Scaling Analysis of Dynamic Heterogeneity in a Supercooled Lennard-Jones Liquid

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We have performed molecular dynamics computer simulations of a dense Lennard-Jones liquid mixture to study dynamic heterogeneity from normal liquid temperatures down to a supercooled temperature 15% above the previously identified mode-coupling temperature T_c of the model. A temperature-dependent correlation length associated with the correlation function of mobility fluctuations is calculated. The results are used to test two sets of scaling hypotheses for the dynamic heterogeneity. The results are in close agreement with the inhomogeneous mode-coupling theory of Biroli *et al.* [Phys. Rev. Lett. **97**, 195701 (2006)] for both the α and β relaxation regimes. Comparison with results for kinetically constrained models suggest that the Lennard-Jones mixture studied is more similar to models of fragile liquids than models of very strong liquids.

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Dynamic heterogeneity has been recognized as a significant feature of supercooled liquids. At any given time, there are regions of such a material in which the molecules are more mobile and hence relaxation takes place at rates that are larger than the average relaxation rates in the material. Moreover, the correlation length that characterizes the sizes of these regions increases as the temperature is lowered. Experimental and computer simulation studies of this phenomenon have been the subject of several reviews [1–4]. For estimates of the dynamic correlation lengths based on experimental studies, see [5]. For recent simulation and theoretical studies of dynamic heterogeneity, see [6–24].

One approach to the theoretical understanding of dynamic heterogeneity is based on the use of kinetically constrained lattice models [4,11,12,15–20,23,25–27]. Another approach is based on generalizations [7,22] of the mode-coupling theory of Götze [28]. The existence of dynamic heterogeneities and an increasing correlation length is also implied by the random first-order transition theory of supercooled liquids [29–32]. Many simulation studies of model liquids [1,6,10,12,21,22,33–36] have given evidence of a growing length scale for correlations of molecular mobility as the temperature of a material is lowered.

Here we present results of extensive molecular dynamics simulations designed to study dynamic heterogeneity in a supercooled Lennard-Jones mixture at equilibrium. The system was that of Kob and Andersen [37], which has been the object of several studies [6,8,12,14,21,24,38]. In the present work, this model was simulated at a fixed reduced density of 1.204, for reduced temperatures 0.9, 0.8, 0.7, 0.6, 0.55, and 0.5 for systems of 1000, 8000, and 27 000 particles. These temperatures extend into the supercooled liquid regime but are above the apparent mode-coupling temperature T_c of the system. For the present purposes, we use a value of $T_c = 0.438$, which we determined by fitting various relaxation times for 27 000 particle systems, for the temperatures mentioned, with a functional form $\tau = A(T - T_c)^{-\gamma}$. The inclusion of the 27 000-particle systems improved the quality of the extrapolation of k-dependent quantities to zero wave vector. For each temperature and for each system size, the length of the equilibration run was approximately 40 times the structural relaxation time τ_α [39] at that temperature and there were five data collection runs for the systems of largest size and ten runs for all the other systems. Each data collection run had a length of $25\tau_\alpha$.

The model is a mixture of 80% A particles and 20% B particles, with the A particles being larger. We use a definition of particle mobility that is identical or similar to definitions used in previous work [33]. We choose a distance d^* and a time t^* and define the mobility of particle i at time t as

$$\begin{aligned} \mu_i(t; d^*, t^*) &= 1 \quad \text{if } |\mathbf{r}_i(t + t^*) - \mathbf{r}_i(t)| \geq d^* \\ &= 0 \quad \text{otherwise} \end{aligned} \tag{1}$$

