Crossover in the Slow Decay of Dynamic Correlations in the Lorentz Model

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The long-time behavior of transport coefficients in a model for spatially heterogeneous media in two and three dimensions is investigated by molecular dynamics simulations. The behavior of the velocity autocorrelation function is rationalized in terms of a competition of the critical relaxation due to the underlying percolation transition and the hydrodynamic power-law anomalies. In two dimensions and in the absence of a diffusive mode, another power-law anomaly due to trapping is found with an exponent -3 instead of -2. Further, the logarithmic divergence of the Burnett coefficient is corroborated in the dilute limit; at finite density, however, it is dominated by stronger divergences.

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Spatial heterogeneities often give rise to intriguing slow dynamics in complex materials, manifested, for example, by broad frequency-dependent relaxation processes in colloidal gels which form stress-sustaining networks close to the sol-gel transition [1–3]. Similarly, the presence of differently sized proteins, lipids, and sugars in the cytoplasm of eukaryotes, summarized as cellular crowding, is identified by slow anomalous transport as its most distinctive fingerprint [4–6]. A further prominent example is sodium silicates, where the formation of a space-filling network of channels allows for slow diffusion of sodium ions in an arrested host matrix [7]. A minimal model that encompasses spatial disorder and slow dynamics is provided by the Lorentz model [8], i.e., classical point particles explore without mutual interaction a d-dimensional space in the presence of a frozen array of randomly distributed (possibly overlapping) hard spherical obstacles of radius σ and concentration n.

Recently, striking behavior of the velocity autocorrelation function (VACF), $\psi(t) := v^{-2}\langle \mathbf{v}(t)\cdot\mathbf{v}(0)\rangle$, has been reported for a dense hard-sphere system ($d = 3$) close to the freezing transition [9]. At intermediate time scales, a regime of anticorrelations emerges due to the well-known "rattling" of particles in their cages [10]. The long-time behavior exhibits an intriguing crossover scenario from long-living positive correlations, $\psi(t) \simeq A_{\mathrm{fl}} t^{-3/2}$, to a high-density regime characterized by slowly decaying anticorrelations, $\psi(t) \simeq -A'_{\mathrm{fl}} t^{-5/2}$. The former corresponds to the celebrated long-time anomaly in simple liquids [11], connected to the formation of a vortex pattern due to local momentum conservation. The mechanism for the latter decay is presumably of totally different origin: in an array of immobilized obstacles, the dynamics of a tagged particle always remembers its frozen cage—a mechanism well known for the Lorentz model [8].

For the Lorentz model itself, there is a long-standing discrepancy between analytic theory and simulations about the manifestation of the long-time tail. The existence of the long-time anomaly in the Lorentz model has been predicted within a rigorous low-density expansion as $\psi(t) \simeq -A' t^{-d/2-1}$ for $t \to \infty$ [12,13]. Earlier computer simulations on two-dimensional systems [14–16] identified a long-time relaxation of power-law type. At low densities, the expected exponent was confirmed; the amplitude, however, differed significantly from the theoretical prediction. At intermediate densities, the simulation results again suggest power-law behavior, which was described phenomenologically by nonuniversal, density-dependent exponents [15,17].

The regime of higher obstacle densities poses considerable challenges for theory; sequences of repeated-ring collisions have been accounted for by a self-consistent variational repeated-ring theory [18]. Götze *et al.* [19] have developed a mathematically consistent theory that covers the physics of the low-density regime up to the predicted localization transition. In particular, they predict a competition between a critical power-law relaxation due to the fractal clusters at the percolation transition and the universal long-time tail. A similar scenario has been proposed for lattice variants of the Lorentz model, and there, evidence for a crossover scenario has been reported [20].

