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Adsorption of benzene from an aqueous solution

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Adsorption of benzene from aqueous solution on a planar carbon wall is studied by molecular dynamics simulations. The density profile and the orientational behavior of a benzene molecule are determined by two methods. In the first one the center of the benzene molecule is fixed while the molecule can freely rotate and the local density is obtained via integration of the mean force on the center of the molecule. In the second method the density profile is determined directly from a freely moving benzene molecule. It turns out that even in the case of strong adsorption the first method is superior. As regards structure, the benzene molecule is preferably adsorbed in a nearly parallel orientation to the wall, but there is also a certain probability for finding it in more remote positions in an almost perpendicular orientation bridging two water layers.

Keywords: Molecular dynamics simulations; Potential of mean force (PMF); Adsorption; Aqueous solution; Benzene

1. Introduction

Adsorptive methods for separation processes from dilute liquid solutions become increasingly important in chemical engineering. In biochemical engineering, e.g. liquid chromatography is widely used in downstream processing for the recovery of high-value substances from dilute solutions and in environmental engineering adsorption is used to purify water from impurities. Despite of this practical relevance, structure and thermodynamics of adsorption from liquid solutions are barely explored on a molecular basis.

Because molecular modeling of adsorption from the gas phase [1,2] turned out to be quite successful, it seems rewarding to address also liquid solutions and in particular dilute solutions. The long term goal of our research is the prediction of structure, thermodynamics, dynamics and fluid dynamics of medium sized and large molecules like biomolecules in dilute solutions via molecular modeling. Tools in molecular modeling of adsorption are density functional theory (DFT), Monte Carlo (MC) simulations and molecular dynamics (MD) simulations. DFT turned out to be quite successful both for gaining physical insight, e.g. into the liquid–vapor interface in pores [3], and for predicting adsorption isotherms of real systems of simple molecules [2].

Regarding molecular simulations, presently Grand Canonical Monte Carlo (GCMC) seems to be the favorite method in adsorption studies [1] as the chemical potential is treated as an independent variable therein. We remind that GCMC actually relies on particle insertion. It has, however, been demonstrated that in standard MD simulations the chemical potential can also be calculated for inhomogeneous fluids by test particle insertion [4]. Hence, with respect to the chemical potential there is no substantial difference between MC and MD in the simulations of adsorption equilibria. On the other hand, MD has the advantage that it allows also to treat dynamics and microfluidics [5]. Hence, in the following we prefer MD. One problem, which we encountered in the previous MD study for simple Lennard–Jones mixtures [6] is that adsorption from a dilute solution may not be easily assessed by usual molecular simulations technics, in which the solute molecule moves freely. The problem arises, e.g. for the calculation of the local density when the minima in the free energy are separated by high barriers difficult to overcome for a freely moving molecule. This has been solved by using the concept of the potential of mean force (PMF): calculate the mean force (MF) on a particle in a fixed position and then integrate the mean force along some path [6] to obtain the potential of mean force.

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In the present contribution we address the adsorption of benzene from an aqueous solution on a carbon wall for several reasons. First, such a system has some practical importance. Second, the system is considerably more complicated than the previously studied Lennard–Jones mixtures [6] and it challenges an application of the simulation method to more complex systems. Third, the interactions of aromatic hydrocarbon molecules, e.g. benzene with water and carbon present a fascinating research field. The charge distribution poses theoretical and experimental questions as the water + benzene system is considered as prototype of hydrophobic hydration interactions. These are thought to cause the immiscibility of bulk fluids [7]. Finally, on our route to biomolecules, we have to switch from special codes written for a particular problem to universal codes. Here we use the universal MD code MACSIMUS [8] where a carbon surface was implemented for the present work.

2. Theory

We have shown recently [6] that the local density in case of adsorption from dilute solutions can be obtained from molecular simulations via two different routes. The first route is to calculate the PMF by integrating the mean force on a fixed particle. The second route is to let the dilute particle move unconstrained.

