A structural study of a two-dimensional electrolyte by Monte Carlo simulations

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Properties of superconducting and superfluid thin films, modeled as a two-dimensional classic Coulomb fluid, are connected to the molecular structure of the system. Monte Carlo simulations to explore structural properties and ordering in the classical two-dimensional Coulomb fluid were performed. The density dependence of translational order parameters at various temperatures and cluster distribution below and above the Kosterlitz-Thouless line were studied, and the percolation temperature threshold was determined. Results show that one could detect the insulator-conductor transition by observing the translational order parameters, average cluster number, or mean cluster size besides dielectric constant and dipole moment of the system. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4905159>]

I. INTRODUCTION

A complete understanding of the properties and behavior of ionic fluids is of high importance due to their vast industrial application and relevance to a variety of biological systems. Dimensionality of the ionic system is related to its properties.¹ Three-dimensional (3D) electrolytes are always conducting and have an infinite dielectric constant, whereas one-dimensional electrolytes are insulating at all temperatures and densities. Electrolytes in two-dimension (2D) are, however, special. They can behave as a conductor and an insulator, depending on the temperature and density of the 2D electrolyte. An example of such a system is the two-dimensional Coulomb fluid, consisting of an equal number of logarithmically interacting positive and negative charges. It serves as a physical model for systems which are effectively two-dimensional and whose important thermal excitations are vortices, examples being superconductive and superfluid thin films.² Systems of this kind undergo a so called Kosterlitz-Thouless (KT)³ transition between an insulating and a conductive phase. At low temperatures, the charges form neutral pairs or larger neutral clusters. As the temperature increases, the pairs unbind and the system transitions into the conductive phase. Evidence suggests^{4–7} that the Coulomb fluid undergoes also a vapor-liquid (VL) transition at finite densities and low temperatures. Even though the position and properties of both phase transitions have been studied extensively by theoretical methods^{8–13} as well as computer simulations,^{5,14–16} there is still some doubt regarding the position and character of the VL critical point. Studies of a fluid of charged disks interacting via a logarithmic pair potential also have relevance for solutions of rigid cylindrical polyelectrolytes. Kholodenko and Beyerlin¹⁷ and Levin¹⁸ discuss the relation between the Manning counterion condensation¹⁹ and the Kosterlitz-Thouless phase transition.³

Properties and behavior of superconducting and superfluid thin films are connected to their topology. Therefore, a topological study of the two dimensional Coulomb fluid might be of interest. Cluster size distributions of 2D Coulomb gas below and above the KT line were already presented by Sahimi and Mehrabi.¹⁵ The authors have shown that the number of clusters with an odd number of ions decays exponentially. This sort of decay is also observed in the geometrical models of phase transitions, such as percolation model. The authors further suggested that through cluster size distributions, one may also locate the KT transition line. In the present paper, we show Monte Carlo results for translational order parameters, cluster size distributions, alongside their first and second moments, and mean cluster sizes at various temperatures and densities and discuss the possibility of predicting the KT transition from structural properties. The percolation temperature thresholds were also determined as they tell us when the system is macroscopically connected. According to our knowledge, this is the first time results for percolation temperature thresholds, translational order parameters, and mean cluster sizes for 2D Coulomb fluid are reported in the literature and a first test if these parameters can be used to determine KT transition line.

The paper is organized as follows. In Sec. II, we present the model with the interaction potential. In Sec. III, we provide the details of MC simulation. Results for structural properties and the percolation curve are presented in Sec. IV. In addition, we show cluster size distributions and pair correlation functions in the vicinity of percolation temperature threshold.

II. THE MODEL

The system of 1:1 2D electrolyte was composed from N_+ positive and N_- negative particles with a positive q_+ and a negative linear charge density q_- . Positive and negative particles have hard core diameter σ . The interaction between

