

# Calculations of electrostatic intermolecular repulsion in tetrafluoromethane: evidence for a 'hedgehog' contribution to perfluoroalkane volatility

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## Abstract

Intermolecular repulsion by peripheral polar bonds is proposed as a contribution to the volatility of perfluoroalkanes, other perhaloalkanes, and possibly octahedral hexafluorides. The calculated electrostatic contribution to the average interaction energy of two tetrafluoromethane molecules is  $0.05\text{--}0.20\text{ kJ mol}^{-1}$ , which would lower the boiling point by only 2-7 K. Electrostatic energies for some pair geometries are much larger, but these are offset by geometries with negative energies. Steric considerations suggest that electrostatic repulsion should be more important for larger perfluoroalkanes. These considerations rationalize trends in boiling points of perfluoroalkanes relative to alkanes, including trends for isomers.

## Introduction

The boiling points of perfluoroalkanes are remarkably similar to those of the corresponding alkanes. Figure 1 shows that the boiling points for normal perfluoroalkanes are somewhat higher than those of the corresponding alkanes in the  $C_1\text{--}C_3$  cases, but become progressively lower than alkane boiling points for the higher homologues. Only the  $C_1$  difference departs from an otherwise regular trend. Evidently, the dispersion energy of a perfluoroalkane is similar to that of the

corresponding alkane. Although the perfluoroalkane has many more valence electrons, its polarizability is not very different, and its ionization energy is considerably higher.

Perfluoroalkanes differ from alkanes in their patterns of isomer boiling points. As Table 1 shows, the boiling points of isomeric alkanes decrease with increasing branching, whereas isomerism has almost no effect on the boiling points of perfluoroalkanes.

Reed [1] attributed these similarities and differences between perfluoroalkane and alkane boiling points to unusually strong attractions between alkane molecules. He presented a variety of evidence for the claim that the greater accessibility of carbon atoms in alkanes allows carbon atoms to contribute far more to dispersion-force attraction in alkanes than in perfluoroalkanes. He also pointed out that branching in alkanes covers carbon atoms with methyl groups, thereby reducing these attractions by carbon.

We propose an additional explanation for the low volatility of perfluoroalkanes, viz. that electrostatic repulsions contribute significantly to the volatility. The surface atoms of these molecules are the negative ends of highly polar bonds. Intermolecular attraction is attenuated by the opposition of bond dipoles on facing sides of adjacent molecules. Attractively oriented bonds are separated by approximately a molecular diameter. Since the interaction between a pair of dipoles weakens rapidly with increasing separation, we expect the net intermolecular electrostatic interaction to be repulsive.

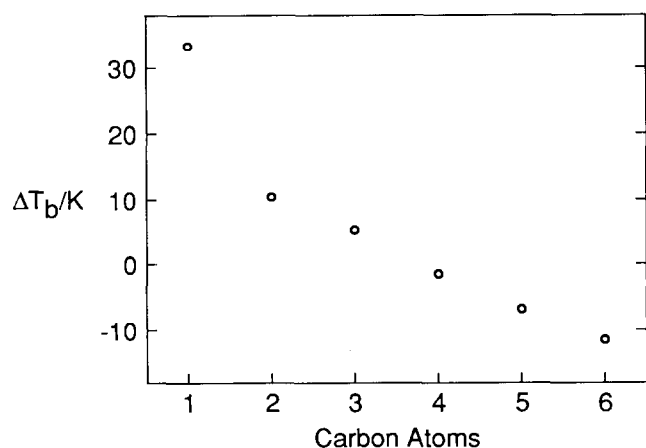


Fig. 1. Boiling-point differences: normal perfluoroalkane minus corresponding alkane.

