Nuclear Induction Lineshape Modeling via Hybrid SDE and MD Approach

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The temperature dependence of the nuclear free induction decay in the presence of a magnetic-field
gradient was found to exhibit motional narrowing in gases upon heating, a behavior that is opposite
to that observed in liquids. This has led to the revision of the theoretical framework to include a
more detailed description of particle trajectories, since decoherence mechanisms depend on histories.
In the case of free diffusion and single component, the new model yields the correct temperature
trends. Inclusion of boundaries in the current formalism is not straightforward. We present a hybrid
SDE-MD (stochastic differential equation - molecular dynamics) approach whereby MD is used to
calculate effective viscosity and the latter is fed to the SDE to predict the lineshape. The theory
is in agreement with experiments. This two-scale approach, which bridges the gap between short
(molecular collisions) and long (nuclear induction) timescales, paves the way for the modeling of
complex environments with boundaries, mixtures of chemical species and intermolecular potentials.

I. INTRODUCTION

During the mid 20th century, when the first nuclear
magnetic resonance (NMR) experiments were performed
in liquids, magnetic-field inhomogeneity was the limiting
factor that determined the properties of nuclear induc-
tion. Rapid signal decay is problematic on so many levels,
especially because it limits the spectral resolution. This
led to the development of the Hahn echo \([1]\), where the
effects of external magnetic field inhomogeneity are re-
moved by a \(\pi\)-rotation about the \(x\) axis in a time-reversal
experiment. Spin echoes enabled more accurate studies
of intrinsic spin-spin relaxation mechanisms and mole-
cular structures. Years later, the deliberate creation and
modulation of magnetization by magnetic-field gradients
formed the basis of modern techniques in magnetic reso-
nance imaging (MRI) \([2, 3]\).

Given the ubiquitous nature and uses of magnetic-field
gradients in modern magnetic resonance experiments, it
is imperative that the nuclear response function and its
dependence on the sample under study in the presence of
applied gradients be properly understood. A correct
understanding of the true limits and capabilities of the
experiment will enable accurate interpretation of experi-
ment results, as well as inform future developments and
applications. In organic and biological chemistries, for
example, NMR spectroscopy is routinely used as a tool
to analyze solution content and composition for chemi-
cal species’ identities and relative content. Limiting fac-
tors that compromise linewidth must be minimized or re-
moved so that spectra can be obtained of sufficiently high
resolution to elucidate molecular structures. The diffu-
sion of molecules can cause undesirable effects such as
altering lineshape or be used advantageously, for exam-
ple, by helping probe transport phenomena. While diffu-
sion can sometimes lead to sharper lines (e.g., increased
spectral resolution due to diffusional averaging of the in-
termolecular magnetic dipole interaction), the presence
of residual gradients does create a complex relationship
between nuclear induction and sample properties and ge-
ometry that obscures the interpretation of results that
rely on lineshape analysis. Diffusion-weighted readouts
have enabled imaging of gases in lungs \([4]\), \(operando\) mon-
toring of chemical reaction \([5, 6]\) as well as biophysical or
mechanical properties of gels and biological tissues \([7, 8]\).
In materials science and engineering, diffusion processes
are essential to fabrication and synthesis.

In light of these various effects, the observation that in
gases lines become narrow with temperature was rather
surprising \([7, 10, 11]\) given that the conventional theory
predicted a broadening instead \([1, 12]\). In liquids,
a broadening is observed experimentally, and this is in
agreement with theory. This led to a revision of the line-
shape theory in gases accounting for the time history of
rapid molecular motions below the timescale of the NMR
experiment \([15]\). It is critical to account for the history
of molecular motions when the process involves motional
averaging due to collisions. Conventional theory ignores
the histories of molecular diffusion and instead assumes
a Gaussian probability distribution for the accumulated
phase of the spins. The Gaussian assumption on phase
accumulation, which neglects the details of molecular tra-
jectories, only appears justified in liquids, where many
collisions occur on the NMR timescale. But in gases the
average separation between molecules is much larger and
this assumption is more difficult to justify. A drawback of
the new theory is its increased complexity. While it pro-
vides good agreement between theory and experiments
in the case of free diffusion, it is unclear how one should
model the effects of realistic boundaries. Stochastic dif-
ferential equations (SDE) can be used to model mole-
cular trajectories but this still requires validation against
experiments.