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two such particles is given by

$$u_{ij}(r_{ij}) = \begin{cases} -\frac{q_i q_j}{2\pi\epsilon\epsilon_o} \ln \frac{r_{ij}}{\sigma} & r_{ij} \geq \sigma \\ \infty & r_{ij} < \sigma \end{cases}, \quad (1)$$

where ϵ is the permittivity of the dielectric in which particles are embedded. The potential is set to zero at contact of particles. The reduced units are used in this work and are defined as $r^* = \frac{r}{\sigma}$, $z_i = \frac{q_i L}{e_o}$, $u_{ij}^* = \frac{u_{ij}}{\lambda_B}$, where $\lambda_B = \frac{e_o^2}{2\pi\epsilon\epsilon_o L^2}$ and L is the characteristic length of the system. In reduced units, potential between two charged particles is simplified to

$$u_{ij}^*(r_{ij}^*) = \begin{cases} -z_i z_j \ln r_{ij}^* & r_{ij}^* \geq 1 \\ \infty & r_{ij}^* < 1 \end{cases}. \quad (2)$$

III. MONTE CARLO SIMULATION DETAILS

Monte Carlo simulations were performed in the canonical (N,V,T) ensemble using periodic boundaries condition and minimum image. The long-range nature of the Coulombic interaction was properly taken into account by means of the Ewald summation method with conducting boundary conditions²⁰

$$U^{ex} = \frac{1}{4} \sum_{i=1}^N \sum_{j=1, j \neq i}^N q_i q_j \sum_{\mathbf{n}}' E_1(\alpha^2 \left| \frac{\mathbf{r}_{ij}}{L} + \mathbf{n} \right|^2) + \frac{1}{4\pi} \sum_{\mathbf{n} \neq 0} \frac{\exp\left(-\frac{\pi^2 \mathbf{n}^2}{\alpha^2}\right)}{\mathbf{n}^2} \left| \sum_{i=1}^N q_i \exp(2\pi i \mathbf{n} \frac{\mathbf{r}_i}{L}) \right|^2 - \frac{1}{4} (\gamma + \ln \alpha^2) \sum_{i=1}^N q_i^2 + \frac{\pi}{2} \left| \sum_{i=1}^N q_i r_i \right|^2. \quad (3)$$

In the above equation, γ is Euler's constant, $E_1(x)$ is the exponential integral, N is the number of particles, and L is the edge of simulation box. α is a parameter that controls the convergence of the sum and is set to 2.5 in the present work. $\mathbf{n}$ is connected to the reciprocal lattice vector $\mathbf{k}$ through $\mathbf{k} = \frac{2\pi}{L} \mathbf{n}$. The sum over $\mathbf{n} = (n_x, n_y)$, with n_x, n_y integers, extends over all vectors with $|\mathbf{n}|^2 \leq 8$.

Another complication in simulating ionic fluids is the occurrence of clustering at lower temperatures when the Coulombic potential energy is large compared to the kinetic

TABLE I. Comparison of our results for energy, heat capacity at constant volume, and pressure for different sized systems at $T^* = 0.6$ and $\rho^* = 0.01$.

N	$\frac{U_{ex}}{N}$	C_v^{ex}	P
102	0.063 95	0.548 4	0.003 74
200	0.063 99	0.515 8	0.003 74
1024	0.063 92	0.521 3	0.003 745

energy, making single particle moves less likely to be accepted. Inadvertently, this means long simulation times will be necessary to correctly sample the configurational space. To speed up the simulation process, cluster move developed by Ferrenberg and Swendsen and modified by Wu *et al.*²¹ was employed alongside single particle moves. A brief explanation of the algorithm goes as follows. Two ions are considered to be a part of the same cluster if they are oppositely charged and less than a cutoff distance σ_c apart. When a cluster is selected, all ions belonging to the cluster are moved by the same distance in the same direction. A move resulting in a formation of a new cluster would break the detailed balance rule in the Markov chain and is for this reason automatically rejected no matter how energetically favorable it is. Otherwise, the move is accepted with the probability $\min(1, \exp(-\beta U))$.

The cutoff distance is determined rather arbitrarily. According to Lomba *et al.*, the optimum value is 1.5σ . They performed a series of analysis using different values of cutoff distances. They report that for σ_c larger than 1.5σ , the cluster distributions are, with the exception of single ions, more or less impervious to the choice of σ_c .¹² Mehrabi *et al.*, who inspected the changes in cluster size distribution accompanying the KT transition, utilized a different cutoff distance, though. They choose $\sigma_c = 1.2\sigma$.¹⁵ In the present work, we inspected the extent of the effect the value of σ_c has on cluster distribution and how, at different values of σ_c , these distributions change as the systems transition from an insulating to a conductive phase.

