculate the VACF, evolving the system an interval of time \(t\) we obtain \(N\) samples for calculating the ensemble average of VACF, since each particle can be equally considered as the tagged particle. In this case, our algorithm can perform the simulation up to \(10^6\) particles. Note that previous numerical simulations are performed with identical particles. Our studies are mainly focused on a more general and often-encountered scenario, i.e., a Brownian particle with different size and mass diffusing in fluid. In this case, only the trajectory of this particle can be applied to calculate the ensemble average, and thus evolving the system to the time \(t\) only obtains one sample. So one has to evolve the system \(N\) intervals to get the same amount of samples for calculating the diffusion coefficient. The efficiency further reduces with the increase of the Brownian particle size, since the size of subsystems should be larger than the Brownian particle and thus limits the value of parameter \(k\). Therefore, to achieve the required accuracy of ensemble average using 240 CPUs (3GHz), we usually use 27000 fluid particles in our simulations. We also check that increasing the particle number to 125000, the results will not significantly change. The maximum size of Brownian particles can be able to handle by our computer resources is about \(R \approx 25\).

Three cases with fluid particles of radius \(b = 2, 3,\) and \(4.5\), which are corresponding to packing fractions of \(\phi = 0.034, 0.11\) and \(0.39\), will be investigated in detail. Usually \(\phi = 0.3\) is considered as the boundary between gas and liquid phases \[23\]. Thus, our studies across both the gas and liquid regions.

Decomposition of \(D_K\) and \(D_H\). The diffusion coefficient can be calculated by the Green-Kubo formula

\[
D(t) = \int_0^t C(t')dt'.
\]

Previous studies have made it clear that the diffusion of a Brownian particle is governed by both kinetics and hydrodynamics \[26, 27, 32–36\]. Consequently, the VACF can be decomposed as \(C(t) = C_K(t) + C_H(t)\).

The kinetic approach of VACF is pioneered by Einstein \[1\]. The key idea is that the decay of the VACF is induced by random collisions from surrounding fluid particles, by which the Brownian particle loses its initial momentum exponentially. The collisions are considered to be uncorrelated. This consideration gives

\[
C_K(t) = C(0) \exp\left(\frac{C(0)}{D_K}t\right),
\]

where \(C(0) = k_B T / M\).

However, it has been known since the 1960s that the VACF also includes a hydrodynamic contribution: The momentum transferred to the fluid can feedback to the Brownian particle through velocity vortex field \[26, 27, 33, 35, 36\] or ring collisions \[32, 34\]. The momentum having been feedback arises \(C_H(t)\). This effect can also be approximately formulated by the extended Langevin equation by involving a memory factor from the random collisions \[27, 59\]. Since the pioneering work of Alder et al., though a fully expression over the entire time interval for this part is still absent, various approaches \[28\] have concreted that \(C_H(t)\) has a long-time tail, i.e.,

\[
C_H(t) \sim [4\pi(D_K + \nu)t]^{-\frac{3}{2}},
\]

where \(\nu = \eta / n\) is the kinematic shear viscosity.

Our idea to decompose \(C_K(t)\) from \(C(t)\) is as follows. In a short time, on the one hand, very little momentum has been transferred into the fluid from the Brownian particle. On the other hand, this part of momentum has
not played a role due to the delay: The Brownian particle collides to a fluid particle and transfers part of its momentum, and until the collision event chain involves the Brownian particle again and thus forming a ring, the Brownian particle has no feedback momentum. Based on such a understanding, we fit $D_K$ by Eq. (4) in a sufficient short time interval begin at $t = 0$. The hydrodynamic effect of the Brownian particle and thus get $C_K$, as shown in this figure too. We see that the hydrodynamic effect of the Brownian particle is significantly larger than that of the fluid particle. At large times, the VACFs converge to the long-time tail of $C(t) \sim t^{3/2}$.

Figure 1(a) and 1(b) show VACFs of a fluid particle and a Brownian particles of $R = 25$ for $M = 24$ respectively in the fluid of $b = 3$. Fitting $D_K$ following the method introduced above, we obtain $C_K$, and thus get $C_H$, as shown in this figure too. We see that the hydrodynamic effect of the Brownian particle is significantly larger than that of the fluid particle. At large times, the VACFs converge to the long-time tail of $C(t) \sim t^{3/2}$.

