Elementary statistical models for collision-sequence interference effects with arbitrary persistence of velocity

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Abstract. Elementary statistical models for collision-sequence interference effects usually assume Gaussian-distributed velocities with zero persistence of velocity. Here we extend the treatment to arbitrary persistences of velocity in the range zero to just less than unity. For vector collision-sequence interference the results show the interference dip narrowing with increasing persistence of velocity as expected. Only partial agreement is obtained with some observations in a molecular dynamics simulation in Lennard-Jonesium.

1. Introduction
1.1. Background
The elementary statistical models developed by Lewis et al. [1-3] to describe collision-sequence interference effects have mostly used Gaussian-distributed velocities with zero persistence of velocity. Persistences of velocity which run from zero to just less than unity can be modelled by an AR(1) (Box-Jenkins) process [4] allowing the effect of varying this parameter on vector and scalar interference in simple models to be determined.

Such processes lead to persistence-of-velocity terms $\langle v_i \cdot v_{i+1} \rangle$, $\langle v_i \cdot v_{i+2} \rangle \ldots \langle v_i \cdot v_{i+k} \rangle$, which form a geometrical progression where $v_i$ is the velocity before the $i$th collision in a collision sequence. More complicated behaviour, however, can be modeled.

1.2. The General Model
We assume an infinite set of statistically independent basis vectors $u_i$ with identical normal distributions and variance $\sigma^2$

$$\langle u_i \cdot u_j \rangle = \delta_{i,j} \langle \sigma^2 \rangle$$

(1)

and a series $a_i$ where the squared series

$$\sum_{i=0}^{\infty} a_i^2 = S$$

(2)
is convergent. Correlated velocities $v_k$ for $k = 0, 1, 2, 3 \ldots$ can be defined through

$$v_k = \frac{1}{\sqrt{S}} \sum_{i=0}^{\infty} a_i u_{k+i}$$  \hspace{1cm} (3)

The velocities in eq.(3) will have a normal distribution with variance $\sigma^2$

$$\langle v_k^2 \rangle = \sigma^2$$  \hspace{1cm} (4)

The value of $\langle v_k \cdot v_{k+j} \rangle$ for $j > 1$ will depend on the choice of the series $a_i$. The vectors $u_i$ could have other distributions but normal is commonly used.

2. The AR Model
A case of particular interest is to take the series $a_i$ as a geometric series. Define velocities $v_k$ in terms of the $u_i$ and a ratio $\gamma$ with $|\gamma| < 1$ as

$$v_k = \sqrt{(1 - \gamma^2)} \sum_{i=0}^{\infty} \gamma^i u_{k+i}$$  \hspace{1cm} (5)

since eq.(3) becomes

$$S = \sum_{i=0}^{\infty} \gamma^{2i} = \frac{1}{1 - \gamma^2}$$  \hspace{1cm} (6)

Then the variance of the $v_k$ will be the same as that of the $u_k$

$$\langle v_i \cdot v_i \rangle = \langle v^2 \rangle = \sigma^2$$  \hspace{1cm} (7)

We have upon assuming a stationary and reversible process

$$\langle v_i \cdot v_j \rangle = \gamma^{|i-j|} \langle v^2 \rangle$$  \hspace{1cm} (8)

where the ratio $\gamma$ is seen to be the persistence of velocity. The definition used here is

$$\gamma = \left( \frac{\langle v_i \cdot v_{i+j} \rangle}{\langle v^2 \rangle} \right)^{(1/j)}$$  \hspace{1cm} (9)

3. Vector Collision Sequences
3.1. Equal Collision Intervals
As in [1] define impulses $f_k = v_{k+1} - v_k$. From eq. (8)

$$\langle f_k^2 \rangle = \langle (v_{k+1} - v_k)^2 \rangle = 2\langle v^2 \rangle (1 - \gamma)$$  \hspace{1cm} (10)

$$\langle f_k \cdot f_j \rangle = \langle (v_{k+1} - v_k) \cdot (v_{j+1} - v_j) \rangle = -\langle v^2 \rangle \gamma^{|k-j|-1}(1 - \gamma)^2$$  \hspace{1cm} (11)

Upon assuming equal time intervals between collisions, which can be scaled so that $t_k = k$ for $k \in [0, N - 1]$ for N collisions, we have

$$f(t) = \sum_k f_k \delta(t - k)$$  \hspace{1cm} (12)
and the corresponding Fourier transform, with $\omega = 2\pi/N$

$$\tilde{f}(t) = \sum_{k=0}^{N-1} f_k e^{i\omega_k}$$

(13)

With the use of eqs.(10) and (11) we have

$$\frac{1}{N} \langle \tilde{f} \cdot \tilde{f}^* \rangle = 2 \langle v^2 \rangle (1 - \gamma) \left[ 1 - (1 - \gamma) \sum_{j=1}^{\infty} \gamma^{j-1} \cos \omega_j \right]$$

(14)

Following [1], after some manipulation, the power spectrum is derived as

$$S(\omega) = 2 \langle v^2 \rangle (1 - \gamma^2) \left[ \frac{1 - \cos \omega}{1 - 2\gamma \cos \omega + \gamma^2} \right]$$

(15)

showing the line shape is dependent on $\gamma$.