Here $\mathbf{r}_i(t)$ is the position of particle i at time t. The position dependent mobility density of A particles is $\mu(\mathbf{r}, t) = \sum_{i=1}^{N_A} \delta(\mathbf{r} - \mathbf{r}_i(t))\mu_i(t)$, where the sum extends over the N_A particles of type A, and, for simplicity, we have not indicated the d^* and t^* dependence. We define a "susceptibility" $\chi(\mathbf{k})$ as $\chi(\mathbf{k}, T) \equiv \mathcal{N}^{-1}\langle|\hat{\mu}(\mathbf{k}, t) - \langle\hat{\mu}(\mathbf{k}, t)\rangle|^2\rangle$, where $\hat{\mu}(\mathbf{k}, t)$ is the Fourier transform of $\mu(\mathbf{r}, t)$. The angular brackets denote an average over an equilibrium canonical distribution of states at temperature T, and $\mathcal{N}$ is a normalization constant chosen to be $N_A\langle\mu\rangle$, where $\langle\mu\rangle$ is the average mobility of the A particles. With this choice, $\chi(\mathbf{k}, T)$ is an intensive dimensionless quantity. The inverse Fourier transform of $\chi(\mathbf{k}, T)$, which we denote $G(\mathbf{r}, T)$, is a correlation function of fluctuations in the mobility density. The correlation length $\xi(T)$ associated with the susceptibility is defined so that for $\mathbf{k} \neq \mathbf{0}$, $\chi(\mathbf{k}, T) = \chi(\mathbf{k} \to \mathbf{0}, T)(1 - k^2\xi(T)^2 + O(k^4))$, where $\chi(\mathbf{k} \to \mathbf{0}, T) \equiv \lim_{\mathbf{k}\to 0}\chi(\mathbf{k}, T)$.

The recognition of the possibility of a long dynamic correlation length in supercooled liquids has led to the use of scaling ideas to analyze the results of theories and data from simulations [7,12,15,19,20,22]. One scaling hypothesis whose implications are equivalent to what is currently being used in studies of dynamic heterogeneity can be summarized in the following way. Assume that $\xi(T)$ is a monotonic function of T. Hence we can write $G(\mathbf{r}, T) = \mathcal{G}(|\mathbf{r}|, \xi(T))$, where $\mathcal{G}$ is a function of two scalar lengths. Assume that $\mathcal{G}(r, \xi) = b^{-(1+\eta)}\mathcal{G}(r/b; \xi/b)$ for large enough values of the arguments of $\mathcal{G}$ on both sides. The quantity η is a constant. This hypothesis implies that for large enough values of $\xi(T)$ and small enough values of $\mathbf{k}$, $\chi(\mathbf{k}, T) = \xi(T)^{2-\eta} f(k\xi(T))$, where the scaling function f has the properties that: $f(0)$ is a finite positive number; $f(x)/f(0) = 1 - x^2 + O(x^4)$ as $x \to 0$; $f(x) \propto x^{-2+\eta}$ as $x \to \infty$. Hence $\chi(\mathbf{0}+, T) \sim \xi(T)^{2-\eta}$; $\chi(\mathbf{k}, T)/\chi(\mathbf{0}+, T) = f(k\xi(T))/f(0)$.

A distinct set of scaling results is suggested by the inhomogeneous mode-coupling theory of Biroli *et al.* [22], namely, that $\xi(T)$ and $\chi(0+, T)$ should be proportional to inverse powers of $\epsilon \equiv T - T_c$ for temperatures above T_c: $\chi(\mathbf{0}+, T) \sim \epsilon^{\phi}$, $\xi(T) \sim \epsilon^{\psi}$ where ϕ and ψ are negative numbers.

In this Letter we test the predictions of these two types of scaling for the Lennard-Jones mixture, and we obtain numerical values of the exponents η, ϕ, and ψ for dynamic heterogeneity in both the α and β relaxation regimes.

For the study of dynamic heterogeneity in the α regime, we choose a value of t^* equal to τ_α at each temperature, and we choose $d = 0.375$, as a reasonable cutoff distance to determine whether a particle is caged on the time scale of interest.

At each temperature, the $\chi(\mathbf{k}, T)$ data were fit to the formula $\ln\chi(\mathbf{k}, T) = \ln\chi(\mathbf{k} \to \mathbf{0}, T) - \xi(T)^2 k^2 + ak^4$. Figure 1 shows the fit for the lowest temperature studied. Such a quadratic function of k^2 fits the data for small k at all temperatures and provides values of $\chi(\mathbf{k} \to \mathbf{0}, T)$ and $\xi(T)$.

The results [40] are in a log-log plot in Fig. 2. A straight line fit to the data gives $\chi(\mathbf{k} \to \mathbf{0}, T) \sim \xi^{4.2\pm0.3}$, providing a test of the scaling hypothesis and an estimate [41] of the exponent $2 - \eta$. Figure 3 shows a scaling plot of $\chi(k, T)/\chi(\mathbf{k} \to \mathbf{0}, T)$ vs $k\xi(T)$ with data for various temperatures. If the scaling hypothesis holds, the data in the scaling regime should lie on a common curve. There appears to be a common curve, defined by the lowest temperature data and smallest wave vectors, but the higher temperature curves depart from it, the departure taking place for smaller $k\xi$ at higher temperatures. This is to be expected, since at any temperature, going to large enough k will involve leaving the range of k values where the scaling equations hold.

