Isothermal compressibility, κ , for one component fluid in three dimension

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0.1 Theory :

For a N-particles System of volume V with density profile $\rho(\mathbf{r}) = \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i)$, the static Structure factor S($\mathbf{k}$) is defined as the Fourier density correlation.

$$S(\mathbf{k}) \equiv \frac{1}{N} \langle \hat{\rho_{\mathbf{k}}} \hat{\rho_{-\mathbf{k}}} \rangle \tag{1}$$

And for K$\rightarrow$ 0 the S(K) is reduced to

$$\lim_{k \to 0} S(k) = \rho K_B T \kappa \tag{2}$$

where κ is the isothermal compressibility and K_B Boltzman constant . In equation (1) $\hat{\rho_k}$ is the Fourier transformation of $\rho(\mathbf{r})$,

$$\hat{\rho}(\mathbf{k}) = \int \rho(\mathbf{r}) e^{i\mathbf{k}.\mathbf{r}}.\mathbf{dr} = \sum_{i=1}^{N} e^{i\mathbf{k}.\mathbf{r}_i} \tag{3}$$

and

$$\rho(\mathbf{r}) = (2\pi)^{-3} \int \hat{\rho_{\mathbf{k}}} e^{-i\mathbf{k}.\mathbf{r}}.\mathbf{dk} = (2\pi)^{-3} \sum_{i=1}^{N} \hat{\rho_{\mathbf{k}}} e^{-i\mathbf{k}.\mathbf{r}} \tag{4}$$

A general expression for $S(\mathbf{k})$ is

$$S(\mathbf{k}) = \frac{1}{N} \left\langle \sum_{i=1}^{N} e^{i\mathbf{k}.\mathbf{r}_i}. \sum_{j=1}^{N} e^{-i\mathbf{k}.\mathbf{r}_j} \right\rangle \tag{5}$$

$$= \frac{1}{N} \left\langle \left| \sum_{i=1}^{N} \cos i\mathbf{k}.\mathbf{r}_i \right|^2 . \left| \sum_{i=1}^{N} \sin i\mathbf{k}.\mathbf{r}_i \right|^2 \right\rangle \tag{6}$$

Here equation (6) is valid for uniform liquid, glasses and periodic structure system e.g. crystal and core equation of this simulaton.

One can choose to calculate $S(\mathbf{k})$ for $(n_k{+}1)^3$ number of $\mathbf{k}$'s, $\Delta k(n_x, n_y, n_z)$ with $n_x, n_y, n_z = 0, 1, 2, 3, ...$ but $n_x = n_y = n_z \neq 0$. For same value of k, $S(\mathbf{k})$ can be counted in the same bin [k + dk] and later an averaged over k for S(k) can be considerd.

0.2 Molecular Dynamic Method :

In this investigation of Isothermal compressibility, a canonical (PVT) system, based on WCA potential, usingNosHoover thermostat and Velocitc Verlet algorithm has been fuctionalised (figure-2). An initial cubic latice box with density$= 0.2\sigma^{-3}$, particle number $= 12 \times 12 \times 12$, mass, m = 1, temperature, T = 1, time unit, $\tau = \sqrt{\frac{m\sigma^2}{\epsilon}}$, characteristic energy unit $= \epsilon$, characteristc length unit $= \sigma$ coupling factor Q = 1.0, has been propagated for dt = 0.0005τ till t $= 7\tau$. As particle number and density is fixed, the box volume is determined. Here, repulsive pairwise Weeks-Chandler-Andersen (WCA) potential(figure-1) is

$$u(r_{ij}) = \begin{cases} 4\epsilon[(\frac{\sigma}{r_{ij}})^{12} - (\frac{\sigma}{r_{ij}})^6] + \epsilon & ; r_{cut} \leq 2^{\frac{1}{6}} \\ 0 & ; \text{otherwise} \end{cases} \tag{7}$$

where $r_{ij} = |\mathbf{r}_j - \mathbf{r}_i|$ is the absolute distance between j^{th} particle and i^{th} particle.