A detailed description of the mean force method has been given by Billes *et al.* [6]. For convenience of the reader, we will give here a brief summary. The first step is to consider the change of the free energy in case that a well defined site on a molecule B is moved from one position in the fluid to another one. For that purpose we first calculate the mean force $\langle F_B \rangle$ on the considered site of molecule B at several fixed positions. Second, we realize that the integral over the mean force is the work done by moving one particle and this equals the change of the Helmholtz free energy ΔA

$$\Delta A = - \int \langle F_B \rangle dz \quad (1)$$

Hence, the change of the free energy equals the change of the PMF, which is usually denoted by Δw . On the other hand it is well known that the PMF is related in general to the pair correlation function, or, in the particular case of a fluid in contact with a wall, to the local density $n_B(z)$ of

particle B at a distance z from the wall according to

$$\Delta w = - \left(\frac{1}{\beta} \right) \Delta \ln(n_B(z)) \quad (2)$$

where $\beta = 1/kT$. Finally, as the change of the free energy (ΔA) is equal to the PMF (Δw), we obtain

$$\Delta \ln(n_B(z)) = \beta \int \langle F_B \rangle dz \quad (3)$$

In the original derivation [6] the considered site has been an interaction site of the solute molecule B. There is, however, no restriction to a particular site and in the same way we may consider any other site. In case of benzene it is natural to consider the center of mass.

3. The model system

The above reviewed method has been implemented into the source code MACSIMUS [8] in order to calculate the local density of the benzene center of mass from equation (3). Moreover, a carbon slit pore has been implemented into MACSIMUS. Therewith the adsorption of a benzene molecule from dilute solution on a carbon wall is studied.

The benzene molecule is described by a fully atomistic model. It is flexible, and in calculations of the interaction potential bond lengths, bond angles, torsional contributions, Lennard–Jones interactions and electrostatic interactions are considered.

The intramolecular potential functions and the intermolecular potential parameters are taken from the CHARMM force field [9]. The most important parameters used to model both types of molecules are given in table 1. The Lennard–Jones parameters for the unlike interactions are constructed using the Lorentz–Berthelot combining rules [10].

We use the CHARMM21 TIP3P [11] water model: the oxygen sites only are endowed with Van-der-Waals interaction sites. The partial positive charges on the hydrogen atoms are exactly balanced by appropriate charges located at the oxygen atoms (see table 1).

On the benzene molecule, six positively charged hydrogen sites are balanced by six negatively charged carbon sites. The net charge of both molecules, water and benzene, is zero.

The volume of the simulation box is kept constant. The simulation box is cubic with fixed number of molecules

Table 1. The quantities σ and ϵ are the Lennard Jones parameters, whereas q is the atomic charge.

Molecule	Atom type	Mass [g/mol]	ϵ [kJ/mol]	σ [nm]	q [e]
C ₆ H ₆	C6R	12.0110	0.20934	0.20400	−0.100
	HA	1.00800	0.17585	0.13300	+0.100
Carbon wall	CR66	12.0110	0.20934	0.18000	–
	HT	1.00800	0.20850	0.09200	+0.417
H ₂ O	OW	15.9994	0.63681	0.18000	−0.834

and density. The box length is calculated from these quantities.

The average pressure counts 1 bar and the model system contains 1 benzene molecule and 500 water molecules. The temperature of the system is fixed at 300 K by the Berendsen (friction) thermostat. The cut off radius of the non-bonded interactions (Lennard–Jones and Coulombic) have been chosen approximately half of the box size (1 nm). A time step of ≈ 1.67 fs has been chosen to integrate the equations of motion.

The distance of the opposing walls of the slit pore is ≈ 2.47 nm. The wall is neither charged nor structured. The carbon walls themselves have been implemented as integrated (9/3) Lennard–Jones potential. Periodic boundary conditions have been applied in directions parallel to the carbon walls.

When calculating the local density via the PMF (equation (3)), the position of the benzene center of mass (CoM) has been fixed at a given value for one simulation run and the MF on the CoM has been calculated. This procedure has been repeated for several CoM positions in subsequent runs. By integration of the MFs along a defined path, the PMF can be calculated.

In the present calculations, the benzene molecule has been moved along a straight line perpendicular to the carbon wall from 1.2 to 0.2 nm distance. This path has been divided into 60 intervals and the CoM has been fixed subsequently at the end points of the intervals. At each position the mean force has been calculated. The averaging has been done by taking the mean value of 95×10^3 individual forces. The first 1.68 ps have been considered as equilibration time, and have not been taken into account for the MF. The total simulation time at each position covers 160 ps.

