# **Coarse-Grain Modeling of Acrylic Latex Polymers**

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#### Abstract

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# **1** Introduction

Many paints and coatings technologies employ organic solvents, and the recent demand for more environmentally friendly materials has sparked interest in replacing these solvents with water. As a result, water-based synthetic latex materials may find an increased importance beyond their current use in adhesives, paper coatings, pharmaceuticals, and other technologies. To realize this potential, it is necessary to achieve precise control over the film properties as a function of time. This requires detailed understanding of the film-forming process, the precursor compositions, and the film's dynamic response to its environment. The properties of a synthetic polymer latex film depend on: the monomer composition(s) used, their glass transition temperatures  $T_g$  (lower  $T_g$  films tend to be softer, while those with higher  $T_g$  are harder), the colloidal formulation (e.g. homopolymers versus blended copolymers), polymerization conditions, the amount of surfactant and crosslinker used, emulsifying and drying conditions, among others.<sup>1</sup>

Latex films are formed from dispersions of polymer nanoparticles in water. The polymer chains are grown by emulsion polymerization within these nanoparticles, which are stabilized (sterically or electrostatically) by a surfactant. The nanoparticle dispersion is cast or sprayed on a substrate, and a film forms upon drying. This drying process is critical to the characteristics of the film, and its mechanism has been the subject of much debate in the literature (see Steward's review<sup>1</sup> and references cited within). The presently accepted model was described by Vanderhoff<sup>2,3</sup> as occurring in three stages:

- 1. concentration of polymerized particles as water evaporates to  $\sim 0.6$  volume fraction, <sup>3-5</sup>
- dramatic decrease in evaporation rate as volume fraction of polymer increases<sup>1</sup> and particles deform to fill the interstitial spaces (above the minimum film formation temperature or MFFT), and

3. polymer chain diffusion  $^{6-8}$  until a mechanically coherent film forms.

During the second stage the particle deformation is thought to be the result of polymer-air,<sup>9</sup> polymer-water,<sup>10</sup> and/or air-water<sup>11</sup> surface tension overcoming the polymer resistance. Water evaporates through any remaining pores in the film and by diffusion through the film, with the rate of evaporation tending toward that of diffusion alone.

Since water is a critical element of synthetic latex drying and film formation, it is important to understand its role during and after synthesis.<sup>8</sup> During film formation, water affects the stabilization and dispersion of polymer particles and can cause plasticization<sup>12,13</sup> (*i.e.*, lowering of  $T_g$ ). However, little is known about the how the dry film interacts with continued exposure to water,<sup>1</sup> including how water uptake and evaporation affect the structure, thermodynamics, and permeability of the latex film over time.

Here we derive and validate a first-principles-based simulation model for (meth)acrylic latex polymers and their interactions with water. We use a molecular dynamics approach to study structural changes in latex films on repeated drying and absorption of water for two formulations: one that is relatively hydrophobic, and one that is relatively hydrophilic, each with respect to the other. The hydrophobic polymer consists of (by mass) 20% butyl acrylate, 40% dodecyl methacrylate, 39% methyl methacrylate, and 1% methacrylic acid. The hydrophilic polymer is made up of 60% butyl acrylate, 39% methyl methacrylate, and 1% methacrylic acid. Both are random copolymers with no crosslinking.

The document is organized as follows: in section 2 we discuss the simulation models and methods employed in this study, in section 3 we present preliminary results obtained to date, and in section 4 we summarize the importance of these results.

# 2 Simulation models and methods

Conventional Molecular dynamics (MD) simulation is a well-established tool for providing atomiclevel details into a variety of material properties and phenomena. However, it is limited by the length and time scales of simulation, especially for polymer systems. Bond vibrations have characteristic time scales  $\tau_{vib} \approx 10^{-13}$ s, while torsional barriers are overcome with a time constant of the order  $\omega^{-1} \approx 10^{-11}$ s. In an unentangled polymer melt (that is, one in which the degree of polymerization n<sub>p</sub> is less than the entanglement length n<sub>e</sub>), the equilibration time according to the Rouse model<sup>14,15</sup> is at least a factor or order n<sup>2</sup><sub>p</sub> larger. In other words,  $\tau \ge n_p^2/\omega$ .