In this Letter, we present high-precision data for the two-dimensional overlapping Lorentz model for reduced obstacle densities $n^* := n\sigma^d$ ranging from the dilute gas $n^* = 0.005$ up to the percolation threshold $n_c^* \approx 0.35907$ [21], and deep into the localized phase. In particular, we focus on the algebraic decay of the VACF at long times which is predicted for asymptotically low densities as [13]

$$\psi(s) \simeq -\frac{n^*}{\pi}\frac{1}{s^2} \quad \text{for} \quad s \to \infty,\ n^* \to 0,\ d = 2, \qquad (1)$$

where $s = t/\tau$ is the mean number of collisions and $\tau^{-1} = 2n^* v/\sigma$ the collision rate, and v denotes the velocity of the particle. We analyze $\psi(t)$ up to times corresponding to several 10^4 collisions, which implies that a noise level in the correlation of the order of 10^{-8} is required. Some 10^6 trajectories per obstacle density have been simulated, each trajectory covering 10^6–10^8 collisions. We have calculated

$\psi(t)$ by directly correlating velocities and obtain accurate data up to a noise level of 10^{-5}. Furthermore, we have measured the mean-square displacement (MSD), $\delta r^2(t) := \langle \Delta \mathbf{R}(t)^2 \rangle$, and extracted the diffusion coefficient D from $\delta r^2(t \to \infty) \simeq 4Dt$. An alternative route to evaluate $\psi(t)$ is to perform a numerical second derivative of $\delta r^2(t)$; we have checked that both methods yield identical results within statistical errors. The second method suppresses the noise level further up to a factor 10^3.

Results for the VACF are shown in Fig. 1 for the full density range in the diffusive phase. On linear scales, the data for the lowest density are indistinguishable from the exponential relaxation, $\exp(-4t/3\tau)$, of the Lorentz-Boltzmann theory. For intermediate densities ($n^* \gtrsim 0.1$), the VACF enters the region of anticorrelation already after two collisions. Since the diffusion coefficient is related to the total area under the VACF by a Green-Kubo relation, $D = (v^2/d) \int_0^\infty \psi(t)dt$, the areas of positive and negative region cancel for $n^* \geq n_c^*$. In a double-logarithmic representation, the data corroborate power-law behavior for time windows covering 1–2 decades or 2–4 decades in correlations. A gradual increase of the density towards n_c^* gives rise to apparent, density-dependent exponents, at least if correlations below 10^{-4} are ignored. Careful inspection of the VACF for $n^* = 0.20$ reveals an intermediate power-law regime as well as a universal long-time tail, consistent with the competition of critical and universal relaxation predicted by Götze *et al.* [19].

As a sensitive test for the crossover scenario, Fig. 2 exhibits the VACF multiplied by the expected power law s^2 of the universal tail. One infers that $s^2\psi(s)$ saturates in the accessible time window for densities up to about 2/3 of the percolation threshold, $n^* \lesssim 0.25$. For densities $n^* \lesssim 0.1$, the constant is approached from above in qualitative agreement with the prediction of Das and Ernst [22] for the subleading long-time behavior,

$$\psi(s) \simeq -\frac{n^*}{\pi s^2}\left(1 + \frac{63}{16s} + \ldots\right). \qquad (2)$$

For higher densities, one observes an increase, following an apparent, density-dependent power law, before the universal tail is attained. The time scale where the crossover occurs shifts to longer times as the percolation threshold is approached, confirming the predicted scenario [19]. The density $n^* = 0.10$ reaches its asymptotic value remarkably early; this is due to a cancellation of the subleading universal tail and the onset of critical slowing down.

Very close to n_c^*, the VACF exhibits the critical relaxation $\psi(t) \sim t^{2/z-2}$, which follows directly from the prediction for the MSD, $\delta r^2(t) \sim t^{2/z}$. The numerical value of the exponent, $z \approx 3.03$ [23], coincides with results of simulations for diffusion on lattice percolation [24], corroborating that the critical transport properties of the Lorentz model share the same universality class.

Long-time tails originating from power-law distributed exit rates of the cul-de-sacs have been predicted even in the localized regime [25,26]. In particular, the VACF should then decay as $\psi(t) \sim t^{-3}$ for $n^* > n_c^*$ and $d = 2$; a prediction that has not been tested so far. Appropriate rectification plots are included in Fig. 2, and one infers that the data follow such a power law for 1 order of magnitude in time, i.e., three decades in correlation.

