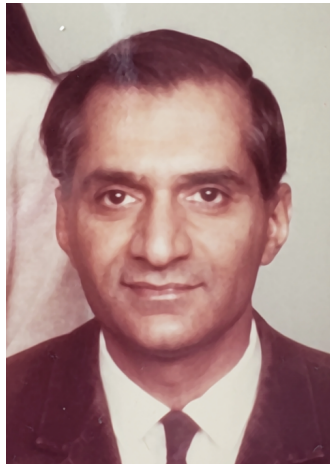
Course 04/1

Molecular dynamics of Lennard-Jones liquid

- Rahman's simulation
- Liquid argon
- Set-up of the simulation
- Lennard-Jones interaction
- Equilibration

Rahman's simulation



Aneesur Rahman
1927-1987

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Correlations in the Motion of Atoms in Liquid Argon*

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(Received 6 May 1964)

A system of 864 particles interacting with a Lennard-Jones potential and obeying classical equations of motion has been studied on a digital computer (CDC 3600) to simulate molecular dynamics in liquid argon at 94.4°K and a density of 1.374 g cm^{-3}. The pair-correlation function and the constant of self-diffusion are found to agree well with experiment; the latter is 15% lower than the experimental value. The spectrum of the velocity autocorrelation function shows a broad maximum in the frequency region $\omega=0.25(k_BT/\hbar)$. The shape of the Van Hove function $G_s(r,t)$ attains a maximum departure from a Gaussian at about $t=3.0\times10^{-12}$ sec and becomes a Gaussian again at about 10^{-11} sec. The Van Hove function $G_d(r,t)$ has been compared with the convolution approximation of Vineyard, showing that this approximation gives a too rapid decay of $G_d(r,t)$ with time. A delayed-convolution approximation has been suggested which gives a better fit with $G_d(r,t)$; this delayed convolution makes $G_d(r,t)$ decay as t^4 at short times and as t at long times.

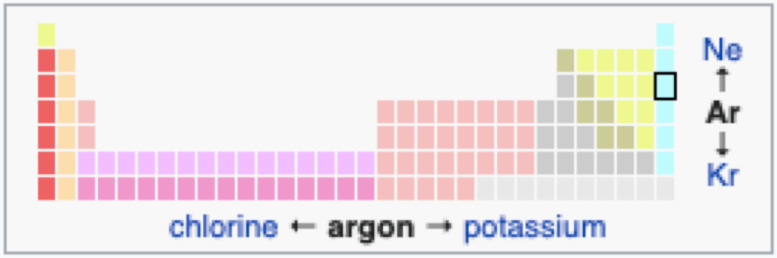
Liquid argon

18

Ar

ARGON

Argon in the periodic table



Atomic number (*Z*)	18
Group	group 18 (noble gases)
Period	period 3
Block	p-block
Element category	Noble gas
Electron configuration	[Ne] $3s^2\ 3p^6$
Electrons per shell	2, 8, 8

Melting point	83.81 K

Density from experimental data

PRESSURE		TEMPERATURE		DENSITY	
BAR	KP/CM^2	KELVIN	CELSIUS	GRAM-MOLE/ CM^3	KG/ DM^3
1.000	1.020	87.160	-185.990	0.034912	1.3947
1.013	1.033	87.284	-185.866	0.034893	1.3939
1.092	1.114	88.000	-185.150	0.034784	1.3896
1.110	1.131	88.150	-185.000	0.034761	1.3886
1.200	1.224	88.911	-184.239	0.034644	1.3839
1.211	1.235	89.000	-184.150	0.034630	1.3834
1.229	1.254	89.150	-184.000	0.034607	1.3825
1.339	1.365	90.000	-183.150	0.034474	1.3772
1.359	1.386	90.150	-183.000	0.034451	1.3762
1.400	1.428	90.452	-182.698	0.034403	1.3743
1.477	1.506	91.000	-182.150	0.034317	1.3709
1.498	1.528	91.150	-182.000	0.034293	1.3699
1.600	1.632	91.834	-181.316	0.034185	1.3656
1.625	1.657	92.000	-181.150	0.034158	1.3645
1.649	1.681	92.150	-181.000	0.034134	1.3636
1.785	1.820	93.000	-180.150	0.033998	1.3581
1.800	1.835	93.091	-180.059	0.033983	1.3576
1.810	1.846	93.150	-180.000	0.033974	1.3572
1.956	1.995	94.000	-179.150	0.033836	1.3517