We have found that the mean force for a given position of the CoM of the benzene molecule converges within 100 ps.

4. Results

4.1. Local density of the benzene

The local density of the benzene molecule has been calculated first from the MF method and second from a freely moving benzene molecule.

In the MF method, the benzene molecule is fixed in its CoM and first inserted near the center of the simulation box. Subsequently it is fixed at other positions approaching the wall along the normal distance z from the wall. For any fixed position the MF on the benzene molecule is calculated. Figure 1 shows a rather structured profile of the MF and PMF calculated by the MF method. Areas where the molecule is repelled from the wall (positive MF) are marked by grey boxes, whereas areas, in which the benzene molecule is attracted towards the wall (negative MF) are marked white. The error of the calculation is within the size of the marks (open circles) and ranges in between 1.1 and 1.7 pN.

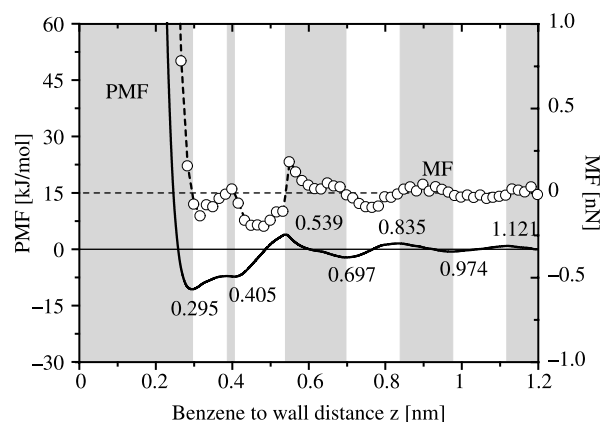


Figure 1. The MF (\circ) on a benzene molecule dissolved in water and the PMF (full line) as function of the normal distance z from the wall. The carbon wall is positioned at $z = 0$ nm. In the grey areas the molecule is repelled, in the white areas it is attracted to the wall.

It is trivial that the minima and maxima of the PMF correlate with the zero values of the MF. The closer the benzene molecule is moved towards the wall, the more pronounced the minima and maxima of the PMF are. Maxima can be found at: 1.121, 0.835 and 0.539 nm, while the minima of the PMF reside at: 0.295, 0.405, 0.697 and 0.974 nm. Note that the benzene molecule has to overcome a potential barrier of 3.905 kJ/mol at 0.539 nm to be adsorbed. The global minimum -10.658 kJ/mol is situated at a distance of 0.295 nm from the carbon wall.

Finally, the local density profile is calculated from the PMF via equation (3) and shown in figure 2. Note that there is some arbitrariness of the local density with respect to the bulk density. Here, the local density was normalized such that the integral over the distance between the two limiting carbon walls became unity.

The alternative route is to calculate the local density profile by allowing the benzene molecule to move unconstrained. In our previous work [6], however, we found that in the unconstrained case the density profile may not converge within affordable time. In order to check

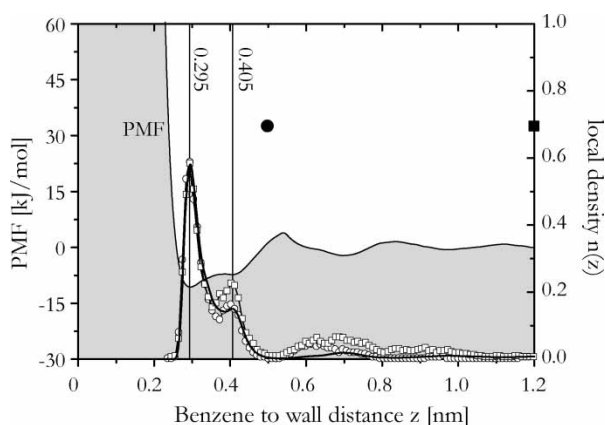


Figure 2. The PMF (grey background) of the benzene molecule and the local density profile obtained therefrom (full line). The circles and squares (\circ , \square) represent the local density profiles of an unconstrained molecule starting from different initial positions (\bullet , \blacksquare).

the situation for the present system, we inserted the unconstrained benzene molecule at two different distances from the wall, namely at $z = 0.5$ and 1.2 nm. In order to make these profiles comparable with the PMF result, their height has been adjusted in the maximum peak. The results are shown also in figure 2. We learn that even after simulation times of 600 ps the simulations has not completely converged. Figure 2 shows that the positions of the two main peaks from the unconstrained simulation match the positions of the PMF profile peaks. The heights of the other peaks of the unconstrained simulations, however, differ already among themselves. Moreover, there are also discrepancies in the tails of the local densities obtained from PMF and from the two unconstrained runs.

