Numerical study of thermodynamics and structure of small clusters in dense gold vapor using EAM potential

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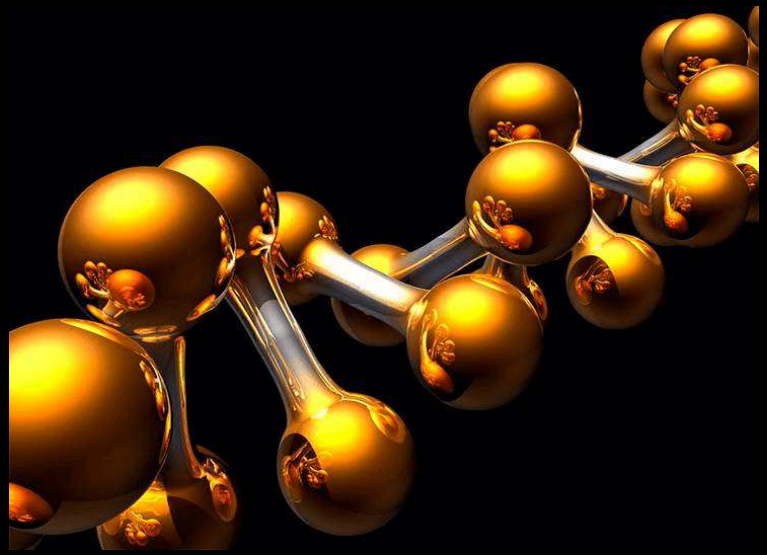
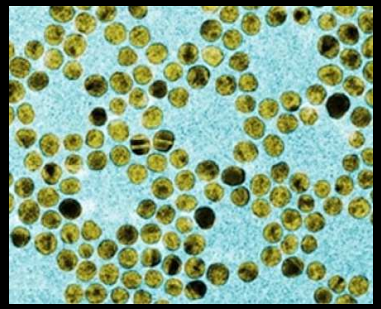
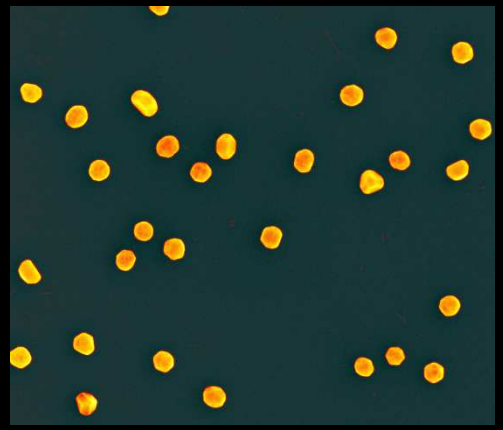
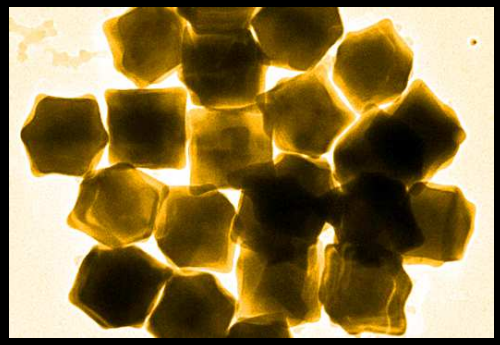
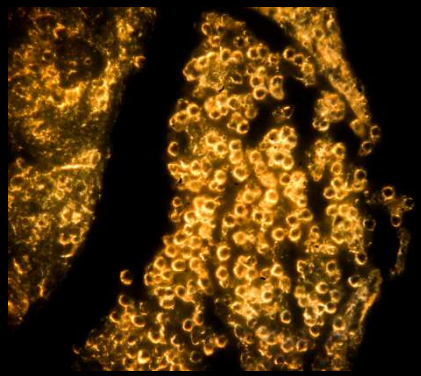
Gold nanoparticles

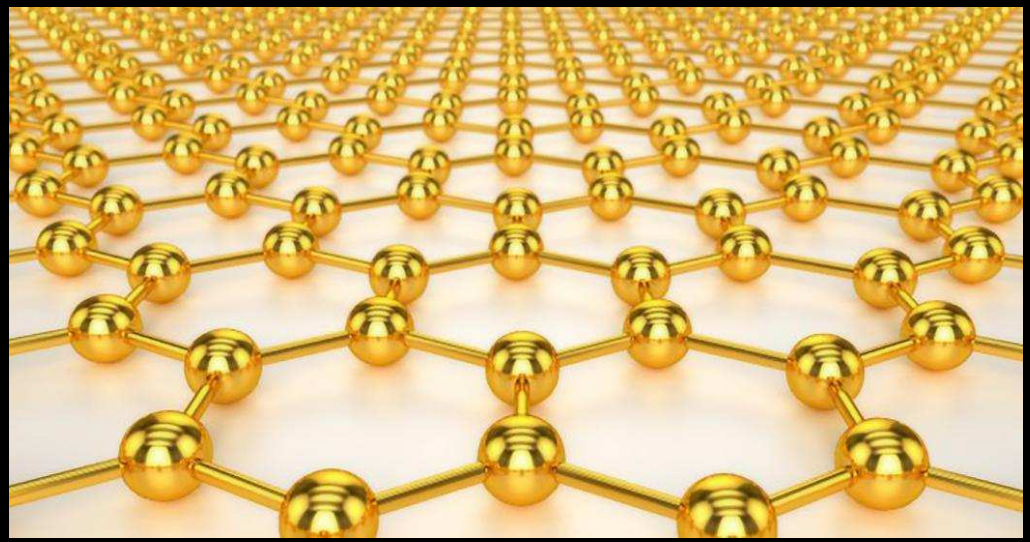


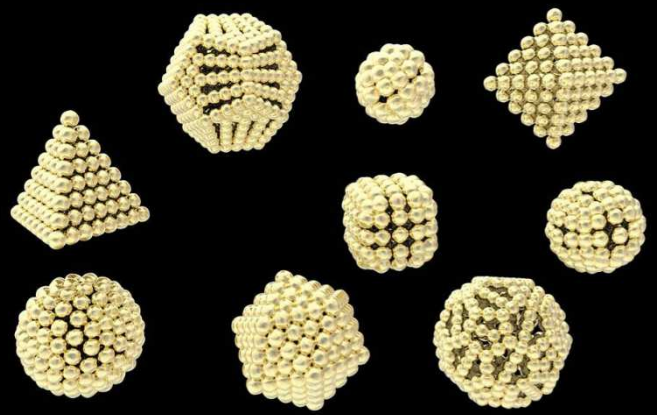












MD simulation with EAM potential

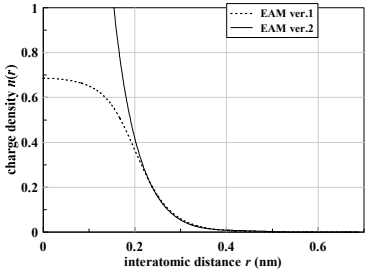
The common form of EAM potential has the form

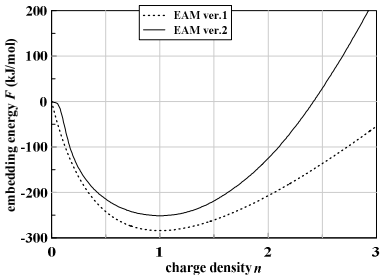
$$E_{\text{tot}} = \sum_i F(\overline{n}_i) + \sum_{i<j} V(r_{ij}), \qquad \overline{n}_i = \sum_{i \neq j} n(r_{ij}),$$