From the temperature dependence of χ and ξ, the exponents ϕ and ψ in the scaling predictions of inhomogeneous mode-coupling theory were determined to be 1.12 ± 0.04 and 0.27 ± 0.03, respectively [42].

For the study of the β regime, we pick values of d^* and t^* that are appropriate for the length and time scales of that regime. For each temperature, a log-log plot of the mean squared displacement of the A particles as a function of time has a well-defined inflection point between the inertial regime and the diffusive regime. The time of that inflection point is chosen as t^* and the square root of the mean squared displacement is chosen as d^*.

The correlation length and $\chi(\mathbf{k} \to \mathbf{0}, T)$ values were determined for each temperature. A plot similar to Fig. 2 gave the result $\chi(\mathbf{k} \to \mathbf{0}, T) \sim \xi(T)^{2.05\pm0.26}$ for the β regime. A scaling plot of the wave vector dependent susceptibility is in Fig. 4. The data for all temperatures follows a common curve quite well for values of $k\xi$ up to about 3, and that curve has the shape of the Ornstein-Zernike function. Note that this function decays for large wave vector as

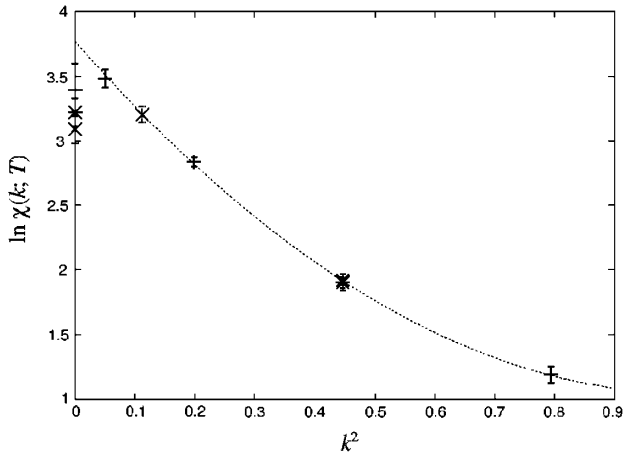

FIG. 1. The logarithm of the wave vector dependent susceptibility χ for α relaxation vs the square of the wave vector for $T = 0.5$.

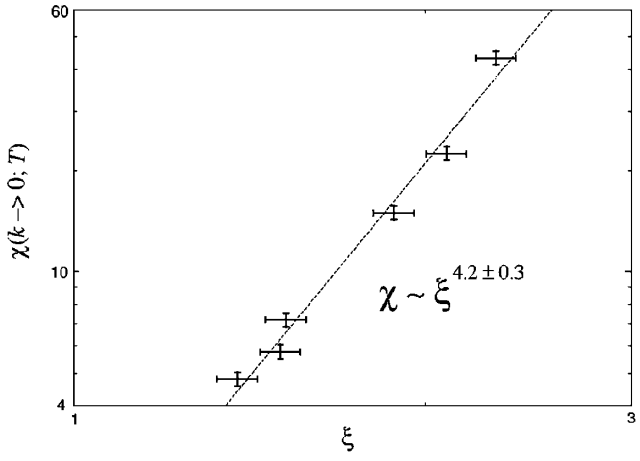

FIG. 2. Log-log plot of the susceptibility χ in the limit of zero wave vector for α relaxation vs correlation length with data for various temperatures.

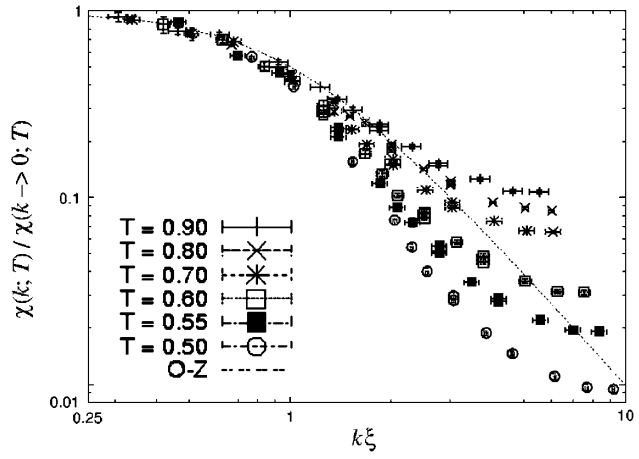

FIG. 3. A scaling plot of the normalized wave vector dependent susceptibility χ for α relaxation as a function of reduced wave vector with data for various temperatures. The dotted curve is the Ornstein-Zernike result.

