Establishing a quantitative connection between the relaxation properties of a liquid and the forces and interactions among its constituent molecules is the *sine qua non* for fundamental understanding and prediction of the dynamical properties. The supercooled regime is of particular interest, since both intermolecular forces and steric constraints (excluded volume) exert significant effects on the dynamics. This makes temperature, pressure, and volume essential experimental variables to characterize the relaxation properties. One successful approach to at least categorize relaxation times of supercooled liquids and polymers is by expressing them as a function of the ratio of temperature, $T$, to mass density, $\rho$, with the latter raised to a material specific constant $\gamma$, viz.

$$x = 3(T/\rho^\gamma)$$

where $x$ is the structural relaxation time, $\tau$, viscosity, $\eta$, diffusion coefficient, $D$, or some other dynamic variable, and $3$ is a function. This scaling was first applied to a Lennard-Jones (LJ) fluid, with $\gamma = 4$ yielding approximate master curves of the “excess” viscosity for different thermodynamic conditions [1]. More recently Eq. (1) has been shown to superpose relaxation times measured by neutron scattering [2], light scattering [3], viscosity [4], and dielectric spectroscopy [5–9] for a broad range of materials, including polymer blends and ionic liquids. The scaling exponent $\gamma$, which varies in the range from 0.13 to 8.5 [10], is a measure of the contribution of density (or volume) to the dynamics, relative to that due to temperature. The only breakdown of the scaling is observed for hydrogen-bonded liquids, in which the concentration of H-bonds changes with $T$ and $P$, causing $\tau$ to deviate from Eq. (1) [4].

The function $3$ in Eq. (1) is unknown *a priori*. Its form can be derived from entropy models for the glass transition, leading to an exponential dependence of $\log \tau$ on $\rho^\gamma/T$ [11, 12]. Another interpretation of the scaling is that the supercooled dynamics is governed by activated processes with an effective activation energy $E(\rho, T)$ [13, 14], in which the $\rho$-dependence of $E(\rho, T)$ can be factored and expressed in terms of a power law of $\rho$. The power law scaling arose from the idea that the intermolecular potential for liquids can be approximated as a repulsive inverse power law (IPL), with the weaker attractive forces treated as a spatially-uniform background term [15–17]

$$u(r) \sim r^{-m} + \text{const}$$

where $r$ is the intermolecular distance. The IPL emphasizes the dominant role of the short-range repulsive interactions for local properties such as structural relaxation. The assumption that the long range forces on a molecule tend to average to zero is consistent with the fact that in liquids, the static structure factor at intermediate and large wave vectors is sensitive only to the repulsive part of the potential [18, 19]. An IPL with density-dependent mean field attractive term was shown indeed to yield a reasonable equation of state for simple liquids [20].

Of course, the exact form of the intermolecular potential for real liquids cannot be deduced from their molecular structure. So a test of whether a spherically symmetric, pairwise additive repulsive potential serves as the basis for the scaling (Eq. (1)) must be drawn from molecular simulations, in which the potential function is known and can be varied. Various groups have explored the relationship of the steepness of the repulsive potential to properties such as the equation of state [21–23], longitudinal wave properties [24], vibrational spectrum [25], liquid [26] and gaseous [27] transport properties, the correlation between fluctuations of energy and pressure [28], and the fragility [29, 30]. Recently two simulations have appeared in which Eq. (1) was used to superpose dynamical data for polymer chains described using an LJ
12-6 with an added term for the intrachain interactions. The results appear contradictory: Tsolou et al. [31] obtained a scaling exponent of \( \gamma = 2.8 \) for the segmental relaxation times of simulated 1,4-polybutadiene, while Budzien et al. [32] superposed diffusion coefficients for prototypical polymer chains using \( \gamma = 6 \) when attraction were included in the simulation and \( \gamma = 12 \) when they were omitted. Thus, the scaling exponent \( \gamma \) is either less than [31] or greater than [32] \( m/3 \), which is the value expected for an IPL with exponent \( m \) [17].

To clarify this situation we carried out simulations for some supercooled LJ \( m-n \) liquids, in which the repulsive exponent \( m \) was systematically varied. Diffusion coefficients, determined as a function of pressure at various temperatures, were superposed using Eq. (1), and the obtained value of \( \gamma \) compared to the \( m \) used in the simulation. The results presented herein show the connection between the thermodynamic scaling and the intermolecular repulsive potential. Moreover, since the steepness of the repulsive forces varies with \( r \), due to the contribution of the attractive term to the intermolecular potential, potentially the \( \gamma \) extracted from master curves of the dynamic data can yield information about the range of \( r \) probed by the structural motions in the supercooled liquid.