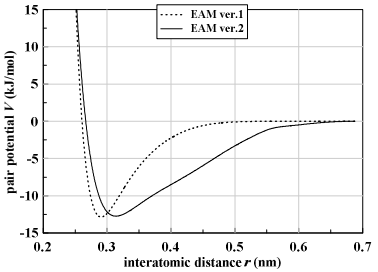
$$n(r) = \sum_{m=1}^{10} a_m (r_c^2 - r^2)^{m+2} \left[1 + \sum_{m=1}^{10} b_m (r_c^2 - r^2)^m \right]^{-1},$$

$$F(n) = \frac{\sum_{m=2}^{11} c_m \left[(n-1)^m - (-1)^m \right]}{1 + \sum_{m=2}^{11} d_m \left[(n-1)^m - (-1)^m \right]},$$

$$V(r) = v_1 \left(r_0^{-2} - r^{-2} \right) \left(r_c^2 - r^2 \right)^{12} \left[\left(r_c^2 - r^2 \right)^6 + v_2 r^6 \right] + \sum_{m=1}^{8} \frac{e_m \left(r_c^2 - r^2 \right)^{m+2}}{1 + \sum_{m=1}^{8} f_m \left(r_c^2 - r^2 \right)^m}.$$







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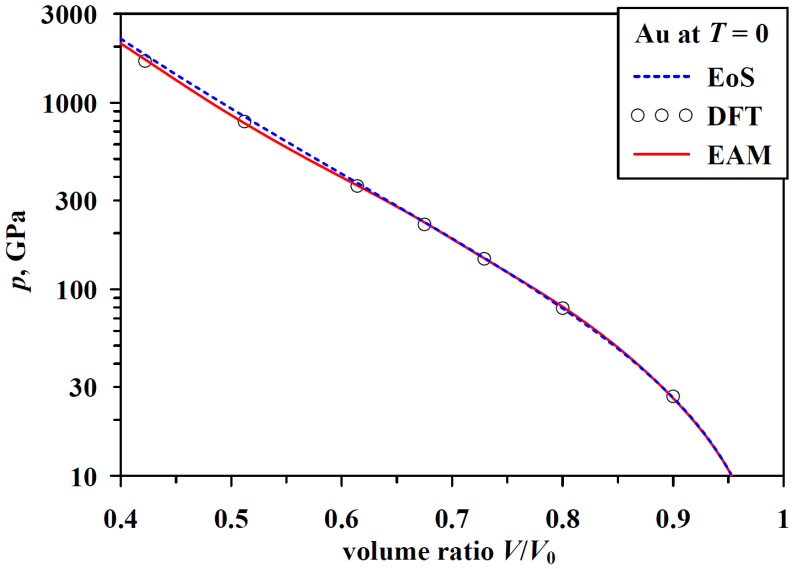


FIG. 1. Cold pressure curves for gold under compression from EAM potential (red line) and from the semi-empirical EoS[4] (blue dashed line). Circles show DFT data.

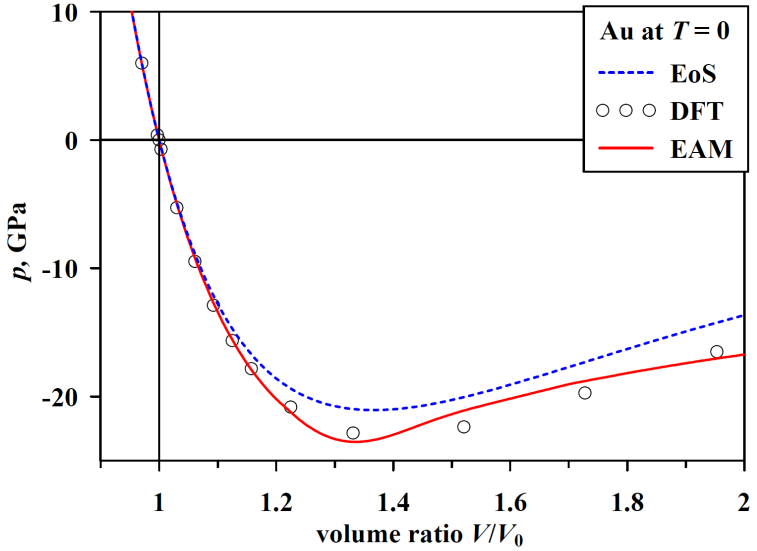


FIG. 2. Cold pressure curves for gold under stretching from EAM potential (red line) and from the semi-empirical EoS[4] (blue dashed line). Circles show DFT data.

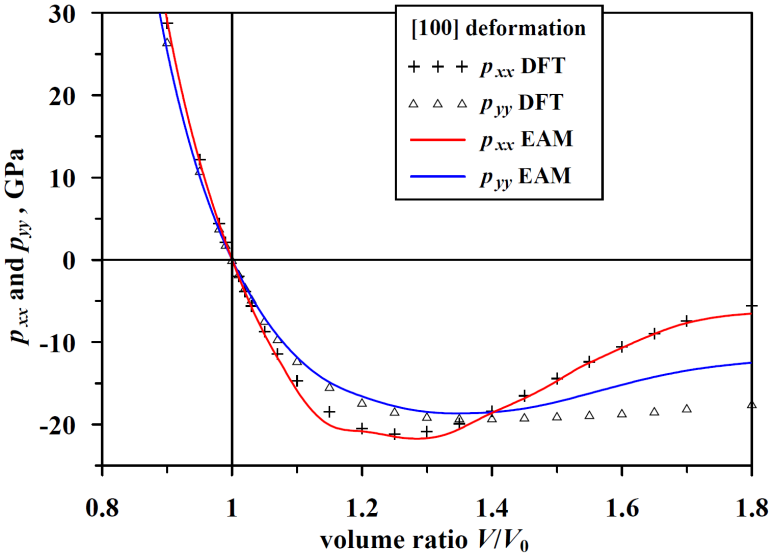


FIG. 3. Components p_{xx} and p_{yy} of the pressure tensor for gold under uniaxial deformation along the axis $x = [100]$ from EAM potential and from DFT calculations.

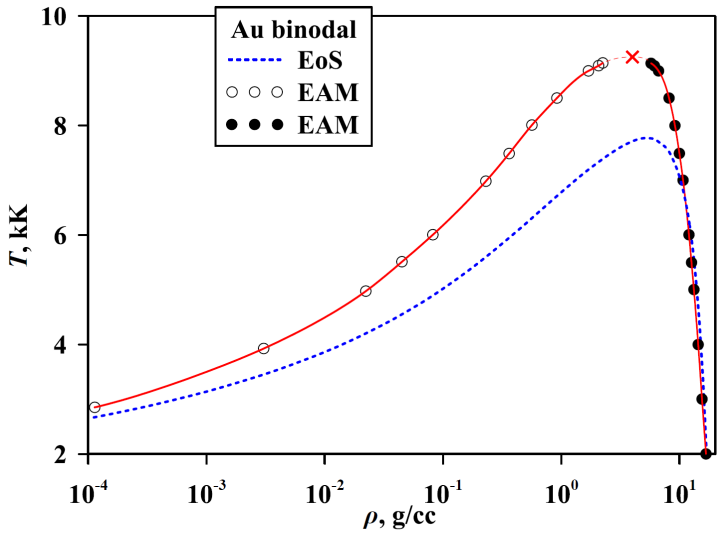


FIG. 4. Liquid–vapor binodal line for gold in $T - \rho$ phase plane. Open circles correspond to the vapor and solid circles, to the liquid coexistence state obtained from MD simulation. Blue dashed line shows data from the wide-range EoS.[14] Red cross denotes the critical point at $\rho_{cr} \approx 3.99$ g/cc and $T_{cr} \approx 9.25$ kK.