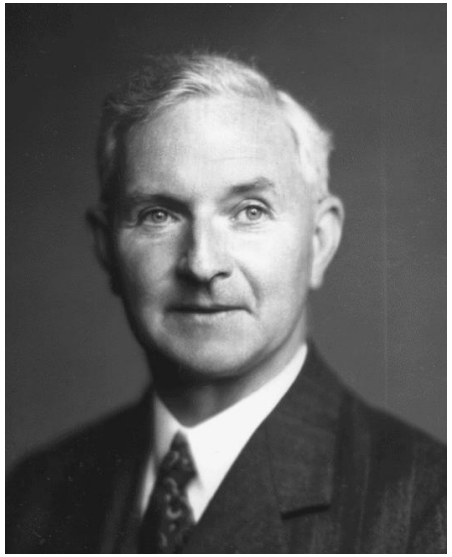
https://nvlpubs.nist.gov/nistpubs/Legacy/TN/nbstechnicalnote361r1.pdf

Set-up of the simulation

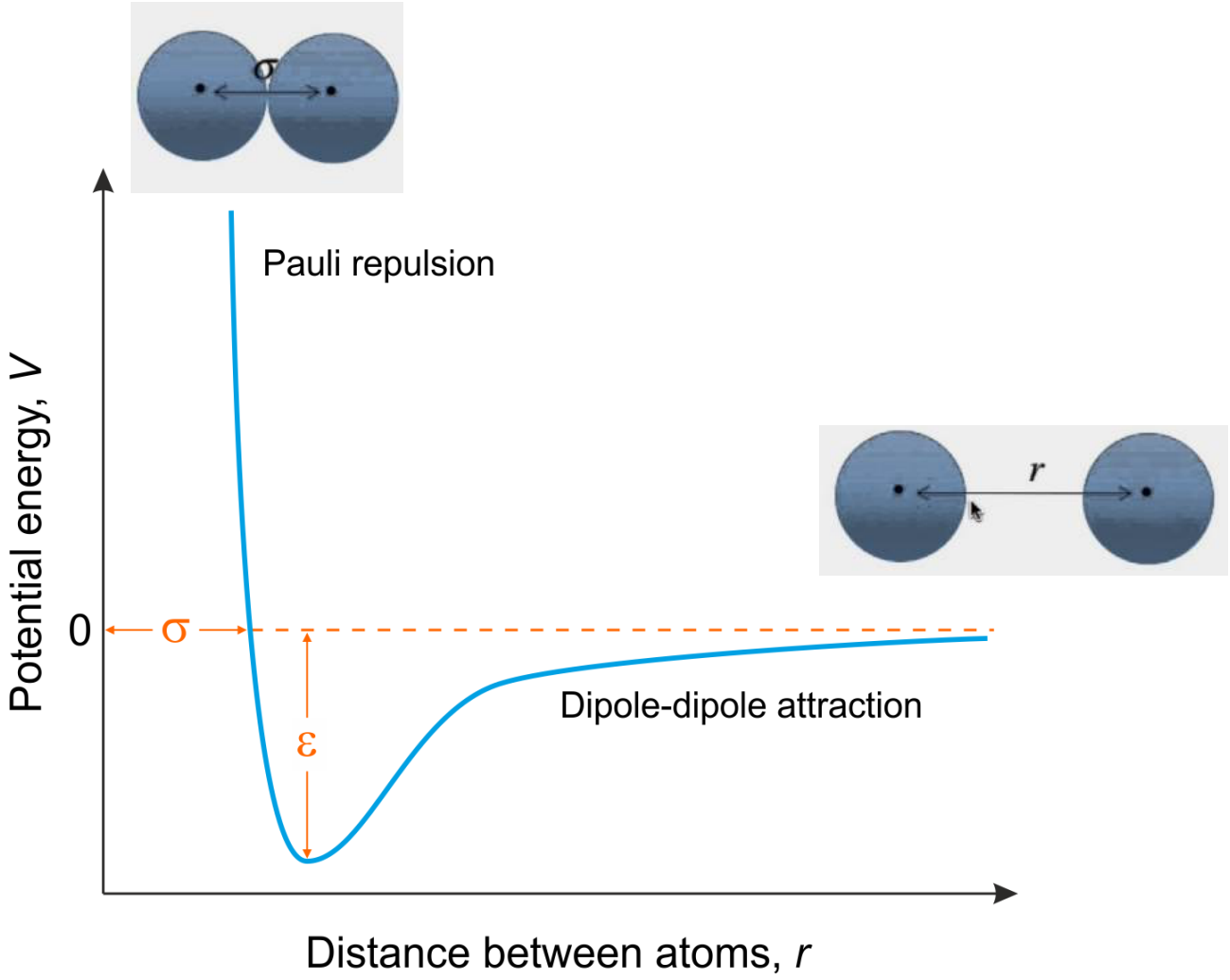
- Number of particles: $N = 864$
- Volume: cubic simulation cell with side $L = 34.8$ Å to achieve the experimental density of 1.374 g/cm^3.
- Microcanonical simulation with conserved energy with fixed volume and fixed number of particles: *NVE* simulation.
- Periodic boundary conditions
- Initialization with random positions
- Predictor-corrector integration algorithm with time step of $\Delta t = 0.01$ ps