The models we study are binary mixtures composed of \( N = 500 \) particles enclosed in a cubic box with periodic boundary conditions and interacting with a modified LJ \( m-n \) potential

\[
u_{\alpha\beta}(r) = 4\epsilon_{\alpha\beta} \left( \frac{\sigma_{\alpha\beta}}{r} \right)^m - \left( \frac{\sigma_{\alpha\beta}}{r} \right)^n \tag{3}\]

where \( \alpha, \beta = 1, 2 \) are indexes of species. We fixed the attractive exponent \( n = 6 \), as in the standard LJ potential, and varied the repulsive exponent \( m = 8, 12, 24, 36 \). The potential \( \nu_{\alpha\beta}(r) \) was smoothed at \( r_c = 2.5\sigma_{\alpha\beta} \) using the cutoff scheme of Stoddard and Ford [33]. Reduced units are used, assuming \( \sigma_{11}, \epsilon_{11} \) and \( \sqrt{m_1\sigma_{11}^2/\epsilon_{11}} \) as units of distance, energy and time respectively. The unit of pressure is given by \( \epsilon_{11}/\sigma_{11}^2 \). The mixture on which we focus is an additive, equimolar mixture with size ratio \( \lambda = \sigma_{22}/\sigma_{11} = 0.64 \), equal masses \( m_1 = m_2 = 1.0 \) and a unique energy scale \( \epsilon_{\alpha\beta} = 1.0 \). The choice \( m = 12 \) corresponds to the AMLj-0.64 mixture studied in [34, 35]. The samples were quenched (almost) isobarically at different pressures \( P = 5, 10, 20 \) by coupling the system to Berendsen thermostat and barostat during the equilibration phase (see [34] for details), and performing the production runs in the NVE ensemble using the Velocity-Verlet algorithm. The timestep \( \delta t \) was varied according to the repulsive exponent, ranging from 0.001 \((m = 36)\) to 0.004 \((m = 8)\) at high \( T \), and from 0.003 \((m = 36)\) to 0.008 \((m = 8)\) at low \( T \). The equilibration criteria used were similar to the ones employed in [34].

The effectiveness of the thermodynamical scaling for modified LJ systems is demonstrated in Figure 1 for different values of the repulsive exponent \( m \). For each \( m \), diffusivity data were gathered along different isobaric paths \((P = 5, 10, 20)\) and the system-specific scaling exponent \( \gamma \) was obtained by maximizing the overlap between \( D \) at different pressures: \( P = 5 \) (squares), \( P = 10 \) (circles), and \( P = 20 \) (triangles). From top to bottom: \( m = 36 \ (\gamma = 13.2), \ m = 24 \ (\gamma = 9.0), \ m = 12 \ (\gamma = 4.8), \) and \( m = 8 \ (\gamma = 3.4) \).

![Figure 1](image-url)
cooled regime first becomes apparent upon cooling the liquid. Analyzing the variation of the scaling exponent in our models, we find that $\gamma$ increases with increasing $m$, but its actual value is systematically larger than $m/3$. For instance, in the case $m = 12$ we obtain $\gamma = 4.8$, a value which we also found to provide scaling of $D$ for other supercooled Lennard-Jones ($m = 12$) mixtures, such as the AMLJ-0.76 mixture introduced in Ref. [34] and the BMLJ mixture of Kob and Andersen [37].

The origin of the discrepancy between $\gamma$ and $m/3$ lies in the fact that the asymptotic region $r \to 0$, in which $u(r) \sim r^{-m}$, is not dynamically accessible in normal simulation conditions. The presence of the fixed attractive term in the potential (Eq. (3)) gives rise to an effective IPL which is steeper in the region of $r$ close to the minimum than in the $r \to 0$ limit. To give a semi-quantitative support to this claim, we first identify, by looking at the radial distribution functions $g_{\alpha\beta}(r)$, the portion of interparticle distances which are dynamically relevant for the present $T$ and $\rho$ conditions. Toward this end, we introduce some useful reference distances: the distance of closest approach between particles $r_0$ (i.e., the value of $r$ for which the radial distribution function first becomes non-zero) and the position corresponding to half of the height of the first peak (i.e., $g_{\alpha\beta}(r_1) = g_{\alpha\beta}(r_m)/2$ where $r_m$ is the position of the first peak and $r_0 < r_1 < r_m$). These quantities depend on the thermodynamic state under consideration, but their variation with $P$ and $T$ is mild within our simulation conditions. In particular, for a given $P$, $r_0$ and $r_1$ show a weak increase with decreasing $T$, but they become almost $T$-independent below $T_D$. Our interest being the supercooled regime, we consider the interval $[r_0 : r_1]$ obtained from the low-$T$ behaviour of the $g_{\alpha\beta}(r)$ and conventionally define it as the relevant range of distance for repulsion.