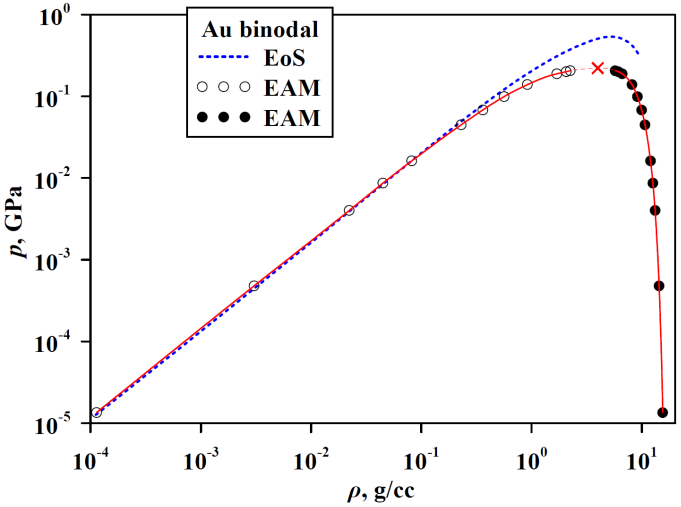


FIG. 5. Liquid–vapor binodal line for gold in $p-\rho$ phase plane. Open circles correspond to the vapor and solid circles, to the liquid state obtained from MD simulation. Blue dashed line shows data from the wide-range EoS.[14] Red cross denotes the critical point at $\rho_{cr} \approx 3.99$ g/cc and $p_{cr} \approx 0.22$ GPa.

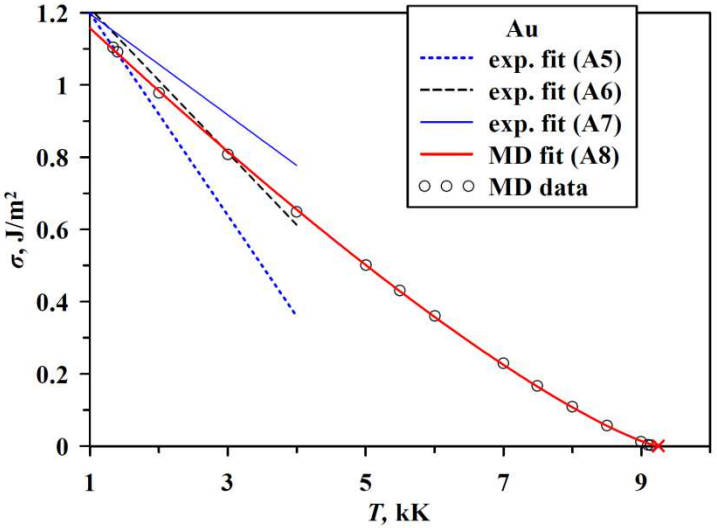


FIG. 7. Surface tension of a flat liquid–vapor interface as a function of temperature from MD simulation (circles) and its approximation by Eq. 8 using the critical index dependence (red line). The experimental fits are presented by Eqs. 5, 6, and 7. The phase separation vanishes at the critical temperature $T_{cr} \approx 9.25$ kK.

TABLE I. EAM binding energies per atom of Au_n clusters (eV) vs. three variants of DFT calculations for various atom configurations. DFT-TPSS and DFT-PBE are obtained from the linear approximations[13] extrapolated to a wide size range (but for n = 55 and 147). For DFT-FSGB, the lowest-energy isomers are presented.

n	EAM	DFT-TPSS[13]	DFT-PBE[13]	DFT-FSGB[7]	Experiment
2	1.126	1.318	1.303		1.15
3	1.594[a]	1.567	1.506	1.66	
4	1.900[b]	1.724	1.635	2.12	
5	2.061	1.836	1.726	2.28	
6	2.210[c]	1.921	1.796	2.56	
13	2.671[d]	2.231	2.050	2.96	
38	3.060[e]	2.548	2.310		
55	3.159[f]	2.632[f]	2.378[f]		
98	3.296[g]	2.748	2.473		
147	3.381[f]	2.818[f]	2.532[f]		
∞	3.970[h]	3.285	2.913		3.81

[a] triangle
[b] tetrahedron
[c] octahedron
[d] icosahedron
[e] octahedra
[f] icosahedra
[g] tetrahedra
[h] fcc

TABLE I. MD simulation parameters: temperature T, pressure p, total atom number density n, number of atoms N_a, cubic box dimension, and simulation time $t_{\rm sim}$

T, K	p, MPa	n, nm^{-3}	N_a	L_x, nm	$t_{\rm sim}$, ns
4006	0.465	0.00897	415292	359	86.6
5005	3.899	0.0649	530604	201	68.6
6004	16.16	0.250	442368	121	68.9

MD simulation procedure

All MD simulations are performed with our in-house parallel code MD-VD^3 utilizing the Voronoi dynamic domain decomposition.[29,30] Atoms of the gas are placed in the MD cubic box with the dimensions $L_x = L_y = L_z$, and the periodic boundary conditions are imposed along all three dimensions. Initially a single crystal sample with the gas density a few percents less than the equilibrium vapor density on the liquid–vapor binodal line $T_s(\rho)$ at a given temperature is generated to ensure that this gas is not supersaturated.

Then this sample is thermalized at the chosen temperature using the Langevin thermostat during a time long enough to reach an almost equilibrium state. At the next stage, the NVE simulation without thermostat is performed until the equilibrium cluster distribution is established. During this stage, the temperature grows slowly by a few degrees while the potential energy drifts down till it reaches a plateau. After this stage, the final production simulations are performed during several tens of nanoseconds with the gas parameters listed in Table I. During the simulation time t_{sim}, all atom coordinates and momenta are saved each 19.2 ps for further cluster analysis. Such time frame separation is sufficiently long to ensure statistical independence of the saved data for each atom.

We have analyzed about 3000 time frames for each set of the state parameters corresponding to three temperatures.

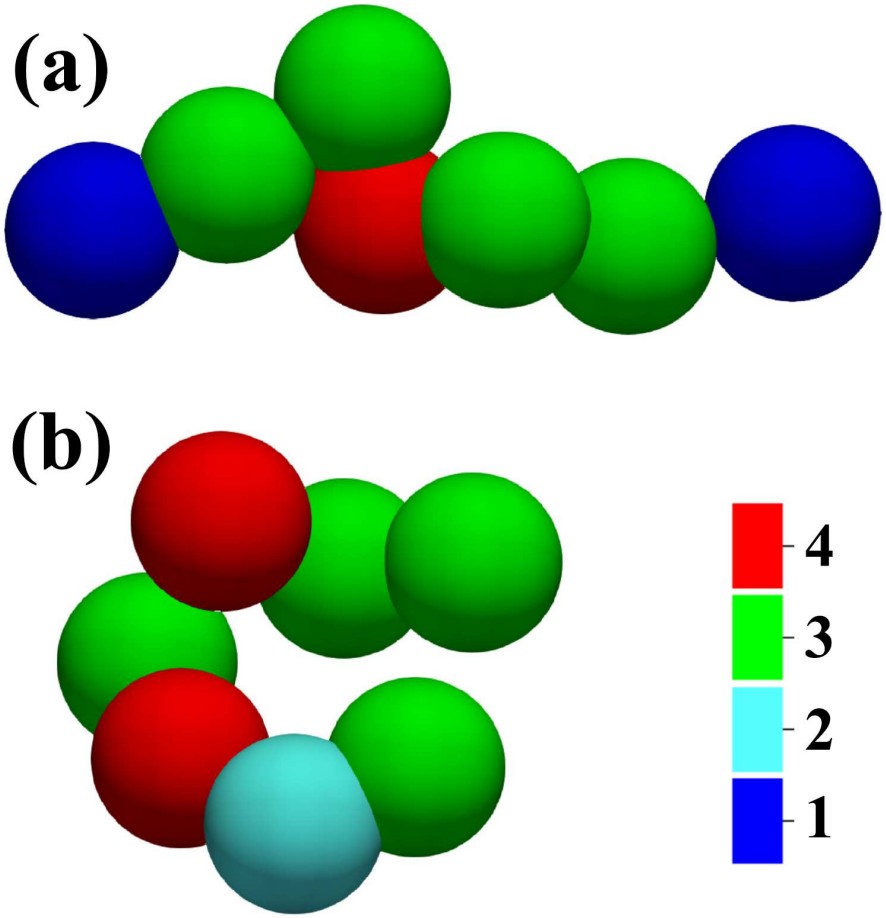


FIG. 1. Typical configurations of the lighter clusters ($k = 7$) at $T =$ 6004 K in (a) the chain-like and (b) the solid-like states. The atom coordination number is color-coded (see legend). The circle diameter is 0.287 nm.