On the other hand, if  $n_p > n_e$ , the relaxation time scales according to the reptation model,<sup>15,16</sup> which gives  $\tau \approx n_p^3/(n_e\omega)$ . For example, a simple polyethylene melt with  $n_e \approx 100$  would have a relaxation time  $^{17} 10^{-7} < \tau < 10^{-4}$  for  $10^2 \leq n_p \leq 10^3$ . While the relaxation time decreases somewhat with temperature, it can increase drastically with lower temperatures near  $T_g$ . The latex systems of interest are significantly more complex than a polyethylene melt, so the relaxation times are even longer. Considering that atomistic simulations are limited in time scale to a few tens of nanoseconds, these methods are impractical for the systems of interest.

One approach to overcome this is to simplify the description of the system by using a coarsegrain (CG) model that represents groups of atoms as a single bead. This enables the simulation of larger systems over longer times. The development of a CG model typically involves two steps:

- 1. choosing a coarsening model (e.g. electronic density model, explicit versus implicit solvent model, chemical moiety or united-atom model, etc.)
- 2. determining the degree of coarsening, and
- 3. determining the effective interaction potentials.

To establish the degree of coarsening for a particular system, a compromise between resolution and computational expense that balances the desired chemical accuracy<sup>18</sup> with efficiently simulating the required length and time scales is required. In principle, one can solve the classical Newtonian equations of motion by considering the beads as point charges, but care must be taken to avoid non-linear effects from velocity-dependent terms<sup>18</sup> which require solving more complex constrained rigid body equations of motions.<sup>19,20</sup> Furthermore, if the model is too coarse, then artifacts in melt properties can result.<sup>21–23</sup> The placement of the beads with respect to the underlying atomic structure is also important in defining a CG model. The coordinates of a bead can be chosen to coincide with a particular representative atom on a polymer backbone or side chain, or with the center of mass of the group of atoms comprising the bead. This choice can have significant impact on the pair radial distribution of the coarsened system,<sup>24</sup> which is typically employed in deriving the effective coarse-grain potential, as discussed below.

Once the degree of coarsening is settled, the effective potential must be derived. One technique for this, applied in the simulation of polymer melts, is the projector-operator formalism.<sup>25–27</sup> A number of other approaches have been described in the literature, many of which entail fitting an effective pairwise potential that accurately reproduces the radial distribution function (RDF) g(r). Levesque, Weiss, and Reatto introduced an iterative predictor-corrector method for this purpose.<sup>28</sup>

Several other methods take as a starting point the potential of mean force

$$F(r) = -k_B T \ln g(r), \tag{1}$$

where  $k_B$  is the Boltzmann constant. This "potential" is in fact a free energy, and is exact only in the infinite dilution limit. The potential is refined by one of several techniques such as reverse Monte Carlo simulation<sup>29,30</sup> or force matching.<sup>31,32</sup> In the so-called iterative Boltzmann inversion<sup>33</sup> method, the potential is updated iteratively according to

$$V_{i+1}(r) = V_i(r) - k_B T \ln\left(\frac{g_i(r)}{g(r)}\right),\tag{2}$$

where  $g_i(r)$  is the radial distribution function computed at the *i*th iteration. Recently, Fu *et al.*<sup>34</sup> proposed a modification of this approach to match the pressure in the coarse-grain system to that in the atomistic model.

Finally, a coarse-grain potential can be derived by fitting distributions based on atomistic simulations to analytic functions instead of using tabulated potentials optimized to fit the RDF. In this case, each frame of an atomistic trajectory is mapped to the CG system, and distributions of bead bond (nearest neighbor) distances, angles (next nearest neighbors), and/or dihedrals are computed. Parameters for the chosen functional form are then fit to the distribution by assuming that for a given potential P(x), the distribution D(x) of values of x is given by

$$D(x) = C \exp\left(\frac{-P(x)}{2k_BT}\right).$$

where *C* is arbitrary. The nonbond interactions are modeled by a simple analytic function (*e.g.*, a Lennard-Jones or Morse function) with parameters chosen to reproduce the RDF. Nielsen *et al.*<sup>35</sup> used this method to model polyethylene with bond, angle, and dihedral terms. Care must be taken in using these methods, as they depend on the conditions of the atomistic simulation.<sup>36</sup> For a more comprehensive description of techniques in coarse-grain simulation, the reader is referred to the review by Müller-Plathe.<sup>37</sup>