All simulations were performed with 102 particles, due to a considerable rise in computational costs at temperatures where the phase transitions are expected. In 2D, 100 particles are equal size as in 3D 1000 particles. Simulations with 200 and 1024 particles were also performed to assure that there were no size effects. Results for energy, pressure, and

FIG. 1. Pair distribution function for (a) equally and (b) oppositely charged ions at $\rho^* = 0.01$ and $T^* = 0.6$ for different sized systems. Red symbols correspond to $N = 1024$, green to $N = 200$, and blue to $N = 102$. Results for different sizes are within the error of the method.

FIG. 2. Cluster size distributions for $\rho^* = 0.01$ and (a) $T^* = 0.075$, (b) $T^* = 0.1$, (c) $T^* = 0.15$, (d) $T^* = 0.2$, (e) $T^* = 0.4$, (f) $T^* = 0.6$, (g) $T^* = 0.8$ for different cutoff distances in clusters. Results for $\sigma_c = 1.2\sigma$ are plotted with black, for $\sigma_c = 1.3\sigma$ with red, for $\sigma_c = 1.4\sigma$ with blue, for $\sigma_c = 1.5\sigma$ with orange, for $\sigma_c = 1.6\sigma$ with green, and for $\sigma_c = 1.7\sigma$ with pink line.

heat capacity at constant volume at selected temperature and density are given in Table I, while radial distribution function for different sized systems can be seen in Figure 1. Expressions for pressure and heat capacity can be found in Ref. 13. All results are in agreement within the error of the method. To equilibrate the system, 10^6 moves per particle were needed.

The statistics were gathered over the next 2×10^6 moves to obtain well converged results.

The dielectric response function was obtained via

$$\epsilon_o^{-1} = \lim_{\mathbf{k} \rightarrow 0} \left(1 - \frac{2\pi}{\mathbf{k}^2 k_B T L^2} \langle q_{\mathbf{k}} q_{-\mathbf{k}} \rangle \right), \quad (4)$$

FIG. 3. Cluster size distributions for $T^* = 0.2$ (red solid line) and $T^* = 0.1$ (blue dotted line) at different densities: (a) $\rho^* = 0.002$, (b) $\rho^* = 0.01$, (c) $\rho^* = 0.05$, (d) $\rho^* = 0.1$, (e) $\rho^* = 0.2$.

FIG. 4. Density dependence of (a) first and (b) second moment of cluster size distribution for $T^* = 0.8$ (red), $T^* = 0.6$ (blue), $T^* = 0.4$ (green), $T^* = 0.2$ (pink), $T^* = 0.15$ (black), $T^* = 0.1$ (orange), and $T^* = 0.075$ (violet).

where $q_k = \sum_i \exp(-i\mathbf{k} \cdot \mathbf{r}_i)$ and $\langle \rangle$ denotes an ensemble average. The limit in Eq. (4) was evaluated by averaging over the three lowest allowed wave vectors $\mathbf{k}$ in the periodic simulation cell as was previously done by Orkoulas and Panagiotopoulos.⁵ The dipole moment of the system was calculated through

$$\mathbf{M} = \sum_{i=1}^N z_i \mathbf{r}_i, \quad (5)$$

with the center of the simulation box taken as the origin of the coordinate system. The square dipole moment was averaged through the entire simulation.

The mean cluster size S is defined as the ratio of the second and first moment of the cluster size distribution,

$$S = \frac{\sum_n n^2 N_n}{\sum_n n N_n}, \quad (6)$$

where N_n is the average number of clusters of size n .^{22,23}

IV. RESULTS AND DISCUSSION

First, we studied the effect of the cutoff distance used in cluster definition on the distribution of clusters. Results for cluster size distributions at different temperatures and cutoff distances while density is held constant at $\rho^* = 0.01$ are presented in Figure 2. At all inspected temperatures, choosing a smaller value of σ_c leads to larger ratios of odd numbered clusters and smaller ratios of even numbered clusters. Nevertheless, at temperatures below $T^* = 0.1$ and above $T^* = 0.4$, cluster size distributions are qualitatively the same regardless of the choice of σ_c . Even numbered clusters predominate at temperatures below $T^* = 0.1$ (Figures 2(a)-2(b)), while at temperatures above $T^* = 0.4$ (Figures 2(e)-2(g)), single ions make up the majority of the system at all studied values of σ_c . The choice of the cutoff distance is only important at temperatures in the vicinity of the KT line. At $T^* = 0.15$ (Figure 2(c)), for example, setting σ_c to 1.2σ leads to a cluster size distribution where single ions predominate, while setting σ_c to 1.3σ or larger results in a system made