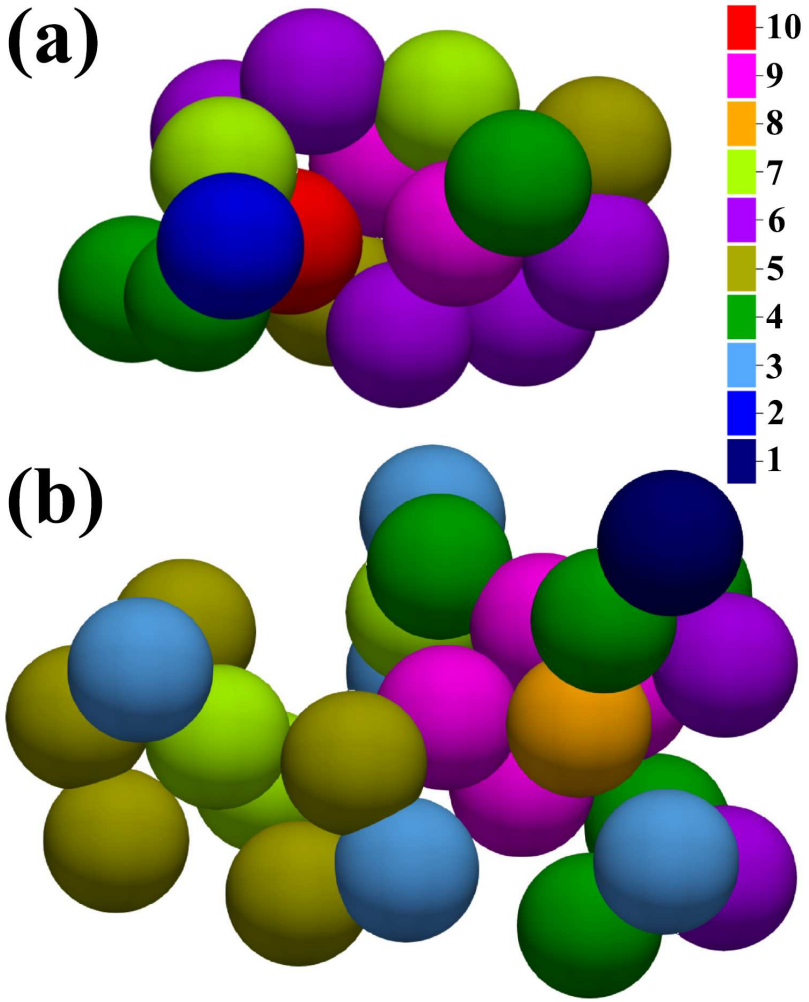
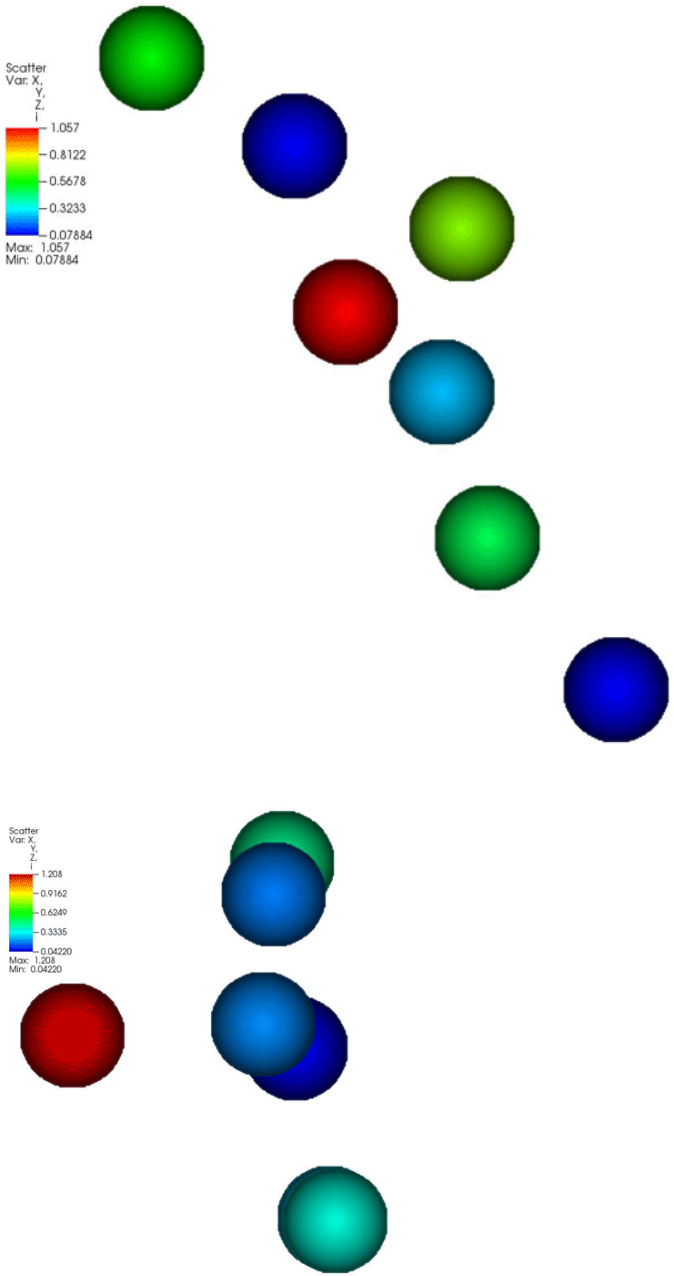


FIG. 2. Typical configurations of the heavier clusters at $T = 6004$ K, (a) $k = 16$ and (b) $k = 26$. The atom coordination number is color-coded (see legend). The circle diameter is 0.287 nm.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0.3233
0.07884
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Min: 0.07884