The coefficient $D$ can be calculated by the Green-Kubo equation. In Table I we list $D$ also for those densities. The integral time in Eq. (3) is truncated at $t = 500$, as we have checked that this truncation time is long enough to guarantee the convergence of $D$. The diffusion coefficient $D$ throughout the present paper is obtained with such a truncation time. The deviations to the theoretical prediction may over 30% in the high density region and are consistent with previous studies [18, 27, 31].

The last line of Table I shows $D_K$ calculated by the decomposition. Surprisingly, it agrees to the theoretical prediction perfectly over the entire fluid region. This fact not only confirm that the Chapman-Enskog equation is precise for the hard-sphere model but also indicate that the proper way to test a pure kinetic theory.

**Examining the original and modified SE relations.** In Fig. 2 we show $D_K$ as a function of $M$ with $R = 20$ [Fig. 2(a)], and as a function of $R$ with $M = 24$ [Fig. 2(b)] for three packing fractions. The former shows that at a fixed $R$, $D_K$ converges to a mass-independent constant. The latter indicates that at a fixed mass, $D_K$ decreases as

$$D_K \sim R^{-2},$$

when $R$ is large. Moreover, $D_K$ can be re-scaled as a universal function (i.e., multiplying it by a $b$--dependent constant and plotting it as a function of $R/b$), see the insert in Fig. 2(b). This finding implies that the original SE relation can’t be precise, since $DR = (D_K + D_H)R \sim R^{-1} + D_H R$ involves a $R$-dependent component.

**Verification of the Chapman-Enskog kinetic theory for the diffusion coefficient.** The diffusion coefficient of spheres in the homogeneous hard-sphere model can be calculated by the Chapman-Enskog theory in the first Sonine approximation [28], that is, $D_{CE} = \frac{3}{8\pi b^2g(\rho)} (\frac{k_BT}{m \pi})^{1/2}$, and $g(\rho) = (1 - \rho/2)/(1 - \rho)^3$ is the value of the equilibrium pair correlation function at contact, where $\rho = 4/3nm\pi b^3$. In Table I, we list $D_{CE}$ for different packing densities calculated by this equation.
converges at large masses, while $D_H R$ keeps mass independent always. Similar behaviors can also be confirmed in $b = 3$ and $b = 4.5$ cases. Therefore, $DR$ and $D_H R$ are mass independent for heavy Brownian particles.

The other three plots in Fig. 3 perform the $R$-dependence test for the three packing densities respectively. The mass of Brownian particles are fixed at $M = 24$ for these cases. We see that $DR$ decreases with the decrease of $R$, while $D_H R$ are size-independent for $R \geq 15$. The converged** value of $D_H R$ in Fig. 3(b) is same as in Fig. 3(a), confirming that $D_H R$ is not only mass but also size independent. It can be checked that the converged values of $D_H R$ in Fig. 3(b) and 3(d) are also mass independent. Therefore, we verify the modified SE relation for Brownian particles of $R \geq 15$, meanwhile the original SE relation fails around this scale.

At what a Brownian particle size the original SE relation applies can be estimated following the scaling behavior shown in Fig. 2(b). We expect that $DR$ should converge to $D_H R$ eventually with the increase of $R$. As Fig. 3 shown, at $R = 15$ the deviation between $DR$ and $D_H R$ is about $300\%$, $170\%$, and $150\%$ for the three packing fractions. Extrapolating $D_K/D_H$ by the universal scaling, we can estimate that if we want the deviation smaller than $1\%$, $R$ should be larger than about $R = 2500, 1500, 1000$, respectively. If we set the water molecule radius (0.3 nanometer) to be the unit of fluid particle diameter in our model, the approximate size-independent $DR$ can be observed till Brownian particles are of the micron scale in gas, and of dozens of nanometers in liquid.

In the particular case of $M = 1$ and $R = b$, i.e., the fluid particle case, we obtain that $DR$ converges to $D_H R = 18.4, 14.8$ and $4.5$ for the three densities. There is a $220\%$ deviation even in the liquid case of $b = 4.5$. Therefore, for fluid particles the original SE relation is far from a precise law.