FIG. 5. Density dependence of (a) mean cluster size and (b) its inverse value for $T^* = 0.8$ (red), $T^* = 0.6$ (blue), $T^* = 0.4$ (green), $T^* = 0.2$ (pink), $T^* = 0.15$ (black), $T^* = 0.1$ (orange), and $T^* = 0.075$ (violet).

up mostly of dipoles. Generally, if σ_c is set to a lower value, odd numbered ions start to predominate in the system at lower temperatures, than if a larger σ_c value is selected. Systems on the KT line should consist of approximately equal number of odd and even numbered clusters. At $T^* = 0.2$ (Figure 2(d)), roughly where according to our calculation the KT transition should occur, the ratio of odd and even numbered clusters is approximately equal, only if $\sigma_c = 1.5\sigma$. This value was then used in all our subsequent calculations.

We have also inspected the changes observed in cluster size distributions that accompany the increase in density at constant temperature. Results for two temperatures, $T^* = 0.1$ and $T^* = 0.2$, are shown in Figure 3. At $T^* = 0.2$ and low densities, the system is insulating and is mainly made up of dipoles and single ions, the former being more abundant (Figure 3(a)). At $\rho^* = 0.01$, we are very close to the KT transition line; consequently, the numbers of even and odd clusters in the system are similar. When the density is increased even further, the systems become conducting and larger clusters begin to form, making cluster size distributions decay slower. Clusters with odd numbers of ions are more frequently observed than even numbered clusters. At $T^* = 0.1$, dipoles are the most frequent cluster even at high densities. Although the system is in the conductive phase at $\rho^* = 0.1$, even numbered clusters are more likely to be found in the system than odd numbered clusters (Figure 3(d)). At even

higher densities, dipoles are still the predominant cluster, but larger clusters are more likely to be made up of odd than even number of ions (Figure 3(e)). This is in disagreement with results of Mehrabi and Sahimi, who have shown that single ions are the most abundant species in the conductive phase and not dipoles.¹⁵ This disagreement stems from the use of different cutoff distances in cluster definition. As we have already mentioned, the cutoff distance in the present work was set to 1.5σ , while the aforementioned authors used 1.2σ .

First and second moments of cluster size distributions, $\langle n \rangle$ and $\langle n^2 \rangle$, respectively, are also calculated and are presented in Figure 4. The first moment, also called the average cluster number, is larger at higher densities and lower temperatures, when ions are packed closer together and have less thermal energy, making it harder for them to resist the electrostatic attraction that pulls them near oppositely charged ions leading to formation of clusters. Same holds for the second moment. Our numerical results show that at lower temperatures, $\langle n \rangle$ starts out as a concave function of density, which then in the vicinity of KT transition transforms into a convex function, while at temperatures above $T^* = 0.2$ such a transition cannot be observed. $\langle n^2 \rangle$ shows a similar dependence though the inflection is less pronounced. Both $\langle n \rangle$ and $\langle n^2 \rangle$ show a change in density dependence around $\rho^* = 0.2$ at all inspected temperatures, which is somewhat peculiar because other thermodynamic functions show nothing unusual in this density region. We have also explored the density dependence of the mean cluster size at various temperatures. Results are shown in Figure 5. We can see that the inequality $\langle n \rangle < S$, established by Quintanilla and Torquato, holds.²⁶ The mean cluster size increases with density and decreases with temperature. It shows a similar density dependence as $\langle n \rangle$ and $\langle n^2 \rangle$. It displays a transition from a concave to a convex function at lower temperatures, with inflection points coinciding with that of $\langle n \rangle$, as well as a change in density dependence around $\rho^* = 0.2$ at all inspected temperatures. On the other hand, S^{-1} shows no such change. At higher densities, S^{-1} decreases almost linearly with density at all investigated temperatures. At lower temperatures, after the change in the gradient, the linear behavior continues even at low densities. We drew straight lines through linear sections and determined the positions of intersection points (Figure 6). A drop in temperature causes the intersection point to move towards lower densities. The position of intersection points roughly coincides with the position of t_{++} maxima.