$(k\xi)^{-2}$. According to the scaling hypothesis discussed above, this exponent (-2) should be equal to the negative of the exponent in the previous equation (2.05 ± 0.26), and this is in fact the case.

The log-log plots of $\chi(\mathbf{k} \to \mathbf{0}, T)$ and $\xi(T)$ vs $T - T_c$ were not well fit by straight lines in the entire temperature range studied. If the data for $T \leq 0.55$ is not included, the remaining data can be reasonably well described by $\phi \approx -0.5$ and $\psi \approx -0.25$.

The function $\chi(\mathbf{k}, T)$ as defined above would be nonzero even if the mobilities of the particles were statistically independent of each other and of the positions of the particles. Let us define $\chi_0(\mathbf{k}, T)$ to be the $\chi(\mathbf{k}, T)$ evaluated under the assumption that each particle's mobility is statistically independent of the coordinates and the mobilities of different particles are statistically independent. Then it follows straightforwardly that $\chi_0(\mathbf{k}, T) = 1 + \langle\mu\rangle(S_{AA}(\mathbf{k}) - 1)$, where $S_{AA}(\mathbf{k}) = N_A^{-1}\langle\sum_{i,j=1}^{N_A} \exp(-i\mathbf{k} \cdot (\mathbf{r}_i - \mathbf{r}_j))\rangle$ is the usual static structure factor for A particles.

Accordingly, we consider the function $\chi_1(\mathbf{k}, T) \equiv \chi(\mathbf{k}, T) - \chi_0(\mathbf{k}, T)$ as being possibly a better measure of the true correlations of mobility fluctuations. Figure 5 shows a scaling plot of $\chi_1(\mathbf{k}, T)/\chi_1(\mathbf{k} \to \mathbf{0}, T)$ vs $k\xi$. The data for all temperatures fall on a reasonably good scaling curve for $k\xi \leq 4$. The correlation lengths implied by χ_1 are systematically smaller than those obtained from χ, but they agree within the statistical error. The susceptibilities calculated from χ_1 are systematically smaller than those for χ. The difference is temperature dependent, and the resulting value of $2 - \eta$ is 4.8 ± 0.5.

There are several ambiguities in analyzing data to test scaling predictions, including uncertainty about what functions should be tested and what range of data should be tested. Despite these ambiguities, the dynamic heterogeneity data for our definitions of χ is remarkably consistent with both types of scaling over the temperature range discussed here for both the α and β regimes. This consistency with scaling behavior holds despite the fact that the correlation lengths are not in fact much larger than the diameter of the atoms.

The exponents obtained from this analysis (using χ rather than χ_1) are very consistent with the predictions of the inhomogeneous mode-coupling theory of Biroli *et al.* [22] The theory predicts, for the α regime, $2 - \eta = 4$, $\phi = -1$, and $\psi = -1/4$. For comparison, our results are $2 - \eta = 4.2 \pm 0.3$, $\phi = -1.12 \pm 0.04$, and $\psi = -0.27 \pm 0.03$. The theory predicts, for the β regime, $2 - \eta = 2$, $\phi = -1/2$, and $\psi = -1/4$. Our results are $2 - \eta = 2.05 \pm 0.26$, and the data for $0.6 \leq T \leq 0.9$ are con-

