Response to ''Comment on 'Negative velocity correlation in hard sphere fluids' '' [J. Chem. Phys. 103, 9512 (1995)]

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Response to "Comment on 'Negative velocity correlation in hard sphere fluids' " [J. Chem. Phys. 103, 9512 (1995)]

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Pasterny makes interesting points in the above Comment;[1] in particular, the demonstration that if $\gamma=-1$ in the Keilson–Storer model, the transform $\hat{C}_{\text{sign}}(z)$ of the velocity-sign autocorrelation function[2] in terms of the free path time distribution,[3] $\psi(t)$, has the same form as that in terms of the distribution $p(t)$ of the time intervals between successive velocity reversals.[2] However, this is only the beginning: to evaluate $C_{\text{sign}}(z)$ one must obtain physically based functional forms for $\psi(t)$ and/or $p(t)$. Of course, whatever the differences in the underlying physics, if the functional forms for $\psi(t)$, and $p(t)$ are the same, then the $\hat{C}_{\text{sign}}(z)$'s are the same. The correlation function $C_{\text{sign}}(t)$ which, as emphasized by Pasterny,[1] is very similar to the more physically interesting velocity autocorrelation function, usually exhibits a strong negative minimum at a "short" characteristic time $t_{\min}$. The various models that describe this minimum, whatever their physical origins, make use of two characteristic parameters which can be interpreted in terms of two characteristic times; the theory of Variyar *et al.*[2] yields only one such time for hard bodies and so *no* minimum in $C_{\text{sign}}(t)$ for hard spheres.

The theory of Variyar *et al.*[2] expresses $p(t/t_m)$ in terms of a single parameter $\alpha=t_i/t_m$, where t_m is the mean time between velocity reversals and t_i is the characteristic time needed to reverse velocities for two particles remaining in interaction. The time t_m is inversely proportional to the density and is similar to the mean free time that arises in kinetic theories of hard bodies. The novel feature of this theory is the interaction time t_i where

$$t_i \propto \frac{(k_B T m)^{1/2}}{|dU(r_0)/dr|};$$

m is the particle mass and r_0 is the center-to-center distance at which the interparticle potential $U(r_0)=k_B T$. Thus t_i can be described in terms of the potential of interaction, as can $p(t)$ and $\hat{C}_{\text{sign}}(z)$.

Much discussion has focused on $C_{\text{sign}}(t_{\min})$ and on the significance of $t_{\min}$. (It is these features that characterize Poley absorption.)[3] The function $p(t)$ is peaked at a time t_{peak} quite comparable to that ($t_{\min}$) at which $C_{\text{sign}}(t)$ exhibits a minimum. In the model of Variyar *et al.*,[2]

$$t_{\text{peak}}=\frac{\alpha}{(1-4\alpha)^{1/2}} \ln\left[\frac{1+(1-4\alpha)^{1/2}}{1-(1-4\alpha)^{1/2}}\right], \quad \alpha<1/4$$

and for small α, one has t_{peak}, and hence $t_{\min}$, equal approximately to $t_i \ln[t_m/t_i]$. These results have been confirmed by simulations[2,4] and they yield relevant insights. In particular, the model states that (1) for hard disks, $t_i=0$, and the peak in $p(t)$, as well as the negative minimum in $C_{\text{sign}}(t)$, move toward $t_{\min}\to 0$; (2) that for very dilute gases, $t_m\to\infty$, and once again the peak in $p(t)$, as well as the negative minimum in $C_{\text{sign}}(t)$, move towards $t_{\min}\to 0$; (3) that for dense soft disks the maximum in $p(t)$ and the minimum in $C_{\text{sign}}(t)$ occur at a time $t_{\min}$ that is largely determined by the interaction time, t_i.

In conclusion, we believe that the most significant aspect of the theory of Variyar *et al.*[2] is that a model of uncorrelated successive velocity reversals can explain the negative minimum that occurs in the $C_{\text{sign}}(t)$ for soft bodies and that the time to this minimum, $t_{\min}$, is shown to be largely dependent upon the time of interaction, t_i, and not upon correlated intermolecular collisions (librations, vibrations, or coherent rattling). We suggest focusing on the differences between the theories compared by Pasterny rather than on the similarities.

[1] K. Pasterny, J. Chem. Phys. **103**, 9512 (1995).
[2] J. E. Variyar, D. Kivelson, G. Tarjus, and J. Talbot, J. Chem. Phys. **96**, 593 (1992).
[3] A. I. Burshtein and M. V. Krongauz, J. Chem. Phys. **102**, 2881 (1995).
[4] Although the model of Variyar *et al.* predicts no minimum in the $C_{\text{sign}}(t)$ associated with hard bodies in three dimensions, small negative minima are detected in simulations. We believe these weak minima are manifestations of correlated successive velocity reversals, manifestations that for soft bodies may be overshadowed by those associated with uncorrelated successive velocity reversals. This argument is strengthened by the fact that for hard ellipsoids this weak minimum may occur at several times t_m and the corresponding minimum for the angular velocity correlation function may occur at $30t_m$. See J. Talbot, G. Tarjus, D. Kivelson, G. T. Evans, M. P. Allen, and D. Frenkel, Phys. Rev. Lett. **65**, 2828 (1980).

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