In this study, we bridge the gap using molecular dy-
namics (MD) simulations and coupling it to an SDE in
order to describe the nuclear induction. By modeling viscosity of fluids using MD, the lineshape is then derived from the viscosity via its connection to the SDE. Our simulations of particle collisions and trajectories using Lennard-Jones interaction reveals opposite trends in liquid and gas particle viscosity coefficients as function of temperature. This in turn can be used to describe the lineshape trends in gases and liquids. This work establishes feasibility of the hybrid SDE-MD approach and paves the way for modeling of complex interactions with boundaries and other components. The advantages of modeling viscosity by MD include the possibility of including realistic boundaries, multiple components or varying the details of intermolecular interactions. Indeed, models of effective viscosity have already been developed for such situations [16,19].

A. Review of Conventional Theory

Assume that an ensemble of spins is placed in an external magnetic field and a coherent superposition between the states $|↑⟩$ and $|↓⟩$ is created. In an inhomogeneous field, the phase accumulation for each spin is proportional to the local field experienced by the spin over time. Phase accrued by nuclear spins can be refocused by application of a $\pi$ pulse which inverts the direction of spin rotations, or simulating a “time-reversal”, forming a Hahn echo [1] [20] [23]. If the spins are fixed (frozen) in space, evolution is described with a unitary propagator and the entropy remains constant. With diffusion (e.g. liquids and gases) not all initial phases within a spin ensemble can be recovered and the Hahn echo signal will be smaller. Assuming that the molecules undergo a random walk, it has been postulated that they sample random phase increments from a Gaussian distribution [1]. In the presence of a magnetic-field gradient $g$ the phase accrued by a spin from time 0 to $t$ is:

$$\Delta \phi(t) = \int_0^t \omega(t')dt' = \gamma_n \int_0^t g \cdot r(t')dt',$$

where $\omega(t)$ is the time-dependent frequency of a moving spin, $\gamma_n$ is the nuclear gyromagnetic ratio, and $r(t)$ is the time-dependent position of the diffusing particle. The nuclear induction signal is weighted by the ensemble average of these phase factors, written with probability distribution $P(\Delta \phi)$

$$\langle \exp(i\Delta \phi(t)) \rangle = \int_{-\infty}^{\infty} P(\Delta \phi) \exp(i\Delta \phi)d(\Delta \phi).$$

To alleviate the notation we will drop $t$ from the notation and write $\Delta \phi(t) = \Delta \phi$. Assuming a Gaussian distribution for $P(\Delta \phi)$ with variance $\langle (\Delta \phi)^2 \rangle$ proportional to $t$, we get

$$S(t) = \langle \exp(i\Delta \phi) \rangle = \exp(- \langle (\Delta \phi)^2 \rangle /2).$$

Thus for the free diffusion under steady magnetic field of a linear gradient $g$ and duration $t$, attenuation of the NMR signal $S(t)$ was found to be

$$S(t) = \exp\left[(-1/3)\gamma_n^2 g^2 D t^3\right],$$

where $D$ is the self-diffusion coefficient and the $t^3$ decay arises from self-diffusion in presence of a field gradient [23, 24]. This equation shows that for unrestricted diffusion, as $D$ gets larger a wider range of $\Delta \phi$ is sampled resulting in faster damping of the signal. In the Hahn echo experiment, $90^\circ - \tau - 180^\circ - \tau$, at $t = 2\tau$ the decay function is similar:

$$S(2\tau) = \exp(-\frac{2}{3}\gamma_n^2 g^2 D \tau^3).$$

The $t^3$ dependence has been validated experimentally for liquids. This form of signal can be used to describe a Carr-Purcell-Meiboom-Gill (CPMG) experiment with $n$ refocusing $\pi$ pulse and interpulse delay of $2\tau$ [20] [25]. The signal at $t = 2n\tau$ decays according to

$$S(2n\tau) = \exp\left(-\frac{2}{3}\gamma_n^2 g^2 D \tau^2(n\tau)\right).$$

As a result, the signal attenuation at time $t = 2n\tau$ can be reduced by decreasing time delay between the pulses $\tau$ while increasing number of pulses $n$. Equations (4) and (5) have been extensively validated in experiments for the case of liquids. The assumption of Gaussian-distributed phase increments is reasonable for liquids because of the short mean-free paths and large number of collisions during time intervals of duration $\tau$.