#### 2.1 Coarsening model

For this work we use a united atom model with explicit solvent. A pseudo particle that incorporates a group of chemically-stable atoms, which approximately represents the molecular mechanical properties of the group on a larger than atomic scale. The pseudo particles interact as whole groups with each other to determine the physical and chemical properties of the bulk. Here, they interact according to an effective CG potential that incorporates harmonic bonds and integrated van der Waals and electrostatic non-bond interactions described by Morse functions. First-principles-based atomistic simulations were used to characterize and develop the CG potentials; as described in the Supplemental Material. The coarse-grained model was chosen to reproduce the structural and thermodynamical features of the target systems calculated from atomistic MD simulation, considering that both contribute to the dynamics of dry latex films exposed to water.

#### 2.2 Degree of Coarsening

We consider key criteria in determining the degree of coarsening to include ease of mapping from atomistic to CG and the reverse. Unambiguous mapping from the coarse system back to an atomistic structure allows for long CG simulations to obtain a well-equilibrated structure followed by short atomistic simulations to obtain detailed properties of the system. We also choose the bead definitions to give the simplest possible distributions of nearest neighbor distances.

The coarse-grain bead definition for the atomistic components of our latex systems is shown in Figure 1. For each monomer type, one bead is assigned to the backbone and denoted A (for acrylate) or MA (for methacrylate). The bead position is chosen to be that of the  $\alpha$ -carbon. A single bead represents the small side chains in methyl methacrylate (denoted Me for methyl) and methacrylic acid (denoted OH).



Figure 1: Bead definitions for coarse-grain force field. All encircled atoms are represented by a single point located at the position of the dot within the circle.

Multiple beads represent the longer side chains for butyl acrylate and dodecyl methacrylate. The first bead, closest to the backbone, is denoted MB1 ("middle butyl 1"). This bead represents the oxygen and first three carbons (and their associated hydrogens) of the side chain, and is placed on the oxygen. The end methyl (Me) and hydroxide (OH) groups also have their bead center defined at the oxygen. Side chain bead centers are placed on the oxygen to simplify the distribution of distances with respect to the backbone. This leads to a unimodal distribution, while placing the bead on the first carbon leads to a bimodal distribution resulting from rotation around the C-O bond. This complicates the functional form for the corresponding interaction potential; therefore, we use the former in order to fit the bead bond distribution to a harmonic form.

In dodecyl methacrylate, two equivalent beads represent the next eight carbon atoms and the associated hydrogens. These beads are denoted MB2 ("middle butyl 2"). The distribution of distances between MB1 (or MB2) and MB2 beads will be multimodal because of the flexibility of the atomistic dihedrals. This has been documented in coarse-grain studies of polyethylene.<sup>38</sup> Finally, a bead denoted EB ("end bead") represents the last carbon in the side chain (and the hydrogens) for both butyl acrylate and dodecyl methacrylate.



Figure 2: Hydrophobic and hydrophilic atomistic and coarse-grain model comparison.

Figure 2 shows the degree of coarsening achieved in this model. The coarse-grained models contain roughly an order of magnitude fewer particles and bonds as compared to the atomistic systems. The low frequency of the force constants (see the following section) allows for the use of a 10 femtosecond timestep in dynamics instead of the 1 femtosecond timestep required by the atomistic simulations. Water is represented using Molinero's mW force field<sup>39</sup> and denoted by W in the current force field. Derivation of the water-polymer interactions is ongoing.

#### 2.3 Effective Coarse-grain Interaction Potential

The effective potential for our coarse-grained model consists of bond terms between neighboring beads and integrated pairwise van der Waals and electrostatic interactions between all other bead pairs (including those separated by one or two bonds). There are no three- or four-body terms. The total potential energy for the coarse-grained chain is written as

$$U_{Total} = \sum_{i} U_{bond}^{CG}(l_i, T) + \sum_{i < j} U_{nb}^{CG}(r_{ij}, T),$$
(3)

where *i* denotes a bond,  $l_i$  the corresponding bond length, and  $r_{ij}$  the distance between any pair of atoms *i* and *j* that are not bonded. The bond interactions are described by a harmonic potential

$$U_{bond}^{CG}(r) = K_{bond}(r - r_0)^2,$$
(4)

where  $K_{bond}$  is the force constant in units of kcal mol<sup>-1</sup> Ångstrom<sup>-1</sup> and  $r_0$  is the equilibrium distance in Ångstroms.