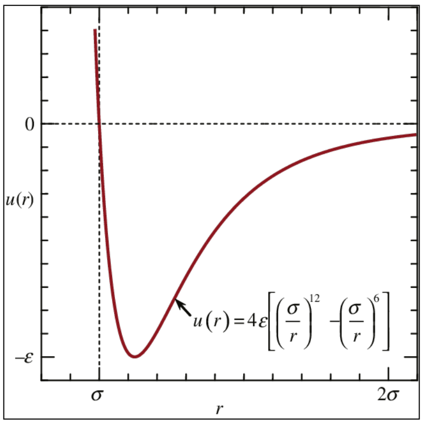

Figure 1: Weeks-Chandler-Andersen (WCA) potential

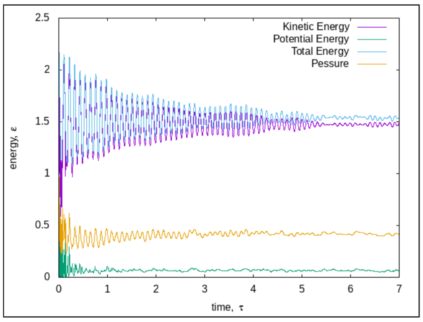

Figure 2: System Energy vs Time

0.3 Static Structure Factor and Isothermal Compressibility :

The system obtained using molecular dynamic method has been implemented to interpret static structure factor and later Isothermal compressibility. In this work, the wave vector component $k_x = k_y = k_z = 30\Delta k$ where $\Delta k = \frac{2\pi}{L}$ and $L = (\frac{N_{part}}{density})^{\frac{1}{3}}$. All the combination of K's components is considered but $k_x = k_y = k_z = 0$. For the same absolute value of $\mathbf{k}$ the corresponding $S(\mathbf{k})$ is accounted in the bin $(k + dk) = (k + \Delta k)$ and later has been averaged by the corresponding number stored in k-bin. Finally, the program, with a constant particle density, for interpreting Static Structure Factor has been run and averaged over the last 5 position space data obtained from MD method at the time steps $(6.9980\tau, 6.9985\tau, 6.9990\tau, 6.9995\tau, 7.0\tau)$. In figure-3 the plot is shown for five different density $(0.1,\ 0.2,\ 0.3,\ 0.4,\ 0.5)\sigma^3$. To calculate Isothermal Compressibility (τ) from equation(2) it is essential to extrapolate the static structure factor at k=0. So, using the taylor series and Symmerty of Static factor

$$S(\Delta k) = S(0) + \frac{\Delta k^2}{2}\alpha + \frac{\Delta k^4}{4}\beta$$

and

$$\kappa = \frac{\lim_{k\to 0} S(k)}{\rho K_B T}$$

Where

$$\alpha = \frac{d^2 S}{dk^2} and \beta = \frac{d^4 S}{dk^4}$$

The obtained Isothermal Compressibility for different density is shown in figure-4. It is clear from figure that $\kappa = 18.9455$ at $\rho = 0.1, \kappa = 3.98956$ at $\rho = 0.2, \kappa = 1.48044$ at $\rho = 0.3, \kappa = 0.937772$ at $\rho = 0.4, \kappa = 0.731694$ at $\rho = 0.5$. And the magnitude of κ is decreasing with increasing density.

