

Structure factors for 2D Lennard-Jones fluids

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Comparing first moment of $h(r)$ and $S(0)$

The integral $1 + \rho \int h(r) d\mathbf{r}$ is truncated at a distance r_t by inspection of the convergence of the numerical integral $\int_0^x rh(r)dr$ (usually $5\sigma \leq r_t \leq 8\sigma$) and compared to $S(0)$ obtained in simulations. All simulation runs use 400 particles.

ρ	T	T/T_c	State	S(0) by 4th virial	$1 + \rho \int h(r) d\mathbf{r}$	$S(0)$
0.0163	0.40	0.71	Vapor	1.35	1.28	1.28
0.02	0.45	0.8	Vapor	1.48	1.45	1.45
0.05	0.50	0.89	Vapor	2.28	2.05	2.07
0.10	0.60	1.07	Supercrit.	2.12	1.97	1.95
0.60	0.55	0.98	Liquid		0.34	0.48
0.60	0.45	0.8	Liquid		0.5–1.0 (Oscillates)	0.96

Therefore $1 + \rho \int h(r) d\mathbf{r}$ agrees best with simulated $S(0)$ at low densities. When the density is higher, the integral converges only at large r and is more prone to noises in the simulated $h(r)$.

Literature for $\tilde{c}(k)$ or $\tilde{h}(k)$

Verlet’s paper¹ talks about two types of decay of $h(r)$: exponential decay at small ρ and damped oscillatory decay at large ρ . The asymptotics of h can be analyzed by the poles of $\tilde{h}(k)$ at small k .

Dijkstra and Evans² report a curious way to “force” long-range information of $h(r)$ from small simulation size. They propose a way to determine if $h(r)$ has exponential decay or damped oscillatory decay, *i.e.* with the transformations:

$$h(r) \text{ from simulation} \rightarrow \tilde{h}(k) \rightarrow \tilde{c}(k) \rightarrow c(r) \rightarrow \text{poles of } \tilde{h}(k) \rightarrow \text{the decay type of } h(r).$$

Because the integral in their second last step is truncated at $r = 2.5\sigma$, the work might be only valid for tasks involving relatively small k , *e.g.* $1 \leq |k| \leq 2$ in their paper. It is

not really helpful to determine the behavior as $k \rightarrow 0$, for the integral $1 + \rho \int h(r) d\mathbf{r} = S(0)$ usually does not converge until $r \geq 5\sigma$. However, it may be instructive to calculate some poles of $\tilde{h}(k)$?

Ref. 3 has a comparison of $1 + \rho\tilde{h}(k)$ with $S(k)$ for liquid water. They also mention significant difference as k go to 0, and that Fast Fourier Transform underestimates $S(0)$ as observed in the previous section.

Fitting of $S(k)$ at small k ($0 \leq k \leq 5$)

The states chosen here for fitting of $S(k)$ are such that $S(k)$ monotonically decreases as k decreases to 0: They are liquid-like supercritical fluids.

ρ	T	T/T_c	Order 3 poly. fit
0.6	2	3.57	$0.026k^3 - 0.1138k^2 + 0.1546k + 0.1219$
0.7	1.5	2.68	$0.0363k^3 - 0.1973k^2 + 0.3155k - 0.0257$
0.7	0.75	1.34	$0.0408k^3 - 0.2286k^2 + 0.3563k - 0.0278$

We note, for the moment, that first and second order polynomials give visibly very inaccurate fit of $S(k)$.

References

- (1) Verlet, L. Computer "experiments" on classical fluids. II. Equilibrium correlation functions. *Physical Review* **1968**,
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- (3) Zhao, S.; Wu, J. An efficient method for accurate evaluation of the site-site direct correlation functions of molecular fluids. *Molecular Physics* **2011**,