To summarize, we observe that the local density profile shows one very pronounced first peak (0.295 nm), which indicates a strong tendency towards adsorption of the benzene molecule. Moreover, also a second peak is found at 0.405 nm and further small maxima at the distances 0.697 and 0.974 nm. A further discussion of these maxima of the local density profile will be given below.

4.2. Orientational distribution of the benzene

Besides the local density of the CoM another interesting point is the orientation of the solute molecule in particular in the first two adsorption peaks, which has been calculated in the framework of the MF method.

At this point we need to introduce the notation for the orientations. First we introduce the normal on the benzene ring directed into the bulk fluid. Thereafter we consider the polar angle θ between this normal and the normal on the carbon wall. As the benzene normal is directed into the bulk fluid, it covers the space angle of 2π while angle θ ranges from 0° to 90° . This angle is by definition also the angle between the carbon wall and the benzene molecule. Thus the benzene molecule is parallel to the wall for $\theta = 0^\circ$ and perpendicular to the wall for $\theta = 90^\circ$. Next, we are interested in the orientational distribution $p(z, \theta)$ of the benzene molecule at a given distance z of the molecule center from the wall. In order to calculate this distribution we keep the CoM of the benzene molecule at a fixed distance z and perform a simulation run. During this run we register the number ΔN of orientations for, which the benzene normal lies between θ and $\Delta\theta$. Keeping in mind that the azimuthal orientation between the benzene and the wall normal is isotropic, we obtain the orientational distribution $p(z, \theta)$ from

$$\frac{\Delta N(z, \theta)}{N} = 2\pi p(z, \theta) \sin\theta \Delta\theta \quad (4)$$

where N is the total number of orientations counted at fixed z . Hence the distribution $p(z, \theta)$ is normalized so that the integration over all orientations of the benzene molecule gives unity for each value of z .

The orientational distribution $p(z, \theta)$ is shown in the density plot in figure 3a. The bright areas mark regions

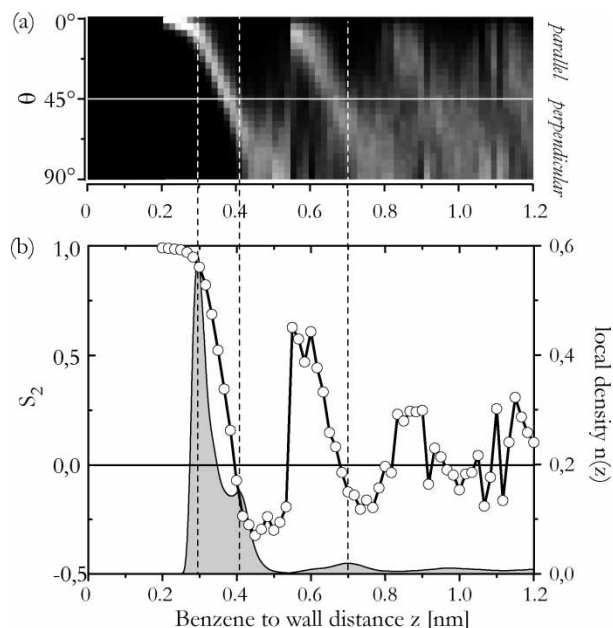


Figure 3. a: Orientational distribution $p(z, \theta)$ of the benzene molecule as function of the distance z from the wall and of the angle θ . A bright square signifies a high probability, a dark square a low probability. b: The orientational order parameter S_2 (\circ) together with the density profile of the benzene molecule (grey plot).

with a high probability $p(z, \theta)$, whereas the dark areas identify regions with a low probability.