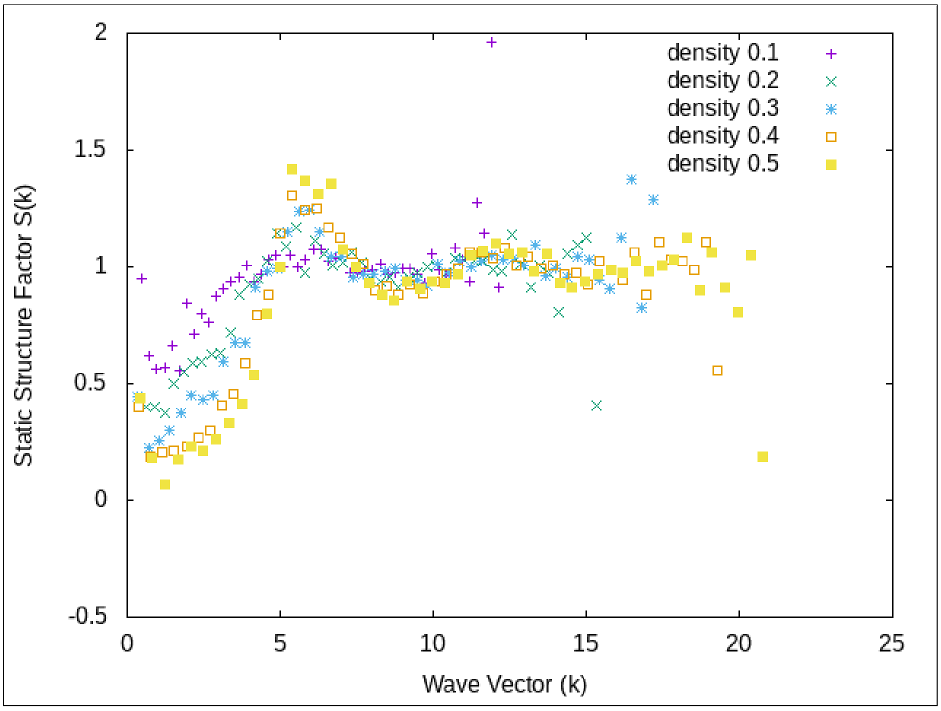

Figure 3: evaluation of Static Factor from wavevector, k

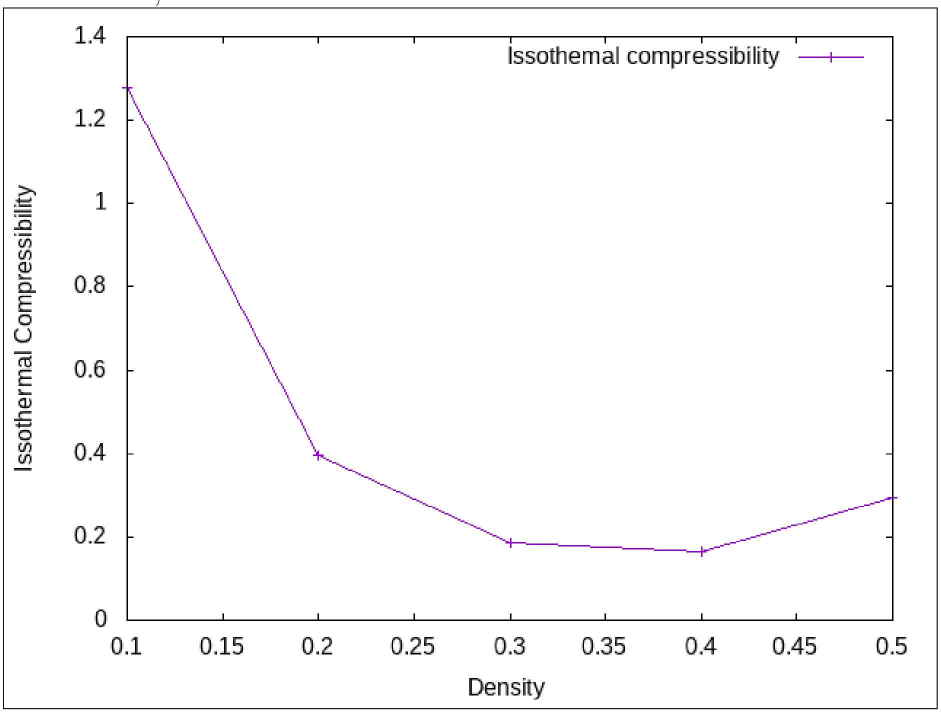

Figure 4: Isothermal Compressibility

0.4 Reference :

1. kai Zhang, On the Concept of Static Structure Factor.
2. J. Horbach, Lecture note