Scatter
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Z,
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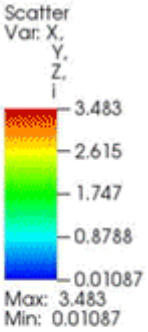
Min: 0.04220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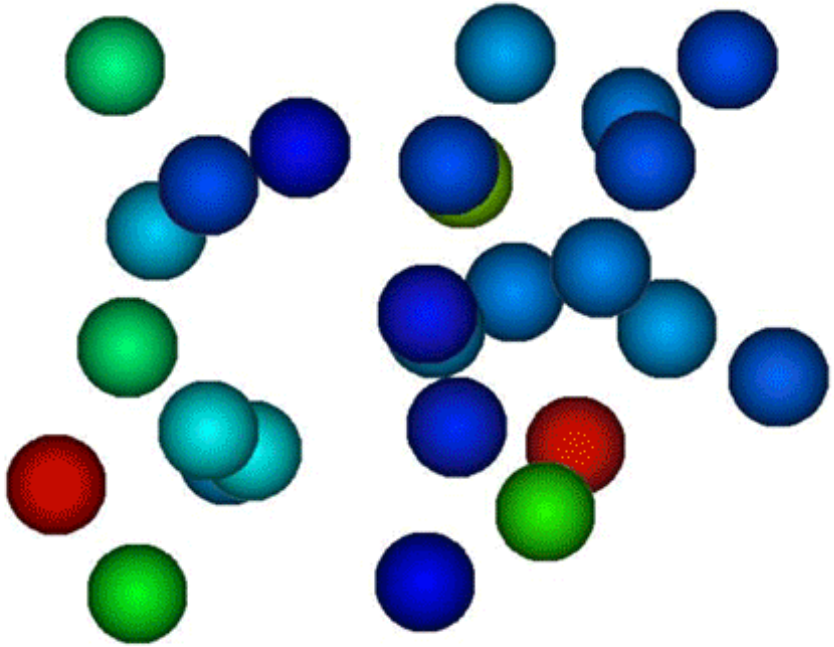
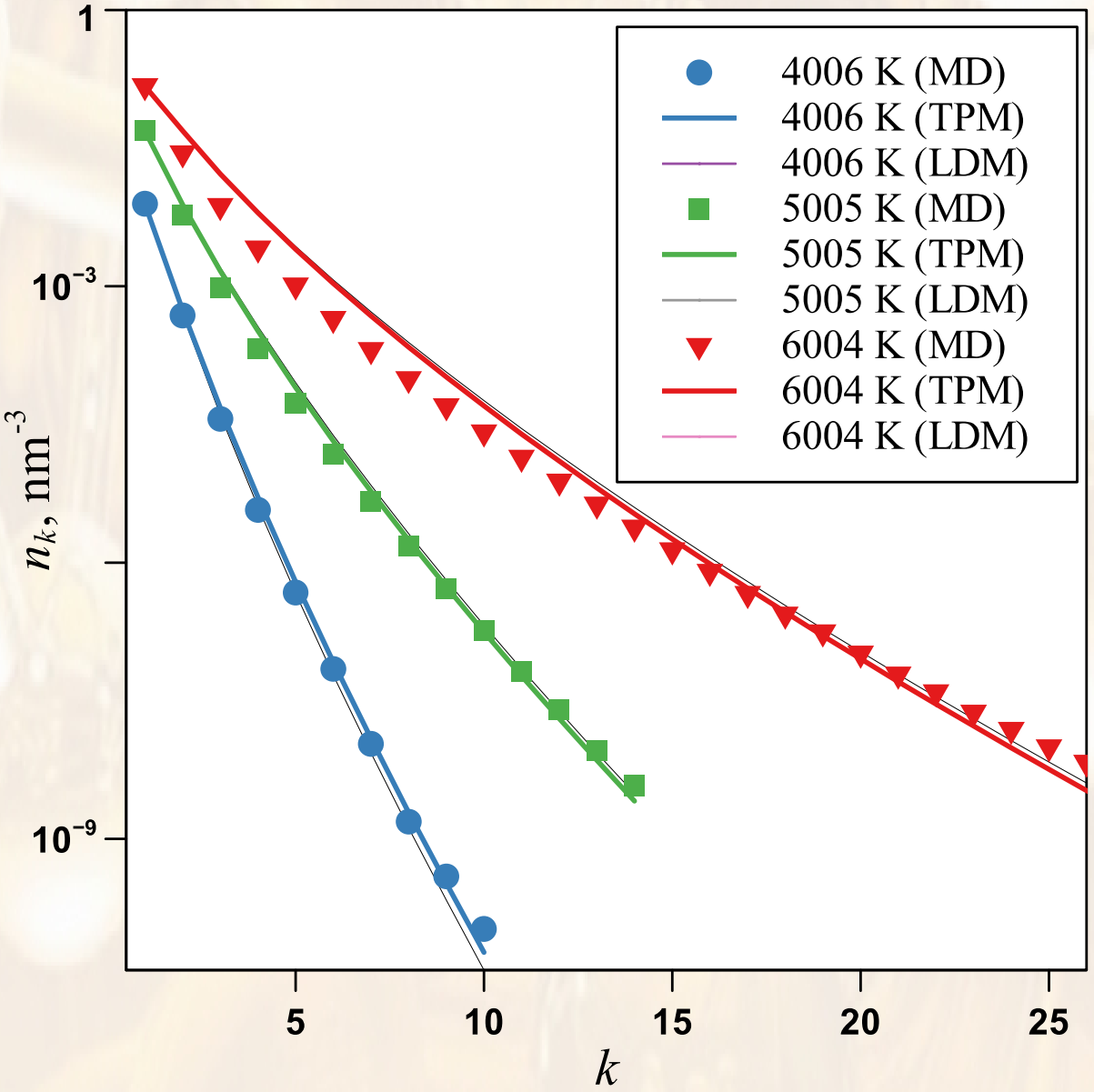
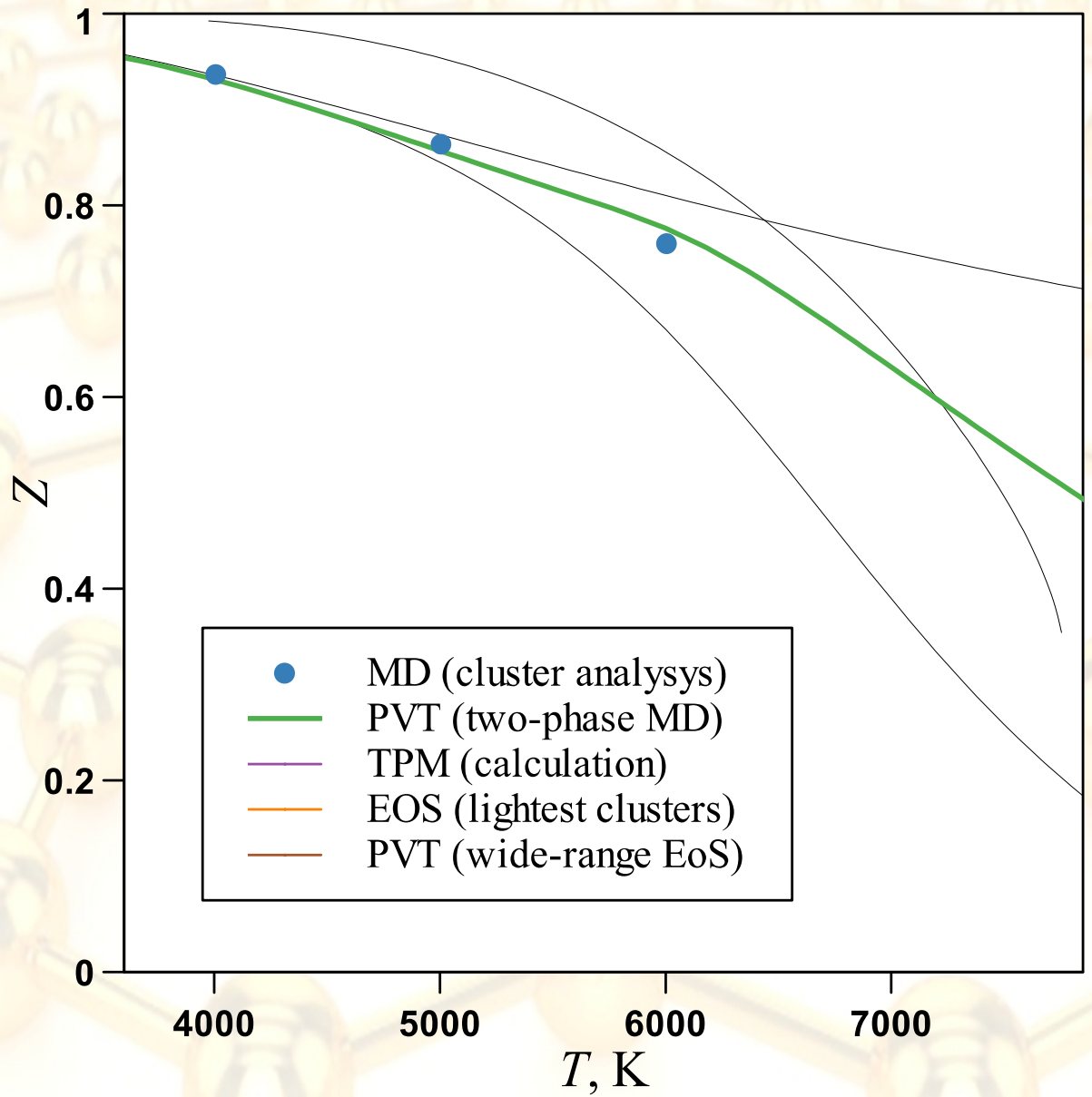