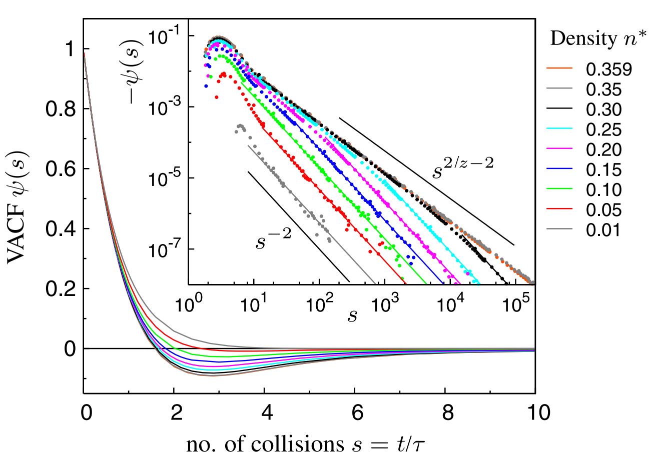

FIG. 1 (color online). Velocity autocorrelation function (VACF) for the two-dimensional Lorentz model. Inset: negative VACF on double-logarithmic scales. Solid lines are fits to the universal long-time tails. The universal and the critical power laws are indicated by thick straight lines, corresponding to exponents -2 and $2/z - 2 \approx -1.34$.

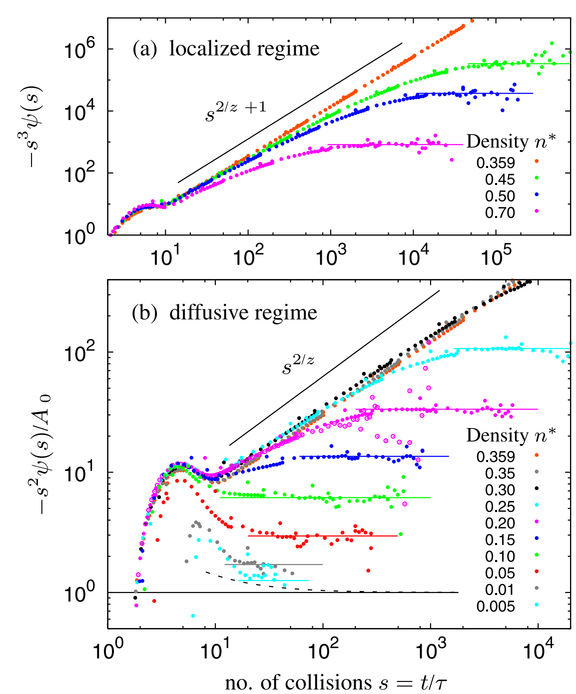

FIG. 2 (color online). Rectification of the universal long-time tail (a) above and (b) below the percolation threshold. Data points are obtained as numerical derivatives of the MSD; open circles for $n^* = 0.20$ correspond to directly correlating velocities; extracted amplitudes are indicated by solid lines. The dashed line in (b) represents the leading correction, Eq. (2).

We have extracted the amplitudes A of the universal tail as the long-time limit of $-s^2\psi(s)$. In the regime of intermediate densities, our data are in semiquantitative agreement with earlier simulations [16,17], see Fig. 3. As has been observed before, the values of A are significantly larger than the low-density prediction, $A_0 = n^*/\pi$. Since the calculation of A_0 relies on a perturbative correction to the Lorentz-Boltzmann equation [13], quantitative agreement requires the diffusion coefficient D to be sufficiently close to the Boltzmann value $D_0 = 3v\sigma/16n^*$. This criterion is not met even at low densities; a 40% suppression of D/D_0 occurs at $n^* = 0.10$ (see Fig. 3), signaling the onset of subdiffusive motion. The diffusion coefficient for $n^* \leq 0.01$ is in agreement with the first nonanalytic correction of the low-density expansion [12,14]

$$\frac{D_0}{D} = 1 - \frac{4n^*}{3}\ln n^* - 0.8775n^* + 4.519(n^*\ln n^*)^2. \quad (3)$$

Although the amplitudes A appear to approach A_0 as $n^* \to 0$, the value for A at $n^* = 0.005$ still deviates by approximately 25%.