The kinematic shear viscosity can be calculated following the method in Refs [13, 30], which gives $\nu = 11.8 \pm 0.1, 6.8 \pm 0.1$, and $18.3 \pm 0.2$ for the three packing densities, respectively. Then, we can determine the parameter $c$ in the SE relation. In Fig.3, the dash lines represent $k_B T/\eta D$ for $c = \pi/4, \pi/6$, and $\pi/8$. The first two are corresponding to the slipping and sticking boundary conditions. We see that both the slipping and the sticking boundary conditions are not exact. Instead, $c = \pi/8$ can well fit the converged $D_H R$ for all of the three densities. Therefore, we find a new universal constant $c$ although its value is inconsistent with the usual expectations.

Mechanisms behind. We propose a phenomenological approach to understand why the modified SE relation works for large Brownian particles and fails for small ones. The idea is similar to Ref. 25 (p. 246), with the key difference that we take the delay effect into account. At time $t = 0$ the Brownian particle localizes at $r = 0$. Then, its initial momentum gradually transfers to the surrounding fluid particles by collisions, and spreads out by the viscosity and sound modes. The momentum density $\Psi(r, t)$ carried by the viscosity mode relaxes diffusively as $\Psi(r, t) \sim \exp(-r^2/4t)$. This mode feeds the momentum back to the Brownian particle and contributes the hydrodynamic component $D_H$. The characteristic radius of the pack region of $\Psi(r, t)$ expands as $r_c = (t/4\nu)^{1/2}$. Assuming the Brownian particle floats as the average velocity of fluid particles within this region, the Eq. (5) can be derived 25. Based on this picture, we further emphasize that for a Brownian particle of radius $R$, the viscosity mode is physically meaningless for $t < 4\nu/R^2$ since $r_c < R$. In other words, the feedback plays a role after $t = 4\nu/R^2$. Then, plugging Eq. (5) into Eq. (3), the lower integral boundary should be larger than $t = 4\nu/R^2$. With this consideration we obtain an estimation of $D_H$, i.e.,

$$D_H \approx \int_{t=4\nu/R^2}^{\infty} C_H(t) dt \sim \sqrt{\nu / R (D_K + \nu)^{3/2}}.$$  

This formula explains, on one hand, $D_H R$ is size-independent for relatively large Brownian particles when $D_K$ can be ignored compare to $\nu$. On the other hand, it is size dependent for small enough Brownian particles when $D_K \approx \nu$. Extrapolating $D_K$ based on the scaling property shown in Fig. 2, we obtain that $R \geq 30$ can assure $D_K/\nu < 1$ for all the three densities. This agrees with the simulation results of Fig. 3, where there is already no remarkable deviations for $R \geq 15$.

Summary and discussion. Diffusion theories of Brownian particles are usually established either on the kinetic or hydrodynamic frameworks, and therefore these theories should be justified by the decomposition scheme proposed by this paper. In doing so, we verify that the Chapman-Enskog theory of kinetic diffusion coefficient is perfectly accurate over the entire fluid region. More importantly, we show that the hydrodynamic law of the SE relation is inaccurate without excluding the kinetic effect. While the modified SE relation excludes the kinetic contribution, and can be applied for Brownian particles down to several times of fluid particle size over the entire fluid region. Contrary to the well-acknowledged view, our size and mass dependent tests indicate that the SE relation could not be a quantitatively law for identical liquid particles.

We would like to point out that a fine experimental test of the size and mass dependence of the SE relation is becoming possible. Indeed, various traditional experimental technologies 12, 13, 30 were able to measure the trajectory of a single Brownian particle of hundreds nanometers. In recent years, thanks to the state-of-the-art experimental techniques, the measurements of

| $b(\phi)$ | 1(0.004) | 2(0.034) | 3(0.11) | 4(0.27) | 4.5(0.39) | 4.7(0.44) |
|----------|---------|---------|---------|---------|---------|---------|
| $D_{CE}$ | 52.3    | 12.1    | 4.35    | 1.50    | 0.763   | 0.552   |
| $D$      | 53.5    | 12.6    | 4.93    | 2.06    | 1.04    | 0.519   |
| $D_K(S)$ | 52.3    | 12.2    | 4.35    | 1.49    | 0.760   | 0.550   |

TABLE I. Kinetic coefficients obtained by the Enskog formula (E) and by simulations (S) for three dimension.
displacement as well as instant velocity of a single Brownian particle are available \cite{41-47}, and thus it is possible to obtain an accurate $C(t)$ experimentally and decompose $D_K$ and $D_H$. We look forward to the experimental investigations in the near future.