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TABLE 1. Boiling points of some saturated hydrocarbons and perfluorocarbons

	$T_b$ (°C)		$\Delta T_b$ (°C)	CX <sub>3</sub> groups	Perfluoro faces
	X = H	X = F			
CX <sub>4</sub>	-161.5	-128.1	33.4	0	4
C <sub>2</sub> X <sub>6</sub>	-88.6	-78.1	10.5	2	8
C <sub>3</sub> X <sub>8</sub>	-42.1	-36.7	5.4	2	12
c-C <sub>4</sub> X <sub>8</sub>	12.5	-6.0	-18.5	0	16
n-C <sub>4</sub> X <sub>10</sub>	-0.5	-2.0	-1.5	2	16
i-C <sub>4</sub> X <sub>10</sub>	-11.8	1.0	12.8	3	16
c-C <sub>5</sub> X <sub>10</sub>	49.3	22.5	-26.8	0	20
n-C <sub>5</sub> X <sub>12</sub>	36.1	29.3	-6.8	2	20
i-C <sub>5</sub> X <sub>12</sub>	27.8	30.1	2.3	3	20
neo-C <sub>5</sub> X <sub>12</sub>	9.5	~30 <sup>a</sup>	~20	4	20
c-C <sub>6</sub> X <sub>12</sub>	80.8	52.7 <sup>a</sup>	-28.1	0	24
n-C <sub>6</sub> X <sub>14</sub>	68.7	57.2	-11.5	2	24
2-(CX <sub>3</sub> )C <sub>5</sub> X <sub>11</sub>	60.3	57.7	-2.6	3	24
3-(CX <sub>3</sub> )C <sub>5</sub> X <sub>11</sub>	63.3	58.4	-4.9	3	24
2,3-(CX <sub>3</sub> ) <sub>2</sub> C <sub>4</sub> X <sub>8</sub>	58.0	59.8	1.8	4	24

<sup>a</sup>Normal sublimation point of the solid. The normal boiling point of the liquid would be lower.

This argument assumes that pairs of these molecules cannot bring adjacent bonds into attractive orientations. We use the term *hedgehog repulsion* to denote electrostatic repulsion between molecules or structural groups due to unavoidable opposition of polar bonds. The bonds repel approach from all directions as do the spines of a rolled-up hedgehog.

Hedgehog repulsion might also contribute to the volatility of other molecular tetrahedral and octahedral halides such as silicon tetrachloride and sulfur hexafluoride. Note, however, that hedgehog repulsion would not apply to boron trifluoride. The positive central atom of this planar molecule is also a surface atom, and polar bonds from overlapping BF<sub>3</sub> molecules can adopt attractive antiparallel orientations.

This investigation uses calculations on pairs of CF<sub>4</sub> molecules to provide evidence regarding two questions: (1) is the electrostatic interaction repulsive for all pair geometries?; and (2) is the magnitude of hedgehog repulsion significant? The electrostatic interactions for individual geometries are found to range from highly repulsive to highly attractive. The average interaction, though positive and hence repulsive, is small.

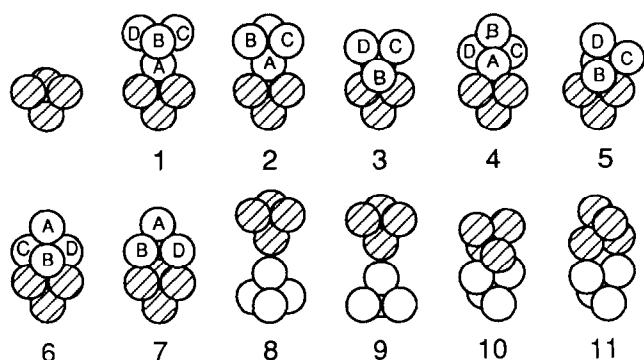
We have not undertaken a quantitative treatment of any compounds other than CF<sub>4</sub>. Instead, we use qualitative arguments to support the conclusion that hedgehog repulsion is more important in the other perfluoroalkanes. These arguments are based on differences between analogous pair geometries for CF<sub>4</sub> and the other perfluoroalkanes. The arguments also predict observed trends in perfluoroalkane boiling points relative to those of the corresponding alkanes, not only for homologous series but among isomers.