Close to the percolation threshold, the crossover scenario suggests that the amplitude should actually diverge. Matching the critical relaxation $\psi(t) \sim t^{2/z-2}$ and the universal tail $\psi(t) \simeq -A(t/\tau)^{-2}$ at the divergent crossover time scale t_* yields $\tau^2 A \sim t_*^{2/z}$. Assuming that t_* also describes the crossover of the MSD from anomalous to diffusive transport, $t_*^{2/z} \sim Dt_*$, entails the prediction

$$\tau^2 A \sim D^{-2/(z-2)} \sim |n^* - n_c^*|^{-(2\nu-\beta)}, \quad (4)$$

as $n^* \to n_c^*$, where β and ν are percolation exponents [23]. The rapid increase of the amplitudes follows this prediction remarkably well; even at $n^* = 0.1$, Eq. (4) deviates by less than 30% from the simulation results, whereas the low-density prediction is off by a factor 6; see Fig. 3.

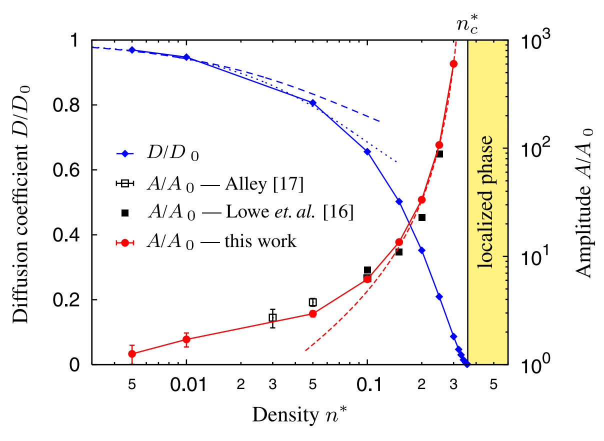

FIG. 3 (color online). Left axis (blue diamonds): suppression of the diffusion coefficient D with respect to the Boltzmann-Lorentz result D_0. The dashed line includes the leading low-density correction, the dotted line corresponds to Eq. (3). Right axis (red dots): reduced amplitude A/A_0 of the long-time tail from low densities up to the divergence at n_c^*. Dashed line: fit to Eq. (4), $A/A_0 = 1.6n^*|n^* - n_c^*|^{-91/36}$.

The VACF or, equivalently, the MSD is only the simplest quantity exhibiting anomalous long-time behavior. Deviations from Fickian diffusion are indicated by a nonvanishing (super-)Burnett coefficient, which reads in two dimensions

$$B(t) = \frac{1}{4!}\frac{d}{dt}\left[\frac{1}{2}\langle\Delta\mathbf{R}(t)^4\rangle - \langle\Delta\mathbf{R}(t)^2\rangle^2\right]. \quad (5)$$

Within a hydrodynamic mode-coupling approach, it has been predicted that the Burnett coefficient diverges logarithmically in $d = 2$ [27]. Indeed, $dB(t)/d\log(t)$ saturates for low densities, see Fig. 4. Again close to n_c^*, this behavior is masked by the critical relaxation. Dynamic scaling predicts a power-law divergence of $\langle\Delta\mathbf{R}(t)^4\rangle \sim t^{4/\tilde{z}}$, where $\tilde{z} = (2\nu - \beta + \mu)/(\nu - \beta/4) \approx 2.95 < z$ [28]. Then, $B(t) \sim t^{4/\tilde{z}-1}$ at the critical density—consistent with Fig. 4. The presence of finite clusters renders the dynamics spatially heterogeneous, even below n_c^*. A superposition of Gaussian processes yields a linearly divergent Burnett coefficient, $B(t) \simeq \bar{\alpha}_2 D^2 t$ for $t \to \infty$, with $\bar{\alpha}_2 = (4/3) \times (1/P_\infty - 1)$, and P_∞ denotes the fraction of mobile particles, see Fig. 4. In the dilute limit, the prefactor is expected to vanish as $\bar{\alpha}_2 D^2 \sim n^*$.