Cluster number density vs. cluster size



Compressibility factor of gold vapor at saturation



Cluster size distribution and the Tolman length

In the virtual chain approximation, the partition function of a "hot" cluster of atoms interacting via the pair additive potential is represented as

$$Z_c^{(k)} = \frac{1}{\lambda^{3k}} \int \cdots \int{}' \exp\left[-\frac{U(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_k)}{T}\right] d\mathbf{r}_1 \ldots d\mathbf{r}_k \simeq \frac{V}{\lambda^{3k}} \left[Z_2 \exp\left(-\frac{D}{T}\right)\right]^{k-1},$$

$$Z_2 = \exp\left(\frac{D}{T}\right) \int{}' \exp\left[-\frac{u(r_1)}{T}\right] d\mathbf{r}_1. \quad \text{Thus,} \quad \mu_k = T \ln p_k + A(T)k + B(T),$$

and the size distribution of the lightest clusters is

$$n_k = n_1 \exp\left(-\frac{\Delta\Phi_k}{T}\right), \Delta\Phi_k = (1-k)T\left(\ln\frac{n_{1s}}{K_2} + \ln S\right), K_2(T) \equiv \frac{n_1^2}{n_2} = \frac{1}{\lambda^3 Z_2} \exp\left(-\frac{D}{T}\right).$$

The case of the lightest clusters and of a macroscopic droplet are unified by a linear interpolation of the cluster chemical potential. Then

$$\Delta\Phi_k = 4\pi\sigma r_\ell^2 \gamma(k) k^{2/3} - (k-1)T \ln S, \quad \gamma = (2/3)(\lambda + 2\delta)^{-1}(k_0 - 1)k^{-2/3},$$

where $k_0 = \frac{1}{2}(\lambda + 2\delta)\left[3(k-k_0)^{2/3} + 3\lambda(k-k_0)^{1/3} + \lambda^2\right]$ is the number of surface atoms. The parameters δ (reduced Tolman length) and λ and define the two-parameter model. They conform to the relationship that ensures correct microscopic and macroscopic extremes so that only one parameter remains (δ):

$$\delta + \frac{\lambda}{2} = -\frac{4\pi}{3}\frac{\sigma r_\ell^2}{T \ln \frac{n_{1s}}{K_2}} \quad \text{(cluster invariant)}.$$

If $k \le k_{\min} = \max\left\{(\lambda^2/2)(\lambda + 2\delta), 2\right\}$ then $k_0 = k$ (no internal atoms).

For the argon-like system, $k_{\min} \sim 10$; for metals, $k_{\min} \sim 1$.

In the widely used self-consistent classical nucleation theory with the Tolman correction

$$\Delta\Phi_k = 4\pi\sigma r_\ell^2 \overline{\gamma}(k) k^{2/3} - (k-1)T \ln S, \quad \overline{\gamma}(k) = k^{-2/3}(k^{2/3} - 1)(1 - 2\delta k^{-1/3}).$$

For a macroscopic drop, both approaches are identical if

$$\frac{5}{4}\lambda^2 = 12\delta^2 + \frac{2}{\lambda + 2\delta}.$$

Vapor compressibility factor (ideal mixture of clusters)

$$Z = \sum_{k=1}^{\infty} n_k \left(\sum_{k=1}^{\infty} k n_k \right)^{-1} = \left[\sum_{k=1}^{\infty} S^{k-1} \left(\frac{p_{1s}}{K_2} \right)^{k_0(k)-1} \right] \left[\sum_{k=1}^{\infty} k S^{k-1} \left(\frac{p_{1s}}{K_2} \right)^{k_0(k)-1} \right]^{-1},$$

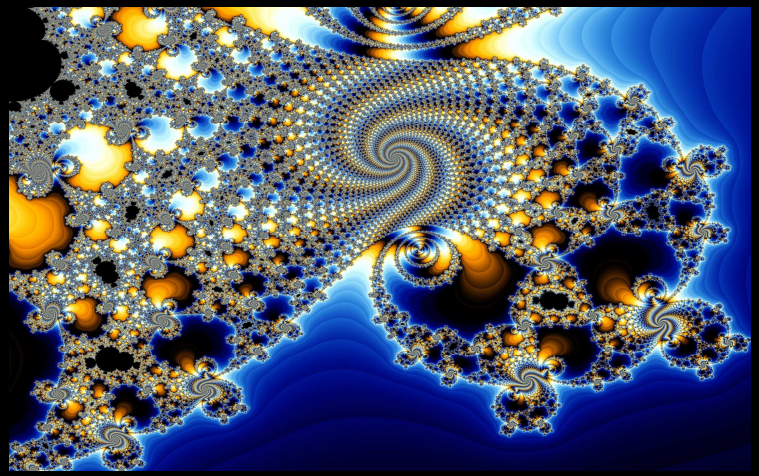
$$p_{1s} = \frac{T \rho_s}{M} \left[\sum_{k=1}^{\infty} k \left(\frac{p_{1s}}{K_2} \right)^{k_0(k)-1} \right]^{-1}.$$

For a rarefied vapor, $Z \simeq \dfrac{1}{1 + p K_2^{-1}}$.

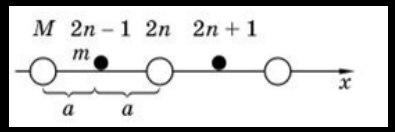
TABLE II. Reduced parameters δ and λ and the ratio S for gold vapor at different temperatures T from MD simulation.

T, K	δ	λ	S
4006	0.1675	1.0877	0.9576
5005	0.1335	0.9517	0.9910
6004	0.1317	0.7125	1.000

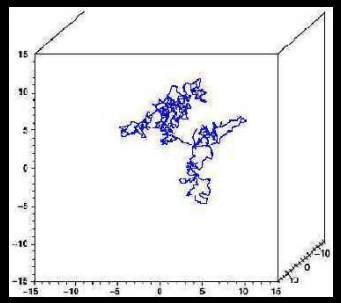
Fractals and fractal dimensionality



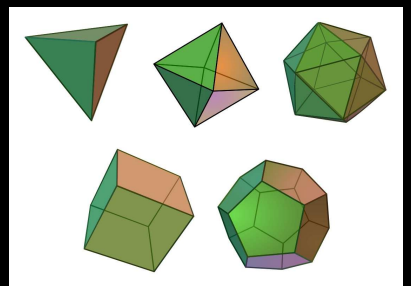
$$D_f = \lim_{r \to \infty} \frac{d \ln N_D}{d \ln r}$$



$D_f = 1$ (linear molecule)