B. Problems With Conventional Theory

In the case of gas molecules, which are characterized by longer mean free paths, the assumption of randomly distributed phase increments becomes more difficult to justify [10, 26]. A simple example can be used to illustrate the need for a more sophisticated model. Take the Ornstein-Uhlenbeck process, which is used to model Brownian particle diffusion. The velocity process obeys the SDE:

$$dv = -\gamma vdt + \frac{\Gamma_f}{M}dW(t),$$

where $\gamma^{-1}$ is a damping time constant, $dW(t)$ is the increment of the Wiener process $W(t)$ at time $t$ ($dW(t) := W(t) - W(t - dt)$). The strength of fluctuations is $\Gamma_f = \sqrt{2\gamma M k_B T}$ (fluctuation-dissipation theorem), where $M$ is the mass of diffusing particle and $k_B$ is the Boltzmann constant. After integration

$$v(t) = \langle v(t) \rangle + \frac{\sqrt{2\gamma k_B T}}{M}e^{-\gamma t} \int_0^t e^{\gamma t'} dW(t'),$$

$$\langle \Delta \phi(t) \rangle = \int_{-\infty}^{\infty} P(\Delta \phi) \exp(i\Delta \phi)d(\Delta \phi).$$
where $\langle v(t) \rangle = \langle v_0 \rangle e^{-\gamma t}$. The position process is the time integral of the velocity process, $dx(t) = v(t)dt$, whose solution is (setting $x(0) = 0$):

$$x(t) = \frac{v_0}{\gamma}(1-e^{-\gamma t}) + \sqrt{\frac{2\gamma k_B T}{M}} \int_0^t dt' e^{-\gamma t'} \int_0^{t'} dW(t'') e^{\gamma t''}.$$ 

Defining a thermal velocity $v_T = \sqrt{k_B T/M}$, the distribution of $x(t)$ is (again, assuming $x(0) = 0$),

$$p(x,t) = \frac{1}{\sqrt{2\pi\sigma_z^2(t)}} \exp\left[-\frac{(x - v_T(1 - e^{-\gamma t})/\gamma)^2}{2\sigma_z^2(t)}\right]$$

where

$$\sigma_z^2(t) := \frac{2v_T^2}{\gamma}t - \frac{v_T^2}{\gamma^2}(3 - 4e^{-\gamma t} + e^{-2\gamma t})$$

at short $t$ is not the usual Gaussian with variance $t$ characteristic of long-time particle diffusion (i.e. the Einstein-Fick limit). Only at long times ($t \gg \gamma^{-1}$) does the distribution become Gaussian with variance $t$:

$$p(x,t) \to \frac{1}{\sqrt{4\pi D}t} \exp\left[-\frac{(x - v_T/\gamma)^2}{4Dt}\right]$$

with diffusion coefficient $D = k_B T/M \gamma$. To compute the accrued phase, which is a time integral of $x(t)$ (c.f. Equation 1), it appears prudent to model the behavior at short times ($t \lesssim \gamma^{-1}$). The timescale $\gamma^{-1}$ of the friction coefficient is associated with molecular collisions.

It has been shown [10] that Eq. (4) or (5) does not describe the nuclear induction decay in gases. Instead, it was observed that in the CPMG experiment:

$$\langle \exp(i\Delta \phi) \rangle = \exp(-\gamma^2 g^2 \kappa(2n\tau)).$$

(6)

Here the decay constant $\kappa$ is a decreasing function of temperature $T$, damping rate $\gamma$, and particle mass $M$, Eq. [17]. Notice the different powers of $\tau$ inside the argument of the exponential function ($\tau^3$ vs $\tau$). This difference was first noticed by observing the linewidth dependence on temperature [7] and subsequently investigated more in-depth in Ref. [10, 26]. The conclusion from these studies is that a more detailed description of diffusion effects is needed. Obviously, exact solutions to the N-body problem are not possible; hence we seek suitable models.