Frequently, the orientation is not represented by the orientational distribution $p(z, \theta)$ but rather by the order parameter S_2 [12] which is defined as

$$S_2(z) = \frac{1}{2} \sum_i (3\langle \cos^2\theta \rangle - 1) \quad (5)$$

Note that $\langle \dots \rangle$ indicates averaging over the orientations of the benzene molecule at fixed position of the center of mass. If the benzene molecule is parallel to the wall then $\langle \cos^2\theta \rangle$ equals 1 and the order parameter $S_2 = 1$. If the benzene molecule is oriented isotropically then $\langle \cos^2\theta \rangle$ becomes $1/3$ and $S_2 = 0$. Finally, if the benzene molecule is perpendicular to the carbon wall the value of $\langle \cos^2\theta \rangle$ becomes zero and the order parameter $S_2 = -1/2$. The simulation results on the order parameter S_2 as function of the distance z from the wall are shown in figure 3b.

The distribution of the orientations presented in figure 3a shows a zig-zag pattern of the bright squares as a function of z . This pattern is asymmetric in the sense that the slope with a positive gradient is shorter in z -direction than the slope with a negative gradient.

For simplification we qualify the orientations of the benzene molecule as follows: a benzene molecule with an angle $\theta > 55^\circ$ will be considered perpendicular whereas all benzene molecules with an average angle $\theta < 35^\circ$ will be considered parallel.

Let us consider an adsorption process in detail, if one follows the orientational distribution of the benzene

molecule in figure 3 from the right to the left, i.e. from the center of the simulation box to the wall.

In the interval between 1.1 and 0.8 nm from the wall the orientation of the benzene molecule is close to isotropic. Figure 3b shows that the order parameter S_2 is close to zero in this interval and figure 3a shows only modest differences in the brightness. Without over-interpretation we find around $z = 1.0$ nm the perpendicular orientation slightly preferred whilst around $z = 0.85$ the parallel orientation is slightly preferred. From 0.8 to 0.7 nm the benzene molecule is preferably found in perpendicular orientation. The dark area in the upper part of figure 3a indicates that parallel orientations hardly occur and this matches with the negative value of S_2 in figure 3b.

If one follows the orientational distribution plot from 0.7 to 0.55 nm a well defined angle-band occurs in figure 3a. This denotes that the benzene molecule no longer arbitrarily flips in different orientations, but covers preferred ones. The deviation from these preferred orientations is rather small. This well defined angle-band correlates with a small maximum in the local density profile of the benzene molecule in figure 3b.

In approaching the wall the benzene molecule flips at 0.54 nm from a parallel orientation to a perpendicular orientation. This rather sharp transition correlates with the jump in the MF in figure 1. Moreover this jump occurs just in the region where the first more pronounced water shell is observed in the simulations and the local density of the benzene is close to zero.

Till 0.405 nm the benzene molecule remains rather perpendicular orientated. We remind that just at 0.405 nm the second local density profile peak occurs. The orientational distribution is rather broad but a maximum can be located at 81° .

Thereafter a gradual transition to a parallel orientation takes place. In this region the orientational distribution is rather narrow. At 0.295 nm this orientational distribution has a pronounced peak at $4-8^\circ$.

These findings from the orientational distribution are observed from the order parameter S_2 in figure 3 as well. At the first peak in the local density close to the wall the order parameter S_2 is near to 1, which shows that the benzene is orientated nearly parallel to the wall. Note that at higher maxima the order parameter S_2 is negative, which indicates a perpendicular orientation.

4.3. Influence of the water structure on the benzene

The key finding from above is that the local density profile of benzene has a very pronounced first peak close to the solid where the benzene lies nearly parallel to the wall. This can be easily understood by the fact that this is the most favorite orientation for the isolated benzene molecule and that in addition the water–benzene interaction surface is minimized by that orientation. What still has to be analyzed are the subsequent minor peaks of the benzene local density, in which the benzene molecules are oriented nearly perpendicular to the wall.