This work is supported by the NSFC (Grants No. 11335006).

\* Current address: Department of Physics, University of Colorado Boulder.

\* zhaoh@xmu.edu.cn

[1] A. Einstein. Un the movement of small particles suspended in stationary liquids required by the molecular-kinetic theory of heat. *Annalen der Physik*, 17:549–560, 1905.

[2] Ernst Rössler. Indications for a change of diffusion mechanism in supercooled liquids. *Physical review letters*, 65(13):1595, 1990.

[3] Mikhail Dzugutov, Sergei I Simdyankin, and Fredrik HM Zetterling. Decoupling of diffusion from structural relaxation and spatial heterogeneity in a supercooled simple liquid. *Physical review letters*, 89(19):195701, 2002.

[4] Stephen R Becker, Peter H Poole, and Francis W Starr. Fractional stokes-einstein and debye-stokes-einstein relations in a network-forming liquid. *Physical review letters*, 97(5):055901, 2006.

[5] Marco G Mazza, Nicolas Giovambattista, H Eugene Stanley, and Francis W Starr. Connection of translational and rotational dynamical heterogeneities with the breakdown of the stokes-einstein and stokes-einstein-debye relations in water. *Physical Review E*, 76(3):031203, 2007.

[6] Amine Dehaoui, Bruno Iessmann, and Frédéric Caupin. Viscosity of deeply supercooled water and its coupling to molecular diffusion. *Proceedings of the National Academy of Sciences*, 112(39):12020–12025, 2015.

[7] Yaakov Rosenfeld. A quasi-universal scaling law for atomic transport in simple fluids. *Journal of Physics: Condensed Matter*, 11(28):5415, 1999.

[8] Mikhail Dzugutov. addendum: A universal scaling law for atomic diffusion in condensed matter. *Nature*, 411(6838):720–720, 2001.

[9] Jean-Louis Bretomet. Self-diffusion coefficient of dense fluids from the pair correlation function. *The Journal of chemical physics*, 117(20):9370–9373, 2002.

[10] Charanbir Kaur, Upendra Harbola, and Shankar P Das. Nature of the entropy versus self-diffusivity plot for simple liquids. *The Journal of chemical physics*, 123(3):034501, 2005.

[11] Luhui Ning, Peng Liu, Yiwu Zong, Rui Liu, Mingcheng Yang, and Ke Chen. Universal scaling law for colloidal diffusion in complex media. *Physical review letters*, 122(17):178002, 2019.

[12] TG Mason, K Ganesan, JH Van Zanten, Denis Wirtz, and Scot C Kuo. Particle tracking microrheology of complex fluids. *Physical review letters*, 79(17):3282, 1997.

[13] Suliman Barhoum, Swomitra Palit, and Anand Yethiraj. Diffusion nmr studies of macromolecular complex formation, crowding and confinement in soft materials. *Progress in nuclear magnetic resonance spectroscopy*, 41:4–10, 2016.

[14] Swomitra Palit, Lilin He, William A Hamilton, Arun Yethiraj, and Anand Yethiraj. Combining diffusion nmr and small-angle neutron scattering enables precise measurements of polymer chain compression in a crowded environment. *Physical review letters*, 118(9):097801, 2017.

[15] HJ Parkhurst Jr and J Jonas. Dense liquids. ii. the effect of density and temperature on viscosity of tetramethylsilane and benzene. *The Journal of Chemical Physics*, 63(6):2705–2709, 1975.

[16] DJ Wilbur, T DeFries, and J Jonas. Self-diffusion in compressed liquid heavy water. *The Journal of Chemical Physics*, 65(5):1783–1786, 1976.

[17] Frank H Stillinger and Jennifer A Hodgdon. Translation-rotation paradox for diffusion in fragile glass-forming liquids. *Physical review E*, 50(3):2064, 1994.