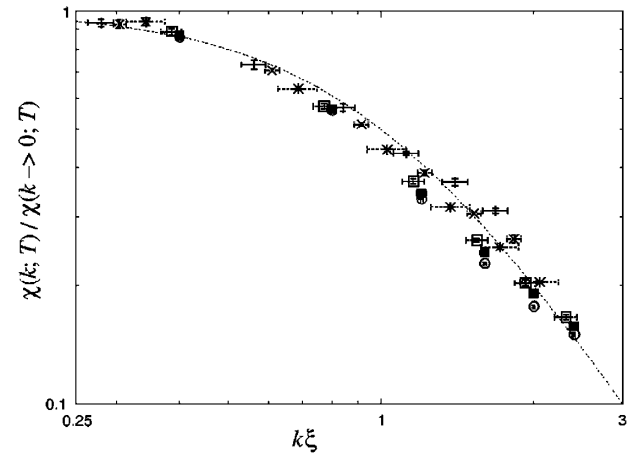

FIG. 4. A scaling plot of the normalized wave vector dependent susceptibility χ for β relaxation as a function of reduced wave vector for various temperatures. See Fig. 3 for more information.

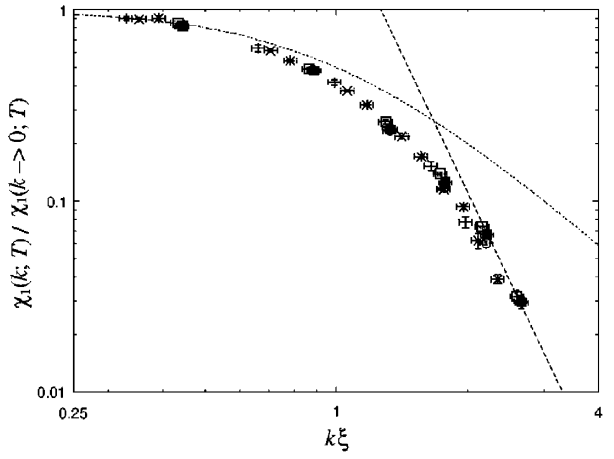

FIG. 5. A scaling plot of the normalized wave vector dependent susceptibility χ_1 for α relaxation as a function of reduced wave vector for various temperatures. The dotted straight line has a slope of -4.8. This is the value of the large wave vector slope of the scaling curve that is consistent with the relationship between $\chi_1(\mathbf{k} \to 0, T)$ and $\xi(T)$. See Fig. 3 for more information.

sistent with $\phi = -1/2$, and $\psi = -1/4$. Moreover, the scaling behavior of the wave vector dependent susceptibility is quite good and follows an Ornstein-Zernike curve, which is consistent with $2 - \eta \approx 2$.

The results for the exponent $2 - \eta$ can be compared with the theory and simulation of kinetically constrained models. A simulation of the Fredrickson-Andersen model [25] in 3 dimensions gave $2 - \eta = 2.15$ [20]. This is a model for strong liquids. Simulations of the NEF model of a very fragile liquid in three dimensions gave $2 - \eta \approx 3.58$ [15]. Our result of $2 - \eta = 4.2 \pm 0.3$ suggests that the Lennard-Jones mixture should be regarded as a fragile liquid.