Lennard-Jones interactions

$$U^{\mathrm{LJ}}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$



John Lennard-Jones
1894-1956



Potential energy for liquid argon

Pair interaction potential

$$U = \sum_{I<J} U_{IJ} = \sum_{I<J} U^{\mathrm{LJ}}(|r_I - r_J|)$$

$$U^{\mathrm{LJ}}(r) = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right] \qquad \varepsilon / k_{\mathrm{B}} = 120\ \mathrm{K}, \quad \sigma = 3.4\ \text{Å}$$

Atomic forces

$$F_{I\alpha} = -\frac{\partial U}{\partial r_{I\alpha}} = \sum_{J \neq I} \left. \frac{\partial U_{IJ}}{\partial r} \right|_{r_{IJ} = |\vec{r}_I - \vec{r}_J|} \cdot \frac{\partial |\vec{r}_I - \vec{r}_J|}{\partial r_{I\alpha}}$$

$$= \sum_{J \neq I} 4\varepsilon \left[\frac{12}{r_{IJ}} \left(\frac{\sigma}{r_{IJ}}\right)^{12} - \frac{6}{r_{IJ}} \left(\frac{\sigma}{r_{IJ}}\right)^{6} \right] \frac{r_{I\alpha} - r_{J\alpha}}{r_{IJ}}$$

Cutoff-radius

$r_c = 2.25\ \sigma = 7.65$ Å (**NB** $L = 34.8$ Å)

Equilibration

Equipartition theorem

$$\langle E_{kin} \rangle = f \cdot \frac{kT}{2}$$

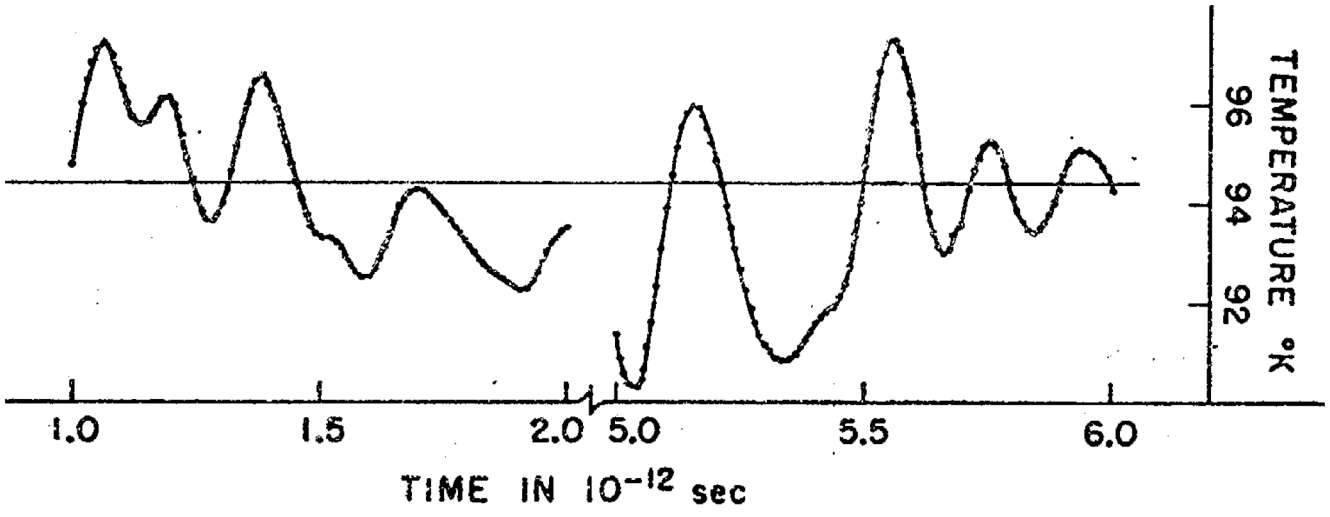
where $f = 3N$ is the number of degrees of freedom