### C. Generalized Langevin Equation (GLE)

The GLE is a well-established model of particle diffusion that accounts for memory effects as the molecules undergo diffusion via collisions. In the gas and liquid phase, nuclear spin degrees of freedom are fairly well isolated from spatial degrees of freedom, at least to first order. Consequently, individual molecular collisions, do not completely depolarize the spins. Instead, decoherence and depolarization processes, which are second-order processes, take place over much longer periods of time. Decoherence is described by a characteristic decay time $T_2$. The motional part of the NMR signal thus can be written as the expectation value of the spin phase factors [c.f. Equation 1] with $\omega(t) = \gamma g \cdot x(t)$ in 1-D which depend on their position $x(t)$ [10, 24]. In Ref. [10] it is assumed that $x(t)$ is a Gaussian random process that is stationary in the wide sense. The expectation value

$$S(t) = \langle \exp\left[i \int_0^t \omega(t')dt'\right] \rangle$$

(7)

takes the form:

$$\exp\left[i\gamma g \int_0^t \langle x(t') \rangle dt' - \gamma g^2 \int_0^t \langle x(t')x(0) \rangle (t - t')dt'\right].$$

The second term determines the lineshape of the signal decay. For liquids, displacements are small $x(t) \approx x(0)$ and this leads to the Einstein-Fick limit $\langle x(t)x(0) \rangle \approx \langle x(t)x(0) \rangle = 2Dt$, where $D$ is a diffusion coefficient, and the classic Hahn result [3] is recovered.

We note that there is no easy way to compute the integral over the function $\langle x(t)x(0) \rangle$ from first principles in the general case of arbitrary physical conditions. Even MD simulations fail because $\langle x(t)x(0) \rangle$ decays on short time scales (tens to hundreds of picoseconds) before reaching a nonzero steady state value, after which the time integral is weighted by the monotonically increasing weight $(t - t')dt'$ over much longer time scales (milliseconds to seconds). The initial decay, and any numerical errors associated with it, is then amplified by orders of magnitude. Instead, a model is needed that bridges the two widely different timescales by analytically solving the integral and reducing it to a function of transport coefficients that are easier to compute. Such a transformation was first presented in Ref. [7]. The main steps of its derivation, although well known to the fluid dynamics community, are recapped below for convenience.

In the “weak collision” regime (see Ref. [10]) a GLE with memory kernel describes particle dynamics

$$M \dot{v} + \int_0^t \Gamma(t - t')v(t')dt' = \eta_f(t)$$

(8)

where $M$ is the mass of diffusing particle, $v(t) = \dot{x}(t)$ and $\dot{v}$ are particle velocity and acceleration. $\eta_f(t)$ on the right-hand side, represents a time-dependent stochastic force. The memory kernel $\Gamma(t)$, is convoluted with the particle velocity to describe the friction asserted by the viscous dynamics. Projecting both sides of the GLE equation with the inner product $\langle v(0), \cdot \rangle$ we get

$$M \langle v(0)\dot{v}(t) \rangle + \int_0^t \Gamma(t - t') \langle v(0)v(t') \rangle dt' = 0.$$ 

(9)

Fluctuation-dissipation, $\langle \eta_f(0)\eta_f(t) \rangle = k_BT \Gamma(t)$, and equipartition, $\langle v(0)v(0) \rangle = k_BT/M$, theorems are in-
voked. Here, $\nu(t)$ is the integral of the velocity auto-correlation function, $\int_0^t \langle v(0)v(t') \rangle dt'$. Then,

$$M\dot{\nu}(t) + \int_0^t \Gamma(t - t')\nu(t')dt' = k_BT. \quad (10)$$

For the memory kernel one often invokes the Ornstein-Uhlenbeck process to model the delayed response of surrounding fluid