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[1] H. C. Andersen, Proc. Natl. Acad. Sci. U.S.A. **102**, 6686 (2005).
[2] R. Richert, J. Phys. Condens. Matter **14**, R703 (2002).
[3] M. D. Ediger, Annu. Rev. Phys. Chem. **51**, 99 (2000).
[4] F. Ritort and P. Sollich, Adv. Phys. **52**, 219 (2003).
[5] E. Hempel, G. Hempel, A. Hensel, C. Schick, and E. Donth, J. Phys. Chem. B **104**, 2460 (2000).
[6] L. Berthier, Phys. Rev. E **69**, 020201 (2004).
[7] G. Biroli and J.-P. Bouchaud, Europhys. Lett. **67**, 21 (2004).
[8] E. Flenner and G. Szamel, Phys. Rev. E **70**, 052501 (2004).
[9] L. Berthier, D. Chandler, and J. P. Garrahan, Europhys. Lett. **69**, 320 (2005).
[10] Y. Gebremichael, M. Vogel, and S. C. Glotzer, J. Chem. Phys. **120**, 4415 (2004).
[11] Y. J. Jung, Juan P. Garrahan, and D. Chandler, Phys. Rev. E **69**, 061205 (2004).
[12] S. Whitelam, L. Berthier, and J. P. Garrahan, Phys. Rev. Lett. **92**, 185705 (2004).
[13] L. Berthier, G. Biroli, J.-P. Bouchaud, L. Cipelletti, D. El Masri, D. L'Hôte, F. Ladieu, and M. Pierno, Science **310**, 1797 (2005).
[14] E. Flenner and G. Szamel, Phys. Rev. E **72**, 031508 (2005).
[15] L. Berthier and J. P. Garrahan, J. Phys. Chem. B **109**, 3578 (2005).
[16] Y. J. Jung, J. P. Garrahan, and D. Chandler, J. Chem. Phys. **123**, 084509 (2005).
[17] S. Léonard and L. Berthier, J. Phys. Condens. Matter **17**, S3571 (2005).
[18] M. Merolle, J. P. Garrahan, and D. Chandler, Proc. Natl. Acad. Sci. U.S.A. **102**, 10 837 (2005).
[19] A. C. Pan, J. P. Garrahan, and D. Chandler, Phys. Rev. E **72**, 041106 (2005).
[20] S. Whitelam, L. Berthier, and J. P. Garrahan, Phys. Rev. E **71**, 026128 (2005).
[21] L. Berthier, G. Biroli, J.-P. Bouchaud, W. Kob, K. Miyazaki, and D. R. Reichman, J. Chem. Phys. **126**, 184503 (2007).
[22] G. Biroli, J.-P. Bouchaud, K. Miyazaki, and D. R. Reichman, Phys. Rev. Lett. **97**, 195701 (2006).
[23] D. Chandler, J. P. Garrahan, R. L. Jack, L. Maibaum, and A. C. Pan, Phys. Rev. E **74**, 051501 (2006).
[24] G. Szamel and E. Flenner, Phys. Rev. E **74**, 021507 (2006).
[25] G. H. Fredrickson and H. C. Andersen, Phys. Rev. Lett. **53**, 1244 (1984).
[26] J. P. Garrahan and D. Chandler, Phys. Rev. Lett. **89**, 035704 (2002).
[27] L. Berthier and J. P. Garrahan, Phys. Rev. E **68**, 041201 (2003).
[28] W. Götze, *Aspects of Structural Glass Transitions*, edited by J. P. Hansen, D. Levesque, and J. Zinn-Justin (Elsevier Science Publishers B.V., Amsterdam, 1991).
[29] T. R. Kirkpatrick and P. G. Wolynes, Phys. Rev. B **36**, 8552 (1987).
[30] T. R. Kirkpatrick, D. Thirumalai, and P. G. Wolynes, Phys. Rev. A **40**, 1045 (1989).
[31] X. Xia and P. G. Wolynes, Proc. Natl. Acad. Sci. U.S.A. **97**, 2990 (2000).
[32] V. Lubchenko and P. G. Wolynes, J. Chem. Phys. **119**, 9088 (2003).
[33] W. Kob, C. Donati, S. J. Plimpton, P. H. Poole, and S. C. Glotzer, Phys. Rev. Lett. **79**, 2827 (1997).
[34] S. C. Glotzer, V. N. Novikov, and T. B. Schrøder, J. Chem. Phys. **112**, 509 (2000).
[35] N. Lačević, F. W. Starr, T. B. Schrøder, V. N. Novikov, and S. C. Glotzer, Phys. Rev. E **66**, 030101(R) (2002).
[36] N. Lačević, F. W. Starr, T. B. Schrøder, and S. C. Glotzer, J. Chem. Phys. **119**, 7372 (2003).
[37] W. Kob and H. C. Andersen, Phys. Rev. Lett. **73**, 1376 (1994); Phys. Rev. E **51**, 4626 (1995); **52**, 4134 (1995).
[38] K. Vollmayr-Lee, W. Kob, K. Binder, and A. Zippelius, J. Chem. Phys. **116**, 5158 (2002).
[39] Here τ_α is defined as the relaxation time of the dynamic structure factor for a wave vector near the first peak of the static structure factor.
[40] Our values for the correlation length in the α regime, obtained using systems containing as many as 27 000 particles, are larger than those of Berthier [6] for the same potential for systems of 1372 particles.
[41] The error estimates for the exponents are ''asymptotic standard errors'' calculated in least squares fitting of functional forms to the data (http://www.gnuplot.info/docs/node86.html). They are only a qualitative estimate of the error.
[42] The exponents were obtained in a way similar to that shown in Fig. 2. Namely, log-log plots of χ and ξ versus $T - T_c$ were fit with straight lines. The exponents quoted are the slopes of the best fits and the error estimates are the standard errors of the linear fits.