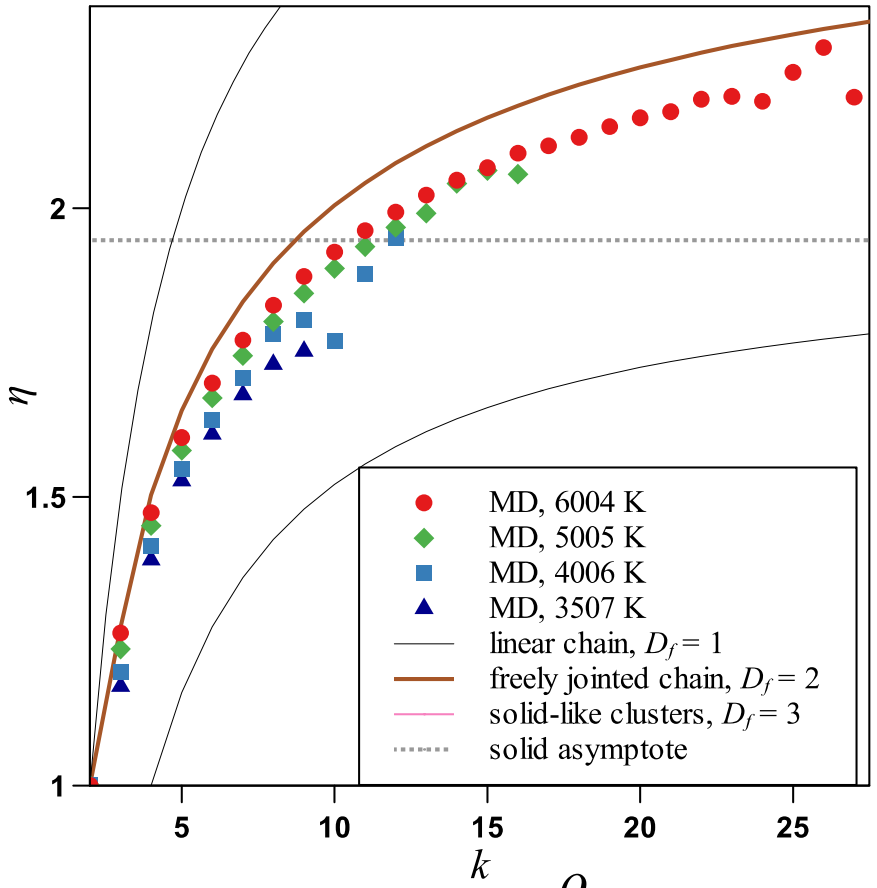


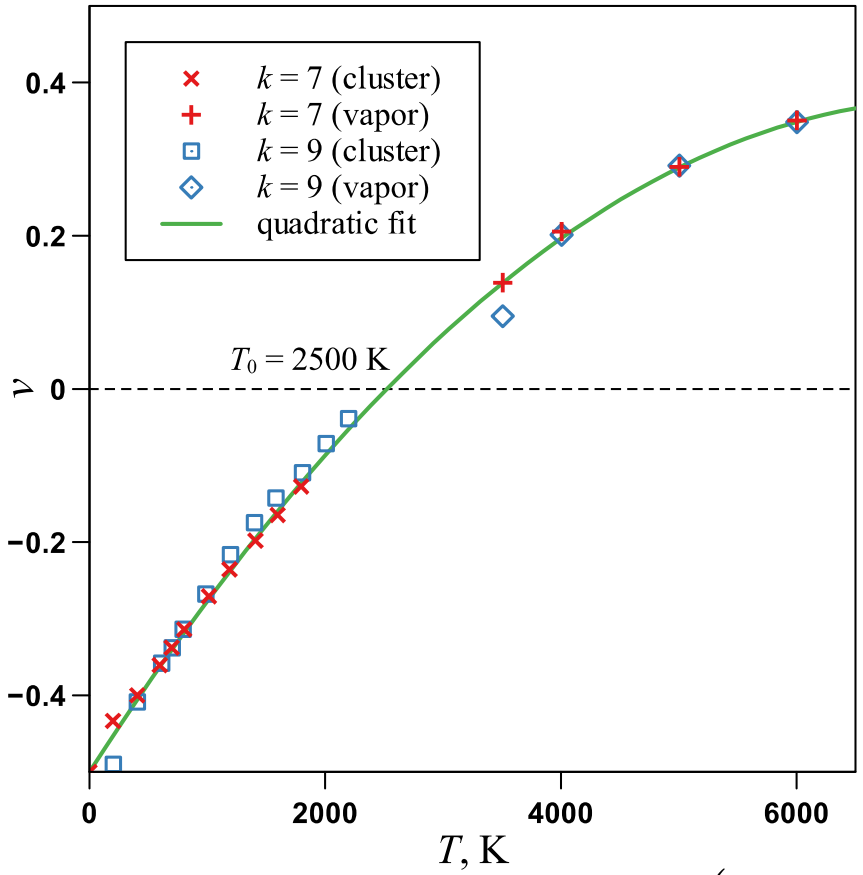
$D_f = 2$ (freely jointed chain)



$D_f = 3$ (solid)