FIG. 6. Extrapolation of linear behavior of the inverse value of the mean cluster size and the resulting intersection points at $T^* = 0.15$ (black), $T^* = 0.1$ (orange), and $T^* = 0.075$ (violet).

FIG. 7. Density dependence of translational order parameter for (a) oppositely charged ions and (b) equally charged ions for $T^* = 0.8$ (red), $T^* = 0.6$ (blue), $T^* = 0.4$ (green), $T^* = 0.2$ (pink), $T^* = 0.15$ (black), $T^* = 0.1$ (orange), and $T^* = 0.075$ (violet).

First, we calculated translational order parameter which measures the degree of pair correlation in the system and is defined as

$$t_{ij} = \int_0^{\xi_c} |g_{ij}(\xi) - 1| d\xi, \quad (7)$$

where $\xi = \rho^{\frac{1}{2}}r$ is the distance r in the units of mean inter-particle separation and $g(\xi)$ is the pair distribution function. ξ_c is the cutoff distance and is set to half of the simulation box in the present paper. For normal fluids, translational order parameter monotonically increases with density. If a different behavior is observed in a certain density range, the fluid is said to exhibit a structural anomaly.^{24,25} In ionic fluid, two translational order parameters can be defined. One describes the extent of correlation between equally charged ions and will be denoted with t_{++} in the present paper, while the other one is in connection with the correlation between oppositely charged ions and will be denoted with t_{+-} . Our results show that t_{+-} monotonically decreases with density at all inspected temperatures. The behavior of translational order parameter in case of equally charged particles, presented in Figure 7(b), is different. For $T^* = 0.1$, for example, t_{++} displays a maximum at $\rho_{max}^* = 0.05$, decreases until it reaches a minimum at $\rho_{min}^* = 0.15$, and then continues with increasing behavior. A

similar behavior was also observed at $T^* = 0.075$ and $T^* = 0.15$ which is shown in Figure 7(b). At lower temperatures, the maximum is more pronounced and lies at lower densities, while the minimum moves towards higher densities. The observed density dependence may be ascribed to the transition of the system from an insulating to a conductive phase. At reduced temperatures above 0.25, the system is always conducting. At such temperatures, t_{++} shows an increasing behavior with respect to density, displaying no maxima within simulation error.

Results for the average square of the dipole moment of the system, M^2 , are presented in Figure 8. At temperatures above the KT line, the square of the dipole moment is a decreasing function of density. At lower temperatures, M^2 shows an increasing behavior at lower densities, reaches a maximum value in the vicinity of the KT line and then decreases if the density is increased even further. The maximum is more pronounced at higher temperatures. At constant density, the average square dipole moment increases with the temperature of the system.

The changes in density behavior of average cluster size and translational order parameter for equally charged particles, observed in the vicinity of the KT line, led us to believe that the KT transition could be detected by observing the aforementioned quantities. When system undergoes KT

FIG. 8. Density dependence of average square dipole moment for $T^* = 0.8$ (red), $T^* = 0.6$ (blue), $T^* = 0.4$ (green), $T^* = 0.2$ (pink), $T^* = 0.15$ (black), $T^* = 0.1$ (orange), and $T^* = 0.075$ (violet).

FIG. 9. Comparison of our results for the KT line (red symbols) with the position of M^2 maxima (blue symbols) and t_{++} (green symbols) and $\langle n \rangle$ (pink symbols) inflection points. Lines are drawn for visual clarity. Black line represents results for KT line obtained by Orkoulas and Panagiotopoulos.⁵

FIG. 10. Density dependence of percolation temperature thresholds.