$$\Gamma(t) = (\gamma^2/m) \exp(-\gamma t/m), \quad (11)$$

where $\gamma$ is a friction coefficient proportional to the viscosity of the fluid and $m$ represents a mass attributed to solvent particles. The solution using $\zeta_+ = \frac{\gamma}{2m}(1 + \sqrt{1 - 4m/M})$ is

$$\nu(t) = \frac{k_BT}{M} \left( \frac{\gamma}{m\zeta_+ - \zeta_-} \right) \left[ (1 - \frac{\gamma}{m\zeta_+}) \exp(-\zeta_+t) - (1 - \frac{\gamma}{m\zeta_-}) \exp(-\zeta_-t) \right]. \quad (12)$$

For the position auto-correlation function one finds

$$\langle x(t)x(0) \rangle = \frac{k_BT}{M(\zeta_+ - \zeta_-)} \left[ \zeta_+^{-1}(1 - \frac{\gamma}{m\zeta_+}) \exp(-\zeta_+t) - \zeta_-^{-1}(1 - \frac{\gamma}{m\zeta_-}) \exp(-\zeta_-t) \right]. \quad (13)$$

In the case that $\gamma t/m$ is sufficiently large, the Ornstein-Uhlenbeck kernel rapidly decays. At this point, it is possible to introduce a dependence on viscosity by invoking Stokes' drag law $\gamma = 6\pi\eta R$ where $R$ is the radius of the "Brownian particle" and $\eta$ is the shear viscosity. The validity of Stokes' law is predicated on the assumption that the Brownian particle is much larger than the solvent particles ($M \gg m$). In the case of self-diffusion all particles are identical. Hence, the Stokes' law appears unjustified. However, the proportionality between $\gamma$ and $\eta$ is always correct \cite{27}. In fact, Einstein developed the concept of "effective viscosity", which has been used to describe the effective viscosity of lubricants \cite{30}.

We are now in a position to replace the integral by a function of the viscosity, a transport coefficient that is easily computed from MD simulations with good accuracy. Viscosity is essentially a coarse-grained quantity describing the relaxation of momentum density to its equilibrium value, after a perturbation. It is directly related to the velocity autocorrelation function. Stokes' law has been extended to the frequency domain to describe dynamical and dissipative effects in rheology \cite{31,33}. The relationship between the Fourier representation of frequency dependent viscosity and the frequency-dependent friction coefficient $\tilde{\gamma}(s)$ is

$$\tilde{\eta}(s) = \frac{\tilde{\gamma}(s)}{6\pi R} \quad (14)$$

where $s$ is the complex frequency in Laplace domain and $\tilde{\gamma}(\omega) = \int_0^\infty \Gamma(t) \exp(i\omega t) \, dt$. This relationship, which has been termed the "correspondence principle" \cite{33}, provides a direct link between the memory function and viscosity. The memory kernel itself encodes the response of particles at all frequencies to collisions and boundary conditions. Therefore, we expect the viscosity to be sensitive to boundary conditions and intermolecular potentials as well. In particular, we expect that changes in the lineshape of the NMR signal, c.f. Eq. (1), as a function of temperature, to be reflected in the memory function as well as viscosity coefficient.

The case of gases. A model for the viscosity and its temperature dependence is needed \cite{33}. Dynamic viscosity of gases was described by Sutherland as

$$\eta = \frac{\mu_0(T_0 + C)}{T^3} \sim \frac{T^{3/2}}{T + C}, \quad (15)$$

where $C$ is Sutherland's constant, and $\mu_0$ is the viscosity at temperature $T_0$. At high temperatures viscosity grows with the square root of the temperature, $\eta \sim T^{1/2}$, while at low temperature $\eta \sim T^{3/2}$. Using Stokes' drag law, we rewrite the nuclear induction signal as \cite{10}

$$S(t) = \exp(-\gamma_\eta^2 g^2 \kappa t), \quad (16)$$

with

$$\kappa(T) = \frac{kT(-m\zeta_+^2 \zeta_- - m\zeta_-^2 \zeta_+ + \zeta_-^2 \gamma + \zeta_- \zeta_+ \gamma + \zeta_+^2 \gamma)}{mMC_3^3 C_4^3}. \quad (17)$$

