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Master thesis in physics submitted by

Jakob Krummeich

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Critical behavior of a 2-D Lennard-Jones mixture under shear

Adviser and first examiner:	Prof. Dr. J. Horbarch
Second examiner:	Prof. Dr. H. Löwen

Abstract

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2.1 Pair correlation function

The partial pair correlation functions for a binary mixture can be defined as

$$g_{\alpha\beta}\left(\vec{r}\right) = \frac{V}{N_\alpha N_\beta} \langle \sum_{i \neq j} \delta\left(\vec{r} - \left(\vec{r}_i - \vec{r}_j\right)\right) \rangle \tag{2.1}$$

where $\alpha, \beta \in \{A, B\}$ label the particle type, V is the total volume, N_α, N_β denote the particle numbers, $\langle . \rangle$ indicates the ensemble average and $\delta(.)$ is the delta function. The sum runs over all pairs of particles i, j where $i \neq j$, so that $\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$ are the distance vectors between particle types α and β. Thus, $g_{\alpha\beta}\left(\vec{r}\right)$ simply is the averaged distribution of $\vec{r}_{ij}$ over the volume space V. Note that this definition implies $g_{\alpha\beta}(\vec{r}) = g_{\alpha\beta}(-\vec{r})$, i.e. $g_{\alpha\beta}(\vec{r})$ is an even function.

In 2 dimensions with the usual map

$$\vec{r} = \begin{pmatrix} r \cdot \cos\phi \\ r \cdot \sin\phi \end{pmatrix} \tag{2.2}$$

for $r \in (0, \infty]$, $\phi \in [0, 2\pi)$ and

$$\phi_{ij} = \sphericalangle\left(\vec{r}_i, \vec{r}_j\right) \tag{2.3}$$

we get

$$g_{\alpha\beta}\left(\vec{r}\right) = \frac{2V}{N_\alpha N_\beta} \langle \sum_i \sum_{i<j} \frac{1}{r} \delta\left(r - \left|\vec{r}_i - \vec{r}_j\right|\right) \delta\left(\phi - \phi_{ij}\right) \rangle. \tag{2.4}$$

To examine structural anisotropy we expand $g_{\alpha\beta}(\vec{r})$ into spherical harmonics:

$$g_{\alpha\beta}(\vec{r}) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} g_{lm}^{\alpha\beta} Y_{lm}(\theta, \phi) \tag{2.5}$$

where $Y_{lm}(\theta, \phi)$ are spherical harmonics with degree l and order m. In 2 dimensions we restrict $\theta = \pi/2$. Since the spherical harmonics form a complete orthonormal set the coefficients $g_{lm}^{\alpha\beta}$ are given by

$$g_{lm}^{\alpha\beta}(r) = \frac{2V}{N_\alpha N_\beta}\langle \sum_i \sum_{i<j} \int_0^{2\pi} \mathrm{d}\phi' \frac{1}{r} \delta\left(r - |\vec{r}_i - \vec{r}_j|\right) \delta\left(\phi' - \phi_{ij}\right) Y_{lm}^*(\pi/2, \phi')\rangle \quad (2.6)$$

$$= \frac{2V}{N_\alpha N_\beta}\langle \sum_i \sum_{i<j} \frac{1}{r} \delta\left(r - |\vec{r}_i - \vec{r}_j|\right) Y_{lm}^*(\pi/2, \phi_{ij})\rangle. \quad (2.7)$$

Note that $g_{lm}^{\alpha\beta}$ depends only on r since the angular dependence of $g_{\alpha\beta}$ is fully included in Y_{lm}. Furthermore, since $g_{\alpha\beta}(\vec{r}) = g_{\alpha\beta}(-\vec{r})$ and $Y_{lm}(-\vec{r}) = (-1)^l Y_{lm}(\vec{r})$ we see that all $g_{lm}^{\alpha\beta}$ with odd l vanish. For isotropic systems all coefficients except $g_{00}^{\alpha\beta}(r)$ vanish.

Of special importance in the context of Couette flow is the imaginary part of $g_{22}^{\alpha\beta}$ as it can be linked to the configurational part of the shear stress. In Cartesian coordinates we have

$$\mathrm{Im}Y_{22} = \sqrt{\frac{15}{8\pi}} \frac{xy}{r^2} \quad (2.8)$$

so that in 2 dimensions we get

$$\mathrm{Im}g_{22}^{\alpha\beta} = \sqrt{\frac{15}{2\pi}} \frac{V}{N_\alpha N_\beta}\langle \sum_i \sum_{i<j} \frac{1}{r^3} \delta\left(r - |\vec{r}_i - \vec{r}_j|\right) (x_i - y_j)(y_i - y_j)\rangle. \quad (2.9)$$

2.2 Static structure factors

We can define partial structure factors by

$$S_{\alpha\beta}(\vec{q}) = \frac{1}{N}\langle \sum_{i,j,i\neq j} \exp\left[-\mathrm{i}\vec{q}(\vec{r}_i - \vec{r}_j)\right]\rangle \quad (2.10)$$

where the sum runs over all distance vectors $\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$ of particles of types $\alpha, \beta \in \{A, B\}$. Thus, the partial structure factors are proportional to the Fourier transform of the partial pair correlation functions $g_{\alpha\beta}(\vec{r})$ given in section 2.1. Furthermore, with this definition it is clear that $S_{\alpha\beta}(\vec{q}) \in \mathbb{R}$ as the partial pair correlation functions are even.

In a system with periodic boundary conditions we need to respect the symmetry, so that only a discrete set of $\vec{q}$ values is allowed. In a 2 dimensional system in a quadratic box with length L these are given by

$$\vec{q} \in \begin{pmatrix} \frac{2\pi}{L} z_x \\ \frac{2\pi}{L} z_y \end{pmatrix}, z_{x,y} \in \mathbb{Z}. \tag{2.11}$$

3 Simulation methods

4 Results

5 Conclusion and Outlook

Attachments

Erklärung

Ich versichere, dass ich diese Arbeit selbstständig verfasst und keine anderen als die angegebenen Quellen und Hilfsmittel benutzt habe.

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Jakob Krummeich