By analyzing the shape of the pair potential within the range $[r_0 : r_1]$, the relationship between the repulsive part of the potential experienced by the particles and the scaling exponent $\gamma$ becomes apparent. To exemplify our procedure, we consider the case $m = 24$ and focus on the radial distribution functions between large particles $g_{11}(r)$, which are shown in the upper panel of Figure 2 at the lowest equilibrated $T$ for $P = 5, 10, 20$. To account for the residual $P$-dependence of $r_0$ and $r_1$, we simply consider their values calculated at $P = 10$. The lower panel of Figure 2 shows a fit of the pair potential $u_{11}(r)$ to an IPL of the form given by Eq. (2) performed in the range $[r_0 : r_1]$. The value $\overline{\gamma} = 27.5$ obtained through this procedure is indeed larger than $m = 24$ and is close to the value expected from the dynamical scaling. Repeating the fit in the range $[r_0 : r_m]$, yields a larger value $\overline{\gamma} = 28.8$, revealing how $\gamma$ is indeed dictated by the portion of $r$ around the distance of closest approach in the supercooled regime.

To proceed in a more systematic way, we considered all $\alpha - \beta$ pairs (1-1, 1-2 and 2-2) in the pair potential $u_{\alpha\beta}(r)$ and performed a simultaneous fit to the following IPL

$$\pi_{\alpha\beta}(r) = r^{\sigma_{\alpha\beta}} \overline{\pi} + \overline{\tau}$$

(4)

For each $\alpha - \beta$ pair we used the corresponding $[r_0 : r_1]$ range for fitting. In Eq. (4) we assumed that the approximating IPL has the same size ratios as the original $u_{\alpha\beta}(r)$ potential. As a further simplification, a single energy scale $\overline{\tau}$ and a common shift term $\overline{\pi}$ are also assumed. Results obtained for different values of $m$ are summarized in Table I. In general, we find a good agreement between $3\gamma$ and the fitted value of $\overline{\pi}$. Thus, the scaling exponent can be reasonably accounted for in terms of an IPL approximation of the pair potential, provided that a sensible choice of the relevant range of distances is made. In principle, the procedure could also be inverted, to find

---

**TABLE I: Summary of effective exponents for IPL.** $3\gamma$ is the value expected from the scaling of diffusion coefficients. The parameters $\overline{\pi}$, $\overline{\tau}$, and $\overline{\kappa}$ of the approximant IPL (Eq. (4)) are also shown.

<table>
<thead>
<tr>
<th>$m$</th>
<th>$3\gamma$</th>
<th>$\overline{\pi}$</th>
<th>$\overline{\tau}$</th>
<th>$\overline{\kappa}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMLJ-0.64</td>
<td>8 10.2 10.9 0.84</td>
<td>-0.83</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>14.4</td>
<td>14.9</td>
<td>1.73</td>
<td>-1.71</td>
</tr>
<tr>
<td>24</td>
<td>27.0</td>
<td>27.2</td>
<td>2.73</td>
<td>-2.67</td>
</tr>
<tr>
<td>36</td>
<td>39.6</td>
<td>39.9</td>
<td>3.01</td>
<td>-2.94</td>
</tr>
</tbody>
</table>
the optimal range of distances in which the effective IPL exponent matches the value expected from the dynamical scaling.

As a check of our procedure, we performed some simulations for a soft-sphere mixture with $\bar{m} = 14.9$ and $\bar{\tau} = 1.8$, which is the approximating IPL (Eq. (4)) for the case $m = 12$. We then compared the diffusivity data for the approximatae soft-sphere model with those of the reference LJ model along two isochores ($\rho = 1.5$, $\rho = 1.7$), which correspond to typical densities attained at low $T$ by the LJ system (at constant $P$). By a slight reoptimization of the energy scale $\bar{\tau}$ (increased by around 10%) we could obtain a good superposition of the diffusion coefficients for both sets of data over more than 3 decades in $D$.

To summarize, the thermodynamic scaling of the diffusion coefficient in supercooled LJ $m = 6$ mixtures reflects the importance of the repulsive part of the pair potential in determining the dynamical properties of these systems. The magnitude of the scaling exponent $\gamma$ is, in fact, strongly related to the steepness of the repulsive part of the potential around the distance of closest approach between particles, which we have identified by inspection of the partial distribution functions. The exponent $\gamma$ is larger than $m/3$ for LJ $m = 6$ liquids, a fact which can be rationalized by approximating the repulsive part of the potential with an IPL having exponent $\bar{m} \approx 3\gamma$. Generalization of such arguments to more realistic models of glass-formers remains a challenge for future investigations.

Acknowledgments

We thank G. Pastore and R. Casalini for discussions and useful suggestions. Computational resources for the present work have been obtained through a grant within the agreement between the University of Trieste and the Consorzio Interuniversitario CINECA (Italy). The work at NRL was supported by the Office of Naval Research.