Note that $\kappa$ determines the linewidth $\Delta f$, and it shows two distinct trends with temperature

$$\Delta f \sim \begin{cases} T^{-7/2} & T < C \\ T^{-1/2} & T > C. \end{cases} \quad (18)$$

Figure 1 represents the decay of gas phase NMR signal in an echo experiment for a range of temperatures. The sample is a sealed tube of liquid tetramethylsilane (TMS), prepared using freeze-pump-thaw method. The sample tube is heated above 25°C to evaporate the TMS. Measurements were performed on a Bruker AV 600 MHz NMR spectrometer equipped with variable temperature and pulsed gradient capabilities. In the presence of a magnetic-field gradient, the line narrows with increasing temperature, a surprising result that was first observed and explained in \cite{7,10,11}. Data points are fitted to exponential decay functions according to Eq. (16) and the resulting linewidths are plotted in the inset of Fig. 1(b). Their temperature trend is in agreement with Eq. (18).

The case of liquids. To model the viscosity of liquids an empirical equation of the form

$$\eta = A \exp(B/T) \quad (19)$$

where $A$ and $B$ are constants can be substituted into the expression for the nuclear induction decay (c.f. Eq. 16). Recalling that $\kappa(T)$ is proportional to $T^{-3}$, we find:

$$\kappa(T) \propto T \exp(-3B/T) = T(1 - 3B/T + \frac{9}{2}B^2/T^2 + \ldots).$$
MD simulations of particle trajectories have been used to model gas diffusion in systems of gas mixtures in complex geometries \[35, 37\]. In particular, for liquids and non-ideal gases in which transport properties are difficult to describe, MD simulations have proven very successful \[16–19\]. At each time step, intermolecular forces between nearest neighbors are enforced to recreate realistic particle trajectories \[38, 39\]. To obtain such trajectories over a large number of particles we used the open source software “Large-scale Atomic/Molecular Massively Parallel Simulator” (LAMMPS) \[40\]. LAMMPS results were then used to compute viscosity coefficients in liquid and gaseous xenon (Xe). We used the Lennard-Jones (LJ) pairing, \[U(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]\], were \(\epsilon = 1.77\) kJ/mol is the depth of the potential well and \(\sigma = 4.1\) Å is the distance where the potential is zero. Simulations were performed for 1,000 Xe atoms in a box with periodic boundary conditions. The simulations ran for a constant number of particles, volume and temperature in the canonical ensemble (NVT). The equilibrium time correlation function approach, a.k.a. Green-Kubo autocorrelation function, was used to derive the viscosity \[19, 34, 39, 41, 42\]

\[
\eta = \lim_{t \to \infty} \eta_{GK}(t)
\]

with

\[
\eta_{GK}(t) = \frac{V}{3k_BT} \int_{0}^{t} \sum_{\alpha<\beta} C_{\alpha\beta}(\tau) d\tau,
\]

where \(\alpha, \beta \in \{x, y, z\}\), \(V\) is the volume and \(T\) is the temperature. \(C_{\alpha\beta}(\tau) = \langle p_{\alpha\beta}(\tau)p_{\alpha\beta}(0) \rangle\) is the autocorrelation function of non-diagonal elements of the pressure tensor, e.g.

\[
p_{xy}(t) = \frac{1}{V} \left\{ \sum_{j} m_{j} v_{jx}(t)v_{jy}(t) + \frac{1}{2} \sum_{i \neq j} r_{ijx}(t)f_{ijy}(t) \right\}.
\]

Here \(f_{ijy}\) represents the \(y\)-component of the force between two particles \(i\) and \(j\). The first term on the right hand side, is the kinetic contribution to the pressure tensor while the second term indicates the potential contribution. Other components \(p_{\alpha\beta}\) of the pressure tensor are defined analogously.