Let us briefly comment on the long-time behavior of the VACF for the three-dimensional Lorentz model. Recently, the critical properties of the localization transition have been analyzed in terms of a scaling Ansatz for the

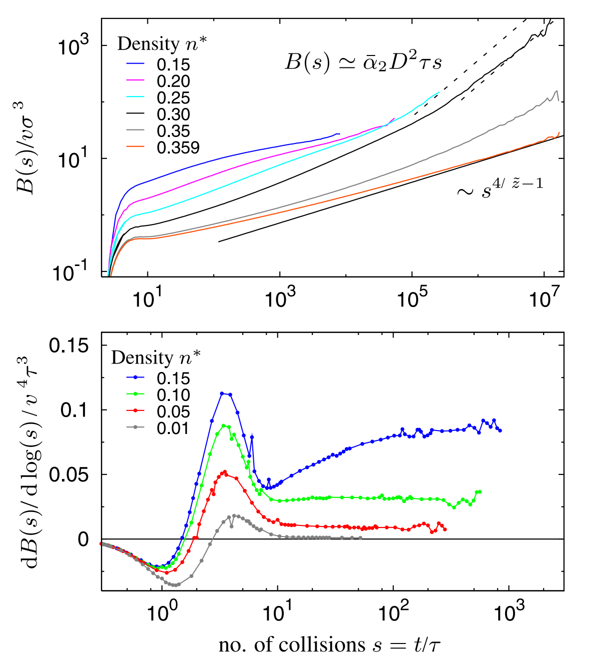

FIG. 4 (color online). Top: Critical (solid line) and linear (dashed line) divergence of the Burnett coefficient at intermediate densities. Bottom: The logarithmic divergence at low densities manifests itself as a finite long-time limit of $dB(s)/d\log(s)$.

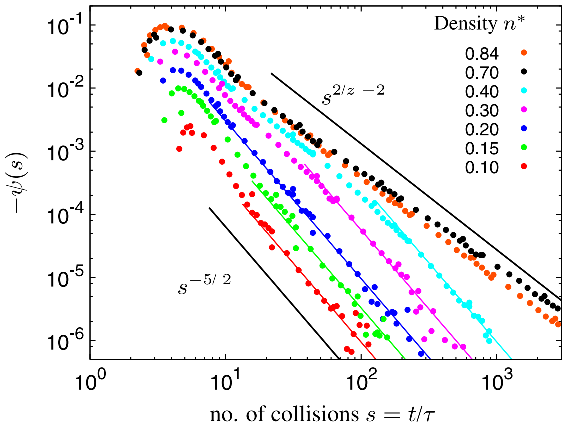

FIG. 5 (color online). VACF for the Lorentz model in $d = 3$; a crossover similar to Fig. 1 from the critical relaxation $\psi(s) \sim s^{2/z-2}$ to the universal long-time tail $\psi(s) \sim s^{-5/2}$ can be observed.

van Hove correlation function [28,29]. The exponent of the universal tail is larger, and the amplitude depends even stronger on the density [13],

$$\psi(s) \sim -\frac{(3\pi)^{3/2}}{16}(n^*)^2 s^{-5/2} \quad \text{for} \quad d = 3, \qquad (6)$$

where $s = t/\tau$ again, and $\tau = \sigma/\pi n^* v$ for $d = 3$. Such a behavior is much more difficult to observe, and only rudimentary evidence has been reported [30]. Our results (Fig. 5) suggest a similar crossover scenario as for $d = 2$: the universal tail with exponent $-5/2$ is preceded by a critical relaxation with exponent $2/z - 2 \approx -1.68$; the latter covers a growing time window upon approaching the localization transition.

Finally, we emphasize again the universality of the negative tail: it relies on the general mechanism that the particle can return in its frozen heterogeneous environment by reversing its path, thus remembering the presence of free volume [8]. For the hard-sphere fluid of Ref. [9], the role of the frozen environment is taken by long-lived cages in the high-density regime. Hence, the negative tail $\psi(t) \simeq -A'_{\mathrm{fl}} t^{-5/2}$ should emerge in a time window, $\tau \ll t \ll \tau_\alpha$, bounded by the time scales for momentum relaxation τ and structural relaxation τ_α; the slowing down of the latter is also reflected in a rapid increase of the viscosity of the fluid, $\eta \sim \tau_\alpha$. At even larger times, the positive hydrodynamic tail $\psi(t) \simeq A_{\mathrm{fl}} t^{-3/2}$ is expected to follow, although its amplitude should vanish rapidly, $A_{\mathrm{fl}} \sim \eta^{-3/2}$ [11].