Instantaneous and average temperature

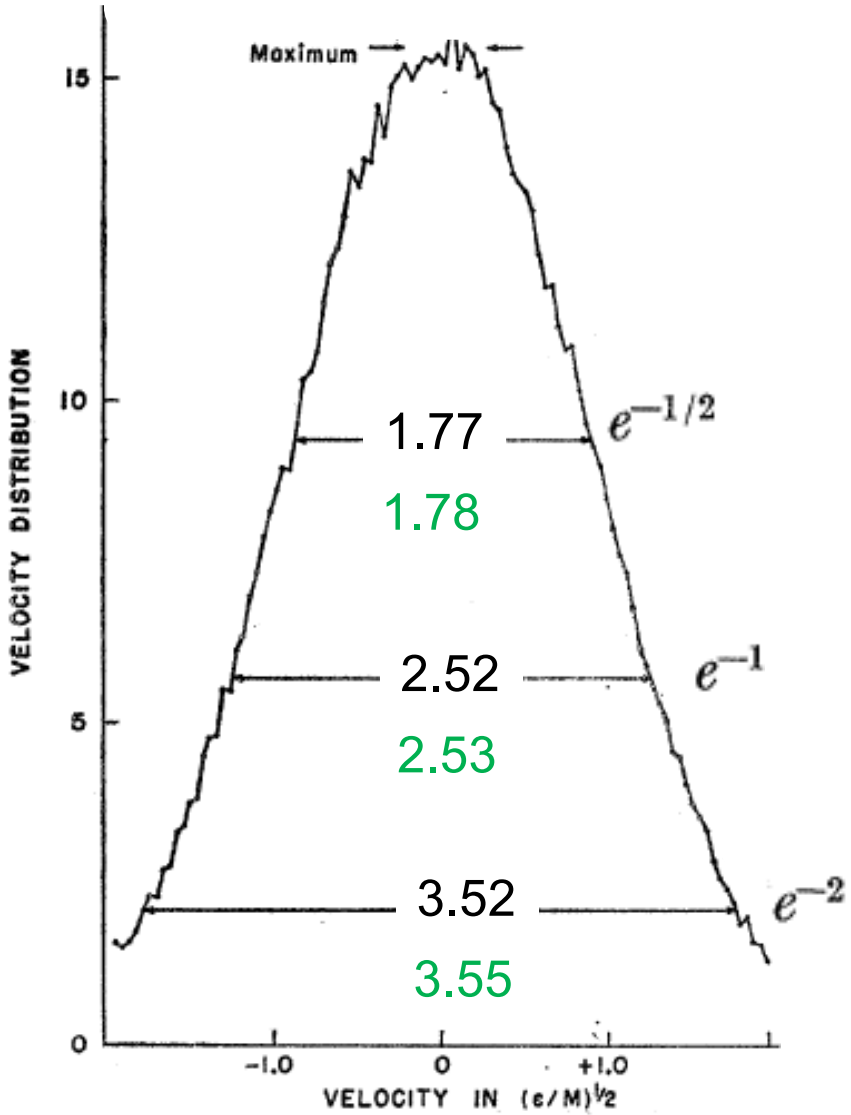
$$kT_{inst} = \frac{2\,E_{kin}}{f}$$

where $$E_{kin} = \sum_{l=1}^{N} \tfrac{1}{2}\, m v_l^{\,2}$$

$$3N \cdot \frac{kT}{2} = \langle E_{kin} \rangle$$



Velocity distribution at equilibrium



Close to the expected Gaussian of the Maxwellian distribution at 94.4 K.

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