Simulations were performed for 21 different temperature values in the range 200-400 K, using a high density \((\rho = N/V)\) of particles compatible with liquid phase, and a low density for gas phase. Particle trajectories were evolved for 10\(^6\) femtoseconds to equilibrate. We evaluated \(C_{\alpha\beta}\) correlation functions 60 times in each simulation, recording them well beyond their saturation point (see Fig. 2). They were then used to evaluate the Green-Kubo integral Eq. (20). For this approach to work, it is critical that the correlation functions decay with similar rates so the resulting integrals converge to an average value.

The shear viscosity coefficient for the liquid state was found to decrease with temperature (see Fig. 3). This behavior is expected and well understood for liquids, and is in agreement with the line broadening observed in the liquid state NMR experiments \[7, 10\]. The verification of simulated viscosity coefficients against experimental values is complicated by the fact that Xe is not in the liquid form above 270 K whereas below that temperature, measurements report viscosity vs temperature but...
FIG. 2. Green-Kubo correlation functions for liquid and gas simulations are evaluated at each temperature for both densities. Here the simulation results at 300 is presented (left). These correlation are integrated to the saturation point to evaluate the viscosity coefficient \(\eta\) (right). Note that the time axis is three orders of magnitude larger for gas simulations.

across different densities [43, 44]. Nevertheless, a matching data point exists: at 220 K our simulated viscosity coefficient lies within 5% of the experimentally measured value [43]. Our simulation results are similar to those from Ref. [45] where the authors performed a general study of LJ potential dynamics vs \(\rho\) and \(T\) and found that the resulting viscosity coefficients are within 6% of experimental values. The decay of \(\eta(T)\) with \(T\) was found to be exponential and was fitted to Eq. (19).

FIG. 3. Viscosity in liquids drops as the temperature increases. Error bars indicate the standard deviation for the set of 60 accumulated correlation functions. The solid line is a fit to Eq. (19) with \(A_0 = 0.38 \pm 0.01\) and \(B = 135 \pm 7\).

The gas phase simulations were performed by first equilibrating the system over a period of \(10^6\) picoseconds. Comparing to the liquid case, the correlation functions were found to decay slower as the frequency of particle collision is smaller (see Fig. 2). The simulated viscosity values were found to be two orders of magnitude smaller as well. Moreover, viscosity coefficients in gases show the opposite trend to those of liquids, i.e. shear viscosity increases with temperature. A comparison to the available experimental data [46, 47] shows that the simulated viscosity coefficients overlap with them. The calculated viscosity coefficients are fitted to Eq. (15). We find that the Sutherland’s constant \((C = 258 \pm 69)\) is in agreement with the experimental results.
with the literature value for Xe gas (C = 252) [16].

Our MD results confirmed that as the temperature of gases increases, the higher frequency of molecular collisions results in greater resistance and larger viscosities. Viscosity results are in agreement with previous studies and experimental results, as expected. On the other hand, what is new here is our ability to predict the correct lineshape for the nuclear induction signal from MD results, and this lineshape is predicted based on the effective viscosity. Equation (17) suggests that the decay rate of the nuclear induction signal is inversely proportional to the viscosity coefficient $\eta$ and as a result, the linewidth narrows at higher temperatures. A depiction of such behavior for the experiment with $g = 0.01$ G/cm, is shown in Fig. 5 where the simulated viscosity coefficients were used to predict the lineshape in gases. The resulting linewidths are very close to the experimental values of Fig. 1. A side-by-side comparison of experiments and theory is shown in the Inset of Fig. 5.

III. CONCLUSION

We have shown the feasibility of using MD simulations to model transport coefficients in liquids and gases; these transport coefficients are then used together with a GLE model to obtain the nuclear induction lineshape. In particular, our MD results correctly indicate that gas phase spectra exhibit narrower lines at higher temperatures. (This is in contrast to the conventional formalism [12–14], which incorrectly predicts the opposite trend.) This work opens the door for the prediction of lineshapes in more complex geometries and boundary conditions. Our work differs from previous studies of diffusion [48] in that memory effects can be explicitly modeled using our method. Future directions may include explicit modeling of boundaries and gas types using appropriate memory kernels, and ultimately, solving the inverse problem of computing molecular and pore parameters from experimentally-measured nuclear induction decays.

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