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[1] A. D. Dinsmore, V. Prasad, I. Y. Wong, and D. A. Weitz, Phys. Rev. Lett. **96**, 185502 (2006).
[2] L. Ramos and L. Cipelletti, Phys. Rev. Lett. **94**, 158301 (2005).
[3] F. Sciortino, S. Mossa, E. Zaccarelli, and P. Tartaglia, Phys. Rev. Lett. **93**, 055701 (2004).
[4] A. Caspi, R. Granek, and M. Elbaum, Phys. Rev. E **66**, 011916 (2002).
[5] I. M. Tolić-Nørrelykke, E.-L. Munteanu, G. Thon, L. Oddershede, and K. Berg-Sørensen, Phys. Rev. Lett. **93**, 078102 (2004).
[6] M. Weiss, M. Elsner, F. Kartberg, and T. Nilsson, Biophys. J. **87**, 3518 (2004).
[7] A. Meyer, J. Horbach, W. Kob, F. Kargl, and H. Schober, Phys. Rev. Lett. **93**, 027801 (2004); T. Voigtmann and J. Horbach, Europhys. Lett. **74**, 459 (2006).
[8] For a review see, e.g., H. van Beijeren, Rev. Mod. Phys. **54**, 195 (1982).
[9] S. R. Williams, G. Bryant, I. K. Snook, and W. van Megen, Phys. Rev. Lett. **96**, 087801 (2006).
[10] A. Rahman, J. Chem. Phys. **45**, 2585 (1966); Phys. Rev. **136**, A405 (1964).
[11] B. J. Alder and T. E. Wainwright, Phys. Rev. Lett. **18**, 988 (1967); Phys. Rev. A **1**, 18 (1970).
[12] A. Weijland and J. M. J. van Leeuwen, Physica (Amsterdam) **38**, 35 (1968).
[13] M. H. Ernst and A. Weijland, Phys. Lett. A **34**, 39 (1971).
[14] C. Bruin, Phys. Rev. Lett. **29**, 1670 (1972); Physica (Amsterdam) **72**, 261 (1974).
[15] B. J. Alder and W. E. Alley, J. Stat. Phys. **19**, 341 (1978); Physica (Amsterdam) **121A**, 523 (1983).
[16] C. P. Lowe and A. J. Masters, Physica (Amsterdam) **195A**, 149 (1993).
[17] W. E. Alley, Ph.D. thesis, University of California, Davis, 1979.
[18] A. Masters and T. Keyes, Phys. Rev. A **26**, 2129 (1982).
[19] W. Götze, E. Leutheusser, and S. Yip, Phys. Rev. A **23**, 2634 (1981); **24**, 1008 (1981); **25**, 533 (1982).
[20] G. A. van Velzen, M. H. Ernst, and J. W. Dufty, Physica (Amsterdam) **154A**, 34 (1988); D. Frenkel, F. van Luijn, and P.-M. Binder, Europhys. Lett. **20**, 7 (1992).
[21] J. Quintanilla, S. Torquato, and R. M. Ziff, J. Phys. A **33**, L399 (2000).
[22] S. P. Das and M. H. Ernst, Physica (Amsterdam) **153A**, 67 (1988).
[23] A scaling relation, $z = (2\nu - \beta + \mu)/(\nu - \beta/2)$, connects z to the geometric exponents $\nu = 4/3$ and $\beta = 5/36$ of lattice percolation in $d = 2$ and the conductivity exponent $\mu = 1.30$ describing the suppression of diffusion, $D \sim |n^* - n_c^*|^\mu$ [24].
[24] D. Stauffer and A. Aharony, *Introduction to Percolation Theory* (Taylor & Francis, London, 1994), 2nd ed.
[25] J. Machta and S. M. Moore, Phys. Rev. A **32**, 3164 (1985).
[26] J. Machta, J. Stat. Phys. **42**, 941 (1986).
[27] M. H. Ernst, J. Machta, J. R. Dorfman, and H. van Beijeren, J. Stat. Phys. **34**, 477 (1984); J. Machta, M. H. Ernst, H. van Beijeren, and J. R. Dorfman, J. Stat. Phys. **35**, 413 (1984).
[28] F. Höfling, T. Franosch, and E. Frey, Phys. Rev. Lett. **96**, 165901 (2006).
[29] F. Höfling, Ph.D. thesis, Ludwig-Maximilians-Universität München, 2006.
[30] I.-A. Park and J. M. D. MacElroy, Mol. Simul. **2**, 105 (1989).