[18] BJ Alder, DM Gass, and TE Wainwright. Studies in molecular dynamics. viii. the transport coefficients for a hard-sphere fluid. *The Journal of Chemical Physics*, 53(10):3813–3826, 1970.

[19] Shuang Tang, Glenn T Evans, Carl P Mason, and Michael P Allen. Shear viscosity for fluids of hard ellipsoids: a kinetic theory and molecular dynamics study. *The Journal of chemical physics*, 102(9):3794–3811, 1995.

[20] Bin Liu, J Goree, and OS Vaulina. Test of the stokes-einstein relation in a two-dimensional yakawa liquid. *Physical review letters*, 96(1):015005, 2006.

[21] Kenneth R Harris. The fractional stokes-einstein equation: Application to lemnard-jones, molecular, and ionic liquids. *The Journal of chemical physics*, 131(5):054503, 2009.

[22] Kenneth R Harris. Scaling the transport properties of molecular and ionic liquids. *Journal of Molecular Liquids*, 222-520–534, 2016.

[23] Norikazu Ohtori, Hiroki Uchiyama, and Yoshiki Ishii. The stokes-einstein relation for simple fluids: From hard-sphere to lemnard-jones via wca potentials. *The Journal of chemical physics*, 149(21):214501, 2018.

[24] Ron AM Fouchier, Sander Herfst, and Albert DME Osterhaus. Restricted data on influenza h5n1 virus transmission. *Science*, 335(6069):662–663, 2012.

[25] Drew Shindell and Christopher J Smith. Climate and air-quality benefits of a realistic phase-out of fossil fuels. *Nature*, 573(7774):408–411, 2019.

[26] B. J. Alder and T. E. Wainwright. Velocity autocorrelations for hard spheres. *Physical review letters*, 18(23):988, 1967.

[27] B. J. Alder and T. E. Wainwright. Decay of the velocity autocorrelation function. *Physical review A*, 1(1):18, 1970.

[28] J. P. Hansen and I. R. McDonald. *Theory of Simple Liquids*. Academic Press, 2006.

[29] Jerome J Erpenbeck and William W Wood. Self-diffusion coefficient for the hard-sphere fluid. *Physical Review A*, 43(8):4254, 1991.

[30] R. García-Rojo, S. Luding, and J. J. Brey. Transport coefficients for dense hard-disk systems. *Physical Review E*, 74(6):061305, 2006.

[31] H Sigurgeirsson and DM Heyes. Transport coefficients of hard sphere fluids. *Annalen der Physik*, 1970.

[32] Frank H Stillinger and Jennifer A Hodgdon. Translation-rotation paradox for diffusion in fragile glass-forming liquids. *Physical review E*, 50(3):2064, 1994.

[33] BJ Alder, DM Gass, and TE Wainwright. Studies in molecular dynamics. viii. the transport coefficients for a hard-sphere fluid. *The Journal of Chemical Physics*, 53(10):3813–3826, 1970.

[34] Shuang Tang, Glenn T Evans, Carl P Mason, and Michael P Allen. Shear viscosity for fluids of hard ellipsoids: a kinetic theory and molecular dynamics study. *The Journal of chemical physics*, 102(9):3794–3811, 1995.

[35] Bin Liu, J Goree, and OS Vaulina. Test of the stokes-einstein relation in a two-dimensional yakawa liquid. *Physical review letters*, 96(1):015005, 2006.

[36] Kenneth R Harris. The fractional stokes-einstein equation: Application to lemnard-jones, molecular, and ionic liquids. *The Journal of chemical physics*, 131(5):054503, 2009.

[37] Kenneth R Harris. Scaling the transport properties of molecular and ionic liquids. *Journal of Molecular Liquids*, 222-520–534, 2016.

[38] Norikazu Ohtori, Hiroki Uchiyama, and Yoshiki Ishii. The stokes-einstein relation for simple fluids: From hard-sphere to lemnard-jones via wca potentials. *The Journal of chemical physics*, 149(21):214501, 2018.

[39] Ron AM Fouchier, Sander Herfst, and Albert DME Osterhaus. Restricted data on influenza h5n1 virus transmission. *Science*, 335(6069):662–663, 2012.