The bond parameters were determined by fitting to data obtained from one nanosecond atomistic NVT ensemble (i.e. constant number of atoms, constant volume, and constant temperature) dynamic trajectories at room temperature sampled at intervals of 500 femtoseconds. The procedure used is described in the SM. For each of snapshot, the coordinates of the beads were determined from the bead definitions given in the previous section. The distance between neighboring beads was calculated at each step, and from the distribution of this distance for each possible bead-bead bond interaction, the force constant and equilibrium distance were determined by assuming Boltzmann statistics as discussed above.

ADD ONE EXAMPLE DISTRIBUTION AND FIT FOR BONDS ... REFER THE REST THE SM

For multimodal distributions a single equilibrium distance was determined as the average of the  $r_0$ 's of the constituent peaks weighted by the peak height. The force constant was chosen to be small enough to give a single broad Gaussian distribution covering both peaks in the target

distribution. In this manner we allow the CG force field to be soft enough to sample either of the two bond states. The bond parameters fit in this manner are shown in 1.

Bond Type	K (kcal mol <sup><math>-1</math></sup> Å <sup><math>-1</math></sup> )	$r_0$ (Å)
MA-Me	73.534	2.507
MA-MB1	61.947	2.492
MB1-MB2	2.047	4.713
EB-MB2	4.091	5.065
MB2-MB2	2.549	5.062
MA-MA	89.374	2.863
A-MA	76.578	2.772
MA-OH	109.422	2.519
A-MB1	55.244	2.472
A-A	83.514	2.706
MB1-EB	2.409	4.855

Table 1: Bond Parameters

Typically, nonbond interactions in coarse-grained models are determined by fitting Lennard-Jones parameters to a total radial distribution function and/or experimental data.<sup>28,33,35,40,41</sup> These approaches are very effective, but they are not generally transferable<sup>36</sup> to systems other than the one to which they were fit. Since the main goal of this work is to predict properties across a wide range of polymer composition and water content, an approach that more rigorously preserves the underlying physics of the atomistic model is desired.

ADD ONE EXAMPLE DISTRIBUTION AND FIT FOR NONBOND ... REFER THE REST THE SM

We base the nonbond parameters on atomistic models of the van der Waals and Coulomb interaction between beads. In these simulations, the atoms corresponding to the centers of the beads as defined in 1 were attached by a spring. At each step of the calculation, a harmonic restoring force with a force constant of 2500 kcal mol  $^{-1}$  Å<sup>-1</sup> was applied to maintain a desired equilibrium distance. The equilibrium distance was decreased from 30 to 1 Å. At each step, the van der Waals and Coulomb interactions between atoms in different beads (*i.e.*, all pairs of atoms (A,B) where atom A is in Bead 1 and atom B is in Bead 2) were computed. The sum of these interactions was plotted as a function of the distance between the bead centers, and a Morse function

$$U_{nb}^{CG}(r) = D\left(e^{-2\alpha(r-r_0)} - 2e^{-\alpha(r-r_0)}\right)$$
(5)

was fitted to these data for each pair of beads. Here *D* is the well depth in kcal mol<sup>-1</sup>,  $\alpha$  (kcal mol<sup>-1</sup> Å<sup>-1</sup>) gives the stiffness of the inner wall, and  $r_0$  (Å) gives the distance of minimum energy. Parameters fit in this manner are shown in Table 2.