3.2. Poisson Distributed Intercollisional Intervals

Following [2] assume the collisions times $t_k$ follow a Poisson distribution with frequency $\bar{\nu}$. The intervals $\Delta_i$ will be exponentially distributed. The $N$ collisions lie in the interval $[0, T]$. For large $N$ the random time $T$ can be taken as $N/\bar{\nu}$ and then

$$\frac{1}{N} = \frac{\bar{\nu}}{T}$$

(16)

so the average over $N$ can be replaced by an average over $T$. For the current model, with $f_k = \mu_k$ and $\omega = \omega - \omega_0$, as in the development from [2, eq. 6], we have

$$\frac{S(\tilde{\omega})}{\bar{\nu}} = \langle \tilde{f} \cdot \tilde{f}^* \rangle$$

$$= \langle f^2 \rangle + 2\Re \left\{ \sum_{j=1}^{\infty} \langle f_k \cdot f_{k+j} \rangle \left[ \frac{\bar{\nu}}{\bar{\nu} + i\tilde{\omega}} \right]^j \right\}$$

(17)

(18)

Writing $\kappa = (1 - \gamma)\bar{\nu}$, the power spectrum is found to be

$$S(\tilde{\omega}) = 2 \langle v^2 \rangle \kappa \left[ \frac{\tilde{\omega}^2}{\kappa^2 + \tilde{\omega}^2} \right]$$

(19)

This shows the shape of the interference dip depends on the product $\kappa$ and not on $\bar{\nu}$ and $\gamma$ in a separable manner. The line shape of the dip is an inverted Lorentzian for all values of $\gamma$.

The results of this and the preceding section 3.1 show the interference dip narrowing with increasing persistence of velocity, as predicted earlier [5-8].

4. Scalar Interference

For $\gamma > 0$, only $\langle f_k f_{k+1} \rangle$ and $\langle f_k f_{k-1} \rangle$ are different from $\langle f \rangle^2$ (see [1]). We have from numerical calculations, using the Box-Muller method to construct random normal vectors [10], that $\langle f_k f_{k+1} \rangle$ decreases with increasing $\gamma$ and

$$\langle f_k f_{k+1} \rangle \lesssim (1 - \gamma) \langle f_k f_{k+1} \rangle_{\gamma=0}$$

(20)

$$\langle f_k f_{k+1} \rangle \rightarrow \langle f \rangle^2 \text{ as } \gamma \rightarrow 1$$

(21)

so that $\text{cov}(f_k, f_{k+1}) \rightarrow 0$ as $\gamma \rightarrow 1$. This is to be expected from the argument in [1] on the origin of the covariance: the larger the persistence of velocity, the smaller is the variation in speed from one collision to the next.
4.1. An Analytic Solution for Two Dimensions

Given Gaussian velocities \( v_k \) and \( v_{k+1} \) in two dimensions with unit variance, these will not be independent for \( \gamma > 0 \). The method of [1] can be used by a change of variable since

\[
|v_{k+1} - v_k| = \left| (1 - \gamma) v_k - \sqrt{1 - \gamma^2} u_{k+1} \right| \tag{22}
\]

where \( v_k \) and \( u_{k+1} \) are independent. Since \( u_{k+1} \) and \( v_k \) have Gaussian distributions with unit variance, we have

\[
\langle f^n \rangle = \frac{1}{4\pi^2} \int d^2 v_k d^2 u_{k+1} \exp\left[-\frac{1}{2}(v_k^2 + u_{k+1}^2)\right] |(1 - \gamma) v_k - \sqrt{1 - \gamma^2} u_{k+1}|^n \tag{23}
\]

Set

\[
a = \frac{(1 - \gamma)}{\sqrt{2}} v_k - \frac{1 - \gamma^2}{2} u_{k+1} \tag{24a}
\]

\[
b = \frac{\sqrt{1 + \gamma}}{2} v_k + \frac{\sqrt{1 - \gamma}}{2} u_{k+1} \tag{24b}
\]

Then

\[
a^2 + b^2 = \frac{v_k^2 + u_{k+1}^2}{2} \tag{25}
\]

and

\[
|(1 - \gamma) v_k - \sqrt{1 - \gamma^2} u_{k+1}|^n = |a|^n (\sqrt{2})^n \tag{26}
\]