[40] Drew Shindell and Christopher J Smith. Climate and air-quality benefits of a realistic phase-out of fossil fuels. *Nature*, 573(7774):408–411, 2019.

[41] B. J. Alder and T. E. Wainwright. Velocity autocorrelations for hard spheres. *Physical review letters*, 18(23):988, 1967.

[42] B. J. Alder and T. E. Wainwright. Decay of the velocity autocorrelation function. *Physical review A*, 1(1):18, 1970.

[43] J. P. Hansen and I. R. McDonald. *Theory of Simple Liquids*. Academic Press, 2006.

[44] Jerome J Erpenbeck and William W Wood. Self-diffusion coefficient for the hard-sphere fluid. *Physical Review A*, 43(8):4254, 1991.

[45] R. García-Rojo, S. Luding, and J. J. Brey. Transport coefficients for dense hard-disk systems. *Physical Review E*, 74(6):061305, 2006.

[46] H Sigurgeirsson and DM Heyes. Transport coefficients of hard sphere fluids. *Molecular Physics*, 101(3):469–482, 2003.

[47] J. R. Dorfman and E. G. D. Cohen. Velocity correlation functions in two and three dimensions. *Physical Review Letters*, 25(18):1257, 1970.
[34] J. R. Dorfman and E. G. D. Cohen. Velocity-correlation functions in two and three dimensions: Low density. Physical Review A, 6(2):776, 1972.

[35] Y. Pomeau and P. Resibois. Time dependent correlation functions and mode-mode coupling theories. Physics Reports, 19(2):63–139, 1975.

[36] M. H. Ernst, E. H. Hauge, and J. M. J. Van Leeuwen. Asymptotic time behavior of correlation functions. ii. kinetic and potential terms. Journal of Statistical Physics, 15(1):7–22, 1976.

[37] R. Zwanzig and M. Bixon. Hydrodynamic theory of the velocity correlation function. Physical Review A, 2(5):2005, 1970.

[38] W. B. Russel. Brownian motion of small particles suspended in liquids. Annual Review of Fluid Mechanics, 13(1):425–455, 1981.

[39] X. Bian, C. Kim, and G. E. Karniadakis. 111 years of Brownian motion. Soft Matter, 12(30):6331–6346, 2016.

[40] Neil YC Lin, Matthew Bierbaum, and Itai Cohen. Determining quiescent colloidal suspension viscosities using the green-kubo relation and image-based stress measurements. Physical review letters, 119(13):138001, 2017.

[41] Yilong Han, AM Alsayed, Maurizio Nobili, Jian Zhang, Tom C Lubensky, and Arjun G Yodh. Brownian motion of an ellipsoid. Science, 314(5799):626–630, 2006.

[42] Tongcang Li, Simon Kheifets, David Medellin, and Mark G Raizen. Measurement of the instantaneous velocity of a brownian particle. Science, 328(5986):1673–1675, 2010.

[43] Rongxin Huang, Isaac Chavez, Katja M Taute, Branimir Lukic, Sylvia Jeney, Mark G Raizen, and Ernst-Ludwig Florin. Direct observation of the full transition from ballistic to diffusive brownian motion in a liquid. Nature Physics, 7(7):576–580, 2011.

[44] Thomas Franosch, Matthias Grimm, Maxim Belushkin, Flavio M Mor, Giuseppe Foffi, Laszlo Forro, and Sylvia Jeney. Resonances arising from hydrodynamic memory in brownian motion. Nature, 478(7367):85–88, 2011.

[45] Simon Kheifets, Akarsh Simha, Kevin Melin, Tongcang Li, and Mark G Raizen. Observation of brownian motion in liquids at short times: instantaneous velocity and memory loss. science, 343(6178):1493–1496, 2014.

[46] Ignacio A Martinez, Artyom Petrosyan, David Guery-Odelin, Emmanuel Trizac, and Sergio Ciliberto. Engineered swift equilibration of a brownian particle. Nature physics, 12(9):843–846, 2016.

[47] Xuewen Fu, Bin Chen, Jau Tang, Mohammed Th Hassan, and Ahmed H Zewail. Imaging rotational dynamics of nanoparticles in liquid by 4d electron microscopy. Science, 355(6324):494–498, 2017.