	A-A	A-MB1	A-EB	A-MA	A-Me	A-OH	A-MB2
D	1.21823	13.64010	0.97841	1.99937	9.73157	36.99540	0.99412
α	0.911546	0.72358	1.68954	1.845971	0.852983	0.300566	1.66401
$r_0$	4.53931	3.44451	3.58887	4.51063	3.39255	3.59686	3.60539
	MB1-MB1	MB1-EB	MB1-MA	MB1-Me	MB1-OH	MB1-MB2	EB-EB
D	0.01854	$3.5 \times 10^{-6}$	11.041	0.00647	0.09913	0.00245	$6.4 \times 10^{-5}$
α	0.988729	2.13830	0.688375	1.12682	2.10812	1.56026	2.28513
$r_0$	6.01848	5.99667	3.64017	5.96611	3.53228	5.27521	5.25749
	EB-MA	EB-Me	EB-OH	EB-MB2	MA-MA	MA-Me	MA-OH
D	1.178	0.00401	0.00072	0.00059	3.17578	9.86956	39.737
α	1.34651	2.13966	2.27474	2.48892	0.79115	0.69767	0.299533
$r_0$	3.84266	4.36806	4.59357	4.58164	4.49053	3.68405	3.63646
	MA-MB2	Me-Me	Me-OH	Me-MB2	OH-OH	OH-MB2	MB2-MB2
D	1.50052	0.044619	0.674141	0.53037	0.02357	0.0402597	0.54901
α	1.33821	1.17269	1.93509	1.89022	2.59471	2.36710	2.07872
$r_0$	3.80804	4.96596	3.20421	3.37028	3.49694	3.65916	3.41895

Table 2: Nonbond Parameters From Direct Interactions

This approach does not account for the three- and four-body terms in the atomistic force field. To account for these effects and to maintain the simplicity of the force field, the Morse parameters were optimized with a genetic algorithm to fit the pressure and total radial distribution function in the equilibrated atomistic models of the hydrophobic and hydrophilic systems. In order to ensure that the basis of the effective potential retained as much of the underlying physics of the bead interactions as possible, the search space was confined to stay within 50% of the starting parameters. The results are shown in Table 3.

	A-A	A-MB1	A-EB	A-MA	A-Me	A-OH	A-MB2
D	0.937688	6.857453	1.321671	2.746029	9.895215	33.062637	0.957668
α	0.997094	1.018902	1.935315	2.016018	0.720818	0.259169	1.200222
$r_0$	2.464728	2.464350	4.504014	5.321703	4.195650	4.114898	1.938678
	MB1-MB1	MB1-EB	MB1-MA	MB1-Me	MB1-OH	MB1-MB2	EB-EB
D	0.012211	$5.0 \times 10^{-6}$	15.599783	0.006591	0.129424	0.003299	$5.7 \times 10^{-6}$
α	1.316912	2.400664	0.996278	1.502874	2.508247	1.807169	1.559304
$r_0$	8.800414	7.847842	2.204713	7.159558	1.879322	7.065989	5.581236
	EB-MA	EB-Me	EB-OH	EB-MB2	MA-MA	MA-Me	MA-OH
D	1.229810	0.002123	0.000575	0.000754	2.214245	9.986007	25.657268
α	1.719568	2.513777	3.333890	1.936526	1.171514	0.874015	0.354725
$r_0$	3.781288	6.480567	5.636890	5.608559	5.829590	4.739361	3.858168
	MA-MB2	Me-Me	Me-OH	Me-MB2	OH-OH	OH-MB2	MB2-MB2
D	2.004522	0.041139	0.627254	0.269766	0.021275	0.025456	0.676596
α	1.177286	1.027205	2.104268	2.310941	3.352481	1.707315	1.290063
$r_0$	4.910055	5.023707	4.354317	2.768230	2.329582	4.647946	4.276580

Table 3: Nonbond Parameters Fitted to Pressure and RDF

### 2.4 Reproducing thermodynamic features

As mentioned, we adjust the analytic parameters of the CG force field to structural and thermodynamic properties. We chose to reproduce pressure (from NVT ensemble runs), but other properties such as cohesive-energy density and density (from NPT runs) can be incorporated in the model. This involved augmenting the fitness or penalty function, f(p), used in preparing the CG force field from the atomistic data with an additional term for the pressure to be reproduced, i.e.

$$f(p) = \left[\frac{P(p)}{P_0} - 1\right]^2 + \int_0^{cutoff} w(r) \left[RDF(r, p) - RDF_0(r)\right]^2$$
(6)

where p are the parameters fitted to the CG force field functional forms in Eq.3 and 0-indexed quantities are the target values.