transition, the structure on molecular level of the system changes. t_{++} and $\langle n \rangle$ are related to structure of the system, so we tested if we can use them to determine KT transition line. Figure 9 compares predictions of different methods (the maxima positions of M^2 , the inflection points of t_{++} and $\langle n \rangle$) for the KT line. The KT transition is accompanied by a jump in the dielectric response of the system. Nelson showed that the size of the jump is universal and has a value $\epsilon^{-1} = 4T_{KT}^*$.²⁷ In order to determine the transition points, we calculated the intersection points of the ϵ^{-1} curve and $4T_{KT}^*$ line. Our predictions for the KT transition points are in agreement with results from other studies (see, for example, Ref. 5). The square dipole moment maximum shows the same temperature dependence as ρ_{KT}^* but lies at somewhat higher densities. The connection between the dipole moment of the system and the

TABLE II. Comparison of our results for the ρ_{KT}^* with the position of M^2 maxima and t_{++} and $\langle n \rangle$ inflection points for different sized systems at $T^* = 0.1$.

N	ρ_{KT}^*	$\langle n \rangle$	t_{++}	M^2
102	0.05	0.08	0.07	0.08
200	0.05	0.075	0.07	0.075
300	0.05	0.075	0.075	0.075

dielectric response of the system was already established and formally proven by Caillol.²⁸ Inflection points of t_{++} and $\langle n \rangle$ behave similarly and roughly coincide with maxima positions for dipole moment of the system. To inspect the effect of system size on the phase diagram, we conducted additional calculations with 200 and 300 particles. Our results, reported in Table II, show that the KT transition line is not sensitive on the system size.

Results for percolation temperature thresholds in the density range $\rho^* = 0.01 - 0.3$ are presented in Figure 10. Percolation temperature at a certain density was determined as the temperature where the ratio $\langle \frac{N_{max}}{N} \rangle$ is equal to 0.5. N_{max} is the size of the largest cluster in the system and N is the number of particles in the system. Percolation temperatures rise with increasing density. This is in agreement with our previous finding that at the same temperature, clusters will be larger in a more condense system. Cluster size distributions near percolation temperature threshold at $\rho^* = 0.2$ are presented in Figure 11. Below the percolation temperature, the most frequently observed cluster spans the whole system. Small clusters up to 15 ions are also common; medium size clusters

FIG. 11. Cluster size distributions for $\rho^* = 0.2$ and (a) $T^* = 0.04$, (b) $T^* = 0.055$, (c) $T^* = 0.058$, (d) $T^* = 0.07$.

FIG. 12. Pair distribution function for (a) equally and (b) oppositely charged ions at $\rho^* = 0.2$. Red symbols correspond to $T^* = 0.04$, blue to $T^* = 0.055$, green to $T^* = 0.058$, and black to $T^* = 0.07$. Lines are drawn for visual clarity.

with 40-60 ions, on the other hand, almost do not occur. In the vicinity of the percolation temperature, threshold dipoles are observed most often and clusters of all sizes can be found in the system. As the temperature is further increased, big clusters do not form anymore. Occurrence of clustering can also be observed in pair distribution functions shown in Figure 12. Both pair distribution functions display three peaks, $g_{+-}(r^*)$ at approximately $r^* = 1, 3$, and 5 , while $g_{++}(r^*)$ has peaks around $r^* = 2, 4$, and 6 . The first peak in $g_{+-}(r^*)$ is due to pair formation, the next is due to formation of four-ion clusters and so on. Peaks in $g_{++}(r^*)$ can be similarly explained. At lower temperature, the peaks are more pronounced, as cluster formation is more likely, and slightly moved to lower values of r^* , showing that clusters are more condensed and less likely to be of linear shape.

V. CONCLUSIONS

Monte Carlo simulations to explore structural properties and ordering in the classical two-dimensional Coulomb fluid were performed and the density dependence of translational order parameters at various temperatures and cluster distribution below and above the KT line were studied, and the percolation temperature threshold was determined. It was discovered that at lower temperatures even numbered clusters predominate far into the conductive phase with dipoles being the most likely species, while at higher temperatures odd numbered clusters make up the majority of the system as soon as we cross the KT line. On average, clusters are larger at lower temperatures and higher densities. It was also checked whether any alternative methods could be used to determine the insulator-conductor line. Translational order parameters for like charged ions, average cluster number, mean cluster size, and average square dipole moment all show some kind of change in their density dependence in the vicinity of the KT lines, making them a viable option for qualitative localization

of the KT transition. For a particular temperature, this change occurs at roughly the same density for all quantities.

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