Cluster structure and reduced structure parameter

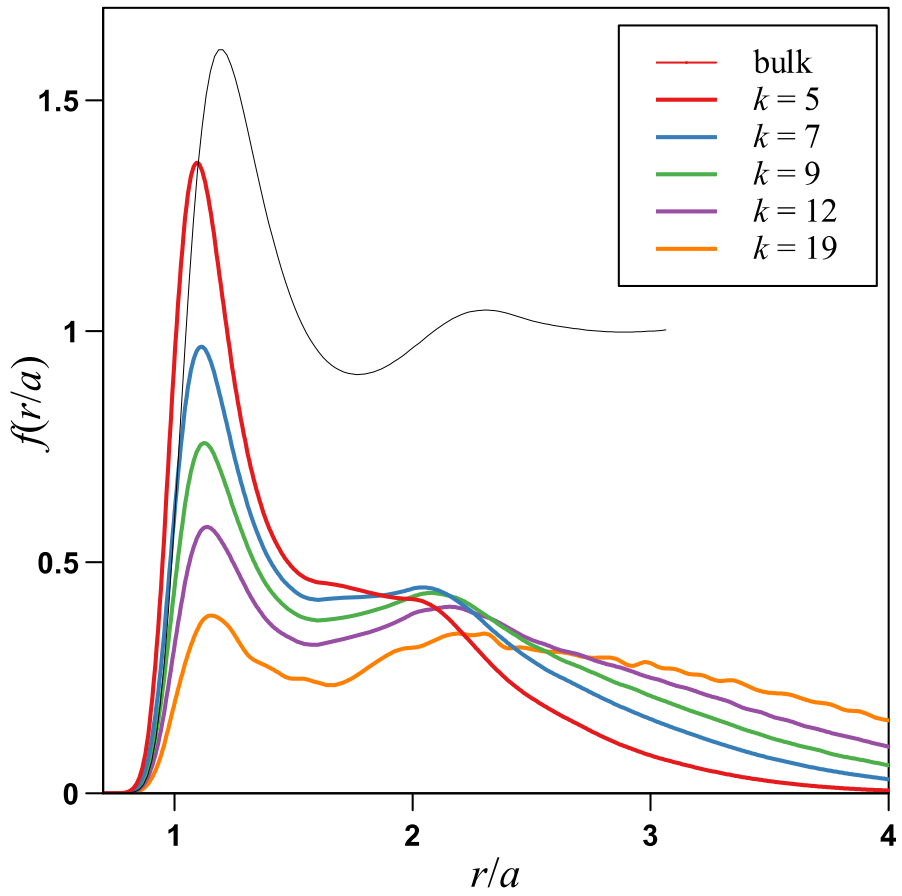


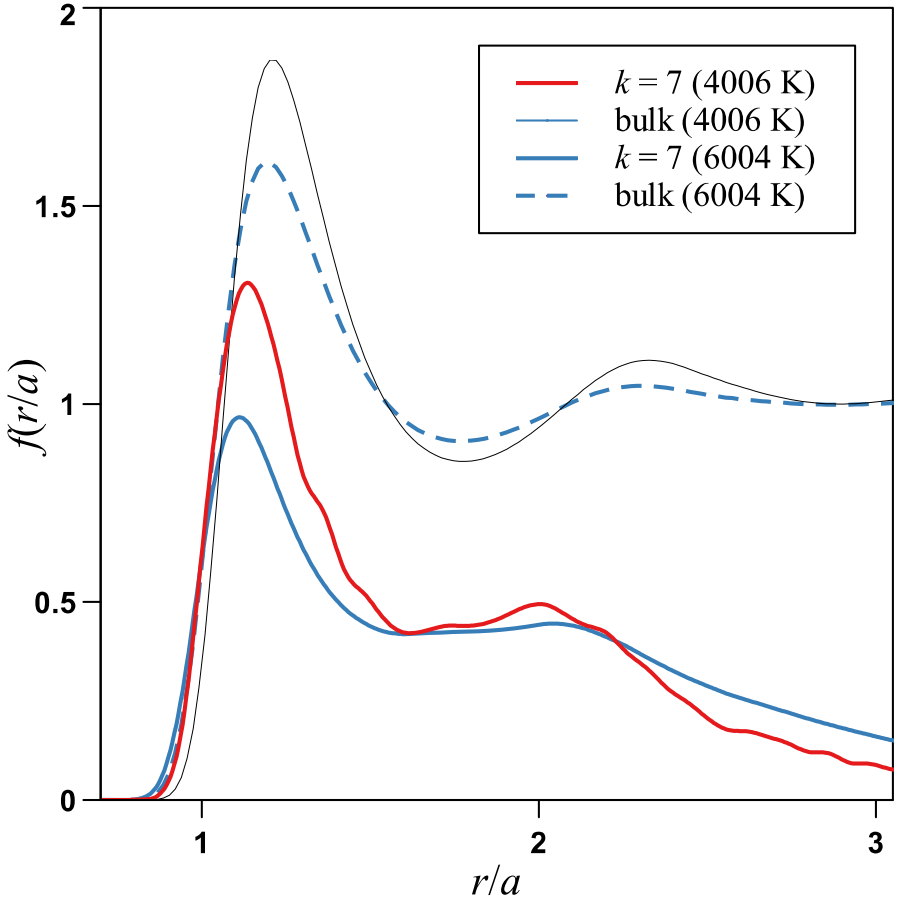


Structure parameter $\eta = \dfrac{\rho_{\max}}{\rho_{\text{av}}}$ and the reduced structure parameter $\nu = \dfrac{(\eta - \overline{\eta})}{\Delta\eta}$,

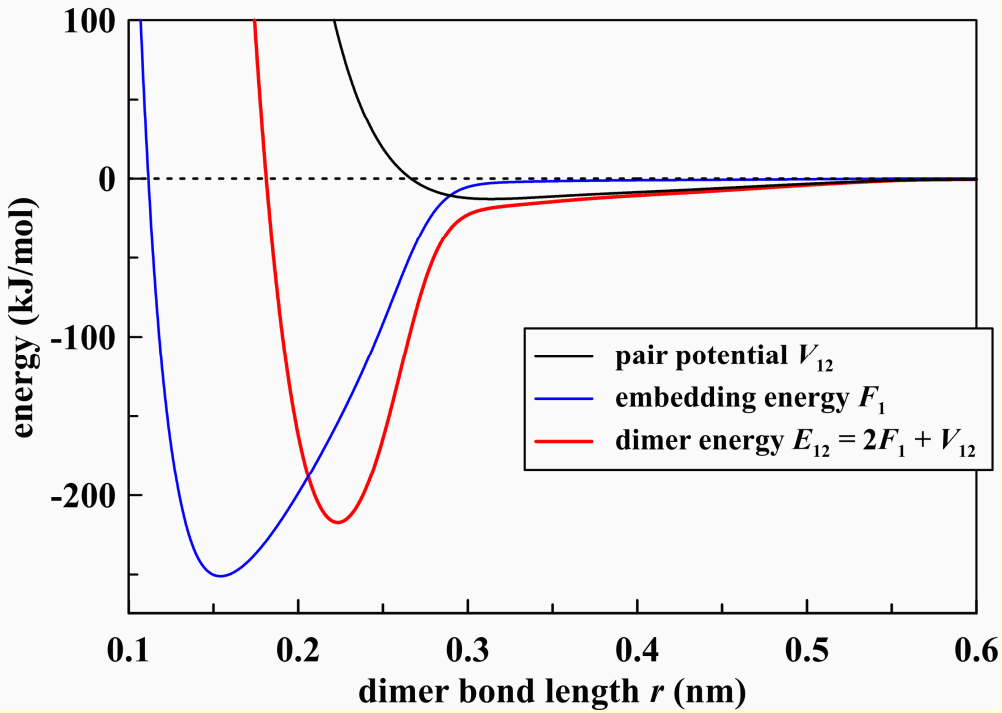
where $\overline{\eta} = \dfrac{\eta_2 + \eta_3}{2}$ and $\Delta\eta = \eta_2 - \eta_3$.

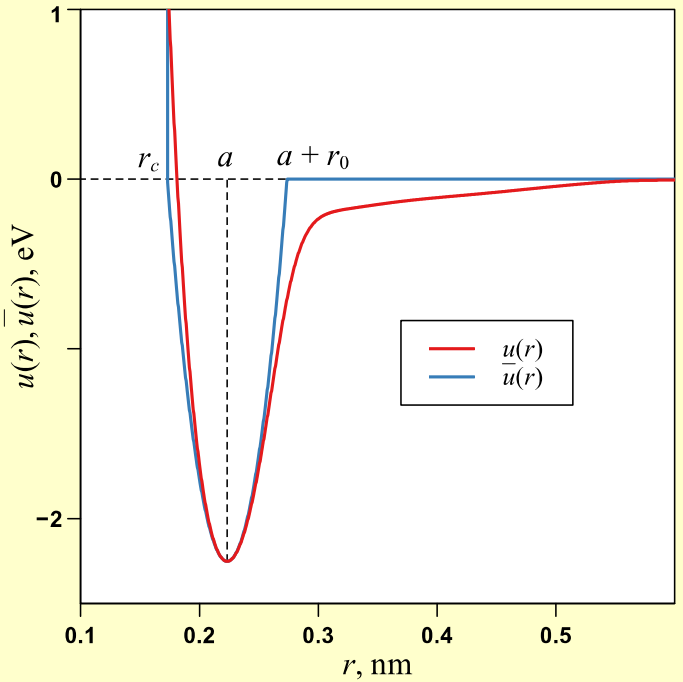
Cluster bond length distributions





Interatomic potential for the dimer Au_2





Assessment of the structural transition temperature

The lightest clusters are liable to the structural transition, whose temperature T_0 can be estimated from the equation

$$\exp(\tau) = \frac{\tau}{\varepsilon}\left(\frac{a}{r_0}\right)^2, \quad \tau = \frac{2\varepsilon D}{T_0}, \quad \varepsilon = \lim_{k\to\infty}\frac{\Delta E_k}{(2k-5)D}, \quad \Delta E_k = E_{\text{ch}} - E_{\text{sol}}.$$

For the saturating metallic interatomic interaction, the estimation is obtained. For Au,

$$\varepsilon = \frac{1}{2}\left(\frac{q}{D} - 1\right) \simeq 0.382.$$

Then, from the solution $\tau = 5.68$, we derive the transition temperature $T_0 = 3500$ K.

Conclusion

- The wide-range EAM potential for gold is constructed. It can be used for simulation of different dynamic processes including vapor nucleation and liquid cavitation.
- The dense gold vapor includes clusters. As temperature is increased, the clusters undergo a structural transition from a compact to chainlike structure. The lightest clusters are quasifractals with the fractal dimensionality close to two.
- The model of an ideal mixture of different clusters is applicable for gold vapor.
- Even the lightest gold clusters conform to the classical thermodynamics of a macroscopic medium due to a special value of the Tolman length.
- Calculated compressibility factor, cluster size distribution, and characteristic temperature of the structural transition are consistent with both MD simulation and independent data.

Thank you for your attention!

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