# **3** Coarse-grain force field validation and preliminary results

The nonbond parameters from Table 2 (direct interactions) and Table 3 (fitted to pressure and RDF) were tested by performing NPT dynamics starting from the CG model corresponding to the

equilibrated atomistic system for both the hydrophobic and hydrophilic cases. A correct force field should give the same density as the atomistic calculations ( $\rho_{CG}/\rho = 1$ ) and match the target RDF for both cases. The target RDF was obtained by computing the RDF over a one nanosecond NVT trajectory of the equilirated atomistic structures mapped to the CG model. That is, each snapshot of the atomistic trajectory was mapped to a CG structure, and the RDF was computed over the resulting trajectory.

The results for density are shown in Table 4, from which it is clear that the direct interactions (Table 2) do not give a sufficiently accurate description. For both the hydrophobic and hydrophilic systems, the density within the CG model is almost five times higher than the corresponding atomistic result. Optimization of the nonbond parameters to reproduce the pressure and RDF of the atomistic model (Table 3) gives much better results, with the hydrophobic and hydrophilic CG models giving densities that are 8.3% and 1.5% higher than the corresponding atomistic results, respectively.

Table 4: Density In CG Models with Different Nonbond Parameters

	Hydrophobic $\rho_{CG}/\rho$	Hydrophilic $\rho_{CG}/\rho$
Table 2	4.975	4.643
Table 3	1.083	1.015

Results for the RDFs are shown in Figures 3 and 4 for the hydrophobic and hydrophilic case, respectively. For both systems it is clear that much better results are obtained from training the force field to reproduce structural (RDF) and thermodynamic (pressure) properties. It is likely that further optimization will improve these results further, and this work is ongoing.





Total RDF for Hydrophobic System

Figure 4: Total RDF in CG System for Hydrophilic Case



Radius of gyration,  $R_g$ , were also computed from the CG model and force field (Table 3) of individual polymer chains in the different systems and compared to their atomistic counterparts (see Figure 5). This serves as an additional validation of the CG force field.

Table 5: Comparison between the  $R_g$  of each polymer chain in the atomistic model versus its corresponding CG model, after equilibration at 300K.

	Chain <sub>1</sub>	Chain <sub>2</sub>	Chain <sub>3</sub>	Chain <sub>4</sub>
Hydrophobic <sub>atomistic</sub>	36.69167	38.1882932	26.5311218	37.7594496
Hydrophobic <sub>CG</sub>	37.2852298	36.2846686	26.6426326	38.9552494
% Change				
Hydrophilic <sub>atomistic</sub>	36.69167	38.1882932	26.5311218	37.7594496
Hydrophilic <sub>CG</sub>	37.2852298	36.2846686	26.6426326	38.9552494
% Change				

# 4 Summary and future Work

We present our results in deriving a CG force field to accurately reproduce the structural and thermodynamic pressure properties of (meth)acrylic latex films, based on atomistic models. We compared this force field with a CG force field derived from using fits to the direct bead interactions and distributions. The results show that thermodynamic and structural properties of the atomistic system are reproduced accurately with the former method. The developed CG model and force field enable a significant reduction in the total number of degrees of freedom, an almost 10-fold increase in the integration time steps (by reducing the range of high frequency vibrations in the model), a reduction in computational effort per integration time step (by way of simpler functional expressions for the interaction potentials) and a smoother effective potential energy surface, when compared to their atomistic counterparts. We are currently adjusting the interactions between the polymer components and the water model, using the changes in volume due to water content as a fitness function. This will allow us to study repeated absorption and evaporation of water in order to study the structural and thermodynamic events that lead to film degradation.

This will involve:

- Validate CG model on bulk MMA mechanical properties at room temperature, and proceed to predict properties of our relatively hydrophobic, hydrophilic and intermediate systems,
- Incorporate temperature-dependence over a range of 260-350K, by introducing new training

cases in the extremes of temperature to systematically adjust the distribution bandwidths as a function of temperature for all interactions,

- Study the thermodynamic free-energy and entropy for all systems through 40% wt water, using gradual water deposit with energy and nearest neighbor distance insertion criterion,
- Study the effects of water evaporation from 40% wt down to dry,
- Perform repeated cycles of water absorption and evaporation to detect significant changes to structural properties (e.g. changes in entanglement)
- Prepare and study Latex surface properties for the different compositions by calculating the water exchange rate between bulk and environment, through a film surface.

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