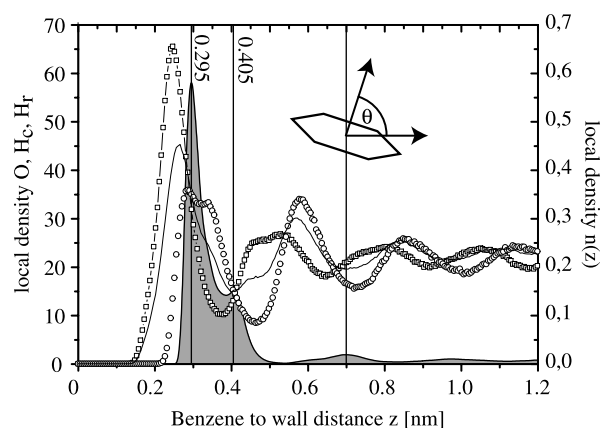


Figure 4. Local density profiles of the water-oxygen sites (O-sites, full line), of the closer water–hydrogen sites (Hc-sites, \square), of the remote water–hydrogen sites (Hr-sites, \circ), and of the center of benzene (grey background).

We assume that the benzene structure in the higher peaks is not in essence a direct consequence of the wall–benzene interaction but rather a consequence of a strong interplay between the water structure and the benzene molecule. In order to work that out we show in figure 4 four local density profiles.

In figure 4 the black line represents the density profile of the oxygen sites (O-sites). Then we show two density profiles of the hydrogen-in-water sites. Looking on the hydrogens in water, one site is closer and the other is more remote with respect to the solid surface. Hence we present the local density of the closer H-sites (Hc-sites) in one curve and the local density of the more remote H-sites (Hr-sites) in the other curve. Moreover, the grey profile in figure 4 indicates the local density profile of the CoM of the benzene molecule. The corners of the benzene model in figure 4 mark the positions of the carbon sites.

First we note that the density profile of the O-sites resembles density profiles from other simulations, e.g. [13]. In any case we observe the usual layered structure for the local density of the O-sites, the Hc-sites and the Hr-sites with the particular finding that starting from the second peak the maxima in the local density of the Hr-sites are close to the local maxima in the density of the O-sites.

Looking now on benzene and starting from the second peak the maxima in the benzene profile are located at the minima of the O-site profile. Therefore a simple picture is that the benzene molecule just bridges two water layers. This picture also accounts for the previous finding that the benzene molecules in the higher peaks are nearly perpendicular oriented. The minor deviations from the perpendicular orientation can be considered as a consequence of a best fit into the water structure.

4.4. Comparison to previous work

From the simulation point of view, O'Dea *et al.* [14] studied the adsorption of sulfonated and unsulfonated aromatic molecules onto flat graphite surfaces from

aqueous solution by semi-empirical quantum mechanical molecular modeling techniques. Whereas the graphite surface and the solute has been modeled fully atomistic by O'Dea *et al.* [14] the solvent has been described by an electrostatic background. Thus, they were not able to take the particular structure of water into account. Despite their main interest rested on the adsorption behavior of sulphonated aromatic carbons, their simulation results considering the adsorption of benzene are of particular interest for this work.

Their key results can be summarized as follows. First they do report no σ - or π -bonding between the surface and the optimized aromatic adsorbate [14]. This is in clear contradiction to the paper of Kim *et al.* [15]. The latter argue for a strong π - π hydrophobic interaction, which is formed between the graphite surface and the aromatic ring of benzene. However our results support the findings of O'Dea *et al.* [14] that adsorption is predominantly due to water-benzene interactions and/or London dispersion forces between the solute and the graphite surface [14].

The advantage of the introduced approach in comparison to O'Dea resides in the fully atomistic description of the model system, which endows the calculation of the favorite positions and orientations of the benzene molecule from the first water layer onwards.

5. Summary

We have carried out MD simulations of one benzene molecule dissolved in 500 water molecules in a carbon slit pore of width 2.24 nm at a temperature of 300 K and a pressure of approximately 1 bar. Structural results are the local density profile and the probability distribution for the orientation of the benzene molecule. In the very pronounced first layer close to the wall at $z = 0.295$ nm the benzene molecule is preferably adsorbed in a nearly parallel orientation to the wall. There exists, however, a second clear peak in the local density profile at $z = 0.405$ nm where the orientation is nearly perpendicular. Going further to the bulk we found still two other comparatively small peaks where the benzene orientation is also preferably perpendicular. Between these peaks the orientation changes from perpendicular to parallel and back. Anyhow, it can be stated that with the exception of its adsorption state closest to the wall the benzene molecule bridges the water layers. In approaching the bulk

the orientation becomes nearly isotropic at a rather small local density.

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