The transformation is

\[
\begin{pmatrix} v_k \\ u_{k+1} \end{pmatrix} = \begin{pmatrix} a/\sqrt{2} \\ b \\ -\sqrt{1 + \gamma}a/\sqrt{2(1 - \gamma)} \\ \sqrt{1 - \gamma}b \end{pmatrix} \tag{27}
\]

giving the Jacobian \( J(\gamma) \) as

\[
J(\gamma) = \left| \begin{array}{cc} \frac{\partial v_k}{\partial a} & \frac{\partial v_k}{\partial b} \\ \frac{\partial u_{k+1}}{\partial a} & \frac{\partial u_{k+1}}{\partial b} \end{array} \right| = \left| \begin{array}{cc} 1/\sqrt{2} & \sqrt{1 + \gamma} \\ -\sqrt{1 + \gamma}/\sqrt{2(1 - \gamma)} & \sqrt{1 - \gamma} \end{array} \right| = \frac{\sqrt{2}}{\sqrt{1 - \gamma}} \tag{28}
\]

Then eq. (23) is evaluated

\[
\langle f^n \rangle = \frac{J(\gamma)^2 (\sqrt{2})^n}{4\pi^2} \int d^2 a d^2 b \exp\left\{-\frac{a^2}{2(1 - \gamma)} - b^2\right\} |a|^n \tag{29a}
\]

\[
= \frac{2}{1 - \gamma} (\sqrt{2})^n \int_0^{\infty} db b \exp\left(-b^2\right) \int_0^{\infty} da \exp\left\{-\frac{a^2}{2(1 - \gamma)}\right\} |a|^{n+1} \tag{29b}
\]

\[
= 2^n (1 - \gamma)^{(n/2)} \Gamma \left( \frac{n}{2} + 1 \right) \tag{29c}
\]

This result is in agreement with previous results for \( \gamma = 0 \) and with numerical calculations for \( \gamma > 0 \).

4.2. Comparison to the \( \gamma = 0 \) Value

From numerical calculations in three dimensions and from eq. (29c), we have for a Gaussian velocity distribution with unit variance

\[
\langle f^n \rangle = (1 - \gamma)^{n/2} \langle f^n \rangle_0 \tag{30}
\]

where \( \langle f^n \rangle_0 \) is the quantity evaluated for \( \gamma = 0 \).
5. Comparison to Lennard-Jones Molecular Dynamics Results

Figs. 1 and 2 show interference dips from molecular dynamics simulations of Lennard-Jonesium mixtures where the parameters were chosen for Ar and H$_2$, with the model induced dipole moment also of Lennard-Jones type. These data were first published in [9]. Taking the induced dipole moment proportional to the force, $\mu_k \propto f_k = v_{k+1} - v_k$, the data of Fig. 1 were well fit using the AR-model eq.(19). The value of $\kappa$ so obtained was then used in a stochastic simulation to fit Fig. 2 with $\mu_k = c_{\mu} f_k |f_k|^\beta$. Note that the physical parameters must be kept the same so the two fits are not independent. In this second fit both $\gamma$ and $\beta$ were varied by generating random velocities with a Gaussian distribution and the desired persistence of velocity. Fig. 3 shows the best fit overlaid with the cusp from Fig. 2. This best fit is for $c_{\mu} \approx 0.34$, $\beta \approx 0.47$ and $\gamma \approx 0$. It was not possible to reproduce the cusp with an expected large value of $\gamma$ as the larger $\gamma$ is the broader the resulting interference dip: normally increasing $\gamma$ would narrow the dip but here the fit to the Fig. 2 case is constrained by the value of $\kappa$ derived from fitting the Fig. 1 case.

6. Conclusions

The theory developed in [1, 2] for the zero persistence of velocity case has been extended to the arbitrary persistence of velocity case using the AR-model although certain quantities could only be evaluated numerically. It is fairly straightforward to generate velocities $v_k$ using eqs. (3) or (5), and then express the induced dipole moment $\mu_k$ as some function of the force (impulse) $f_k = v_{k+1} - v_k$ to do stochastic simulations for cases that are too complex to obtain an analytical solution. The AR-model was successful in reproducing the Lennard-Jones results of [9] for the case $\sigma_\mu = \sigma$ but, using consistent physical parameters, here $\kappa$, a satisfactory fit to the case $\sigma_\mu = 1.1\sigma$ could not be obtained. The reason for this is not clear, but may reflect differing roles for the soft and hard parts of the interaction in the simulation results so that the simple fitting formula used, $\mu_k = c_{\mu} f_k |f_k|^\beta$, is not adequate.

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