### Computational details

Interaction energies for pairs of CF<sub>4</sub> molecules were calculated with and without electrostatic contributions, which were attributed exclusively to bond polarity. Van der Waals contributions were included in all cases; the parameters were those of Williams and Houpt [2].

Bond dipoles were modeled as pairs of point charges, and electrostatic interaction energies were calculated as sums of Coulombic terms between all charges on different molecules. In order to test the sensitivity of calculated energies to the method of modeling charge distribution, two choices of charge sites were used. The atom-bond model placed charges of equal magnitudes but opposite signs at the fluorine nucleus and the center of the bond. The atom-atom model placed charges at the nuclei of both atoms of the bond. In this model, the total positive charge on the carbon atom was four times the magnitude of the negative charge on each fluorine atom. In both models, the magnitude of the fluorine charge was calculated by dividing a widely used estimate of the C-F bond dipole moment, 1.4 D [3], by the intersite distance. The fluorine charge was therefore twice as large in the atom-bond model as in the atom-atom model. The value of the bond length in CF<sub>4</sub> was 1.32 Å [4].

Molecular-pair geometries 1-11 were investigated. In the 'vertex-to-face' geometries (1-5), the fluorine atom A of the top molecule touches the three fluorine atoms which constitute the upper face of the bottom molecule. In the staggered (1) and eclipsed (2) geometries, each molecular pair has three vertical planes of symmetry. Generation of either singly-tipped geometry (3 or 4)



starts from 1 and pivots the top molecule about the nucleus of atom A in a way that preserves one vertical plane of symmetry through the molecular pair. In the 'tipped forward' geometry (3), atom B of the top molecule touches two atoms of the upper face of the bottom molecule. To form the 'tipped back' geometry (4), the top molecule pivots in the opposite direction until atoms C and D touch the third atom of the bottom molecule's upper face. The 'tipped twice' geometry (5) is generated from 3 by rotating the top molecule as far as possible in either direction about the axis through the nuclei of atoms A and B. In the two 'face-to-face' geometries (6 and 7) and the two 'vertex-to-vertex' geometries (8 and 9), each molecular pair has three vertical planes of symmetry. In the 'straddled' geometry (10) and the 'edges' geometry (11), each molecular pair has two vertical planes of symmetry.

Table 2 also lists the number of contact points and the degeneracy for each geometry. A few examples will explain how degeneracies are calculated. In each case,

one molecule is fixed in space. Its faces are distinguishable by orientation, as are its edges and vertices. For the partner molecule, these sites are indistinguishable. The degeneracy of the FF staggered geometry is 4 because there are four distinct orientations, one for each face of the fixed molecule as the contact face. The VF staggered degeneracy is twice as large because the fixed molecule could use either a vertex or a face to make contact. The VF tipped-forward degeneracy is 24 because there are three choices of tipping direction for each VF staggered orientation. The VF tipped-back degeneracy is only 12 because the two molecules play equivalent roles instead of different roles as in the VF tipped-forward case.

For each of the 11 geometries, the van der Waals energy and the total interaction energy (van der Waals plus electrostatic) were minimized separately by varying  $r(\text{F}-\text{F})$ , the single value of internuclear distance for atoms in contact. Degeneracy-weighted Boltzmann averages over these seven geometries at the normal boiling point (145 K) yielded  $\bar{E}_{\text{vdW}}$  and  $\bar{E}_{\text{total}}$ . The average electrostatic energy was calculated from eqn. (1).

$$\bar{E}_{\text{es}} = \bar{E}_{\text{total}} - \bar{E}_{\text{vdW}} \quad (1)$$

Average pair energies were assumed to be proportional to the enthalpies of vaporization and hence, by Trouton's rule, to the absolute boiling points. The contribution of hedgehog repulsion to the boiling point (experimental boiling point,  $T_b$ , minus the hypothetical boiling point without electrostatic contributions) was estimated from eqn. (2)

$$\Delta T_b(\text{hedgehog}) = T_b(\bar{E}_{\text{es}}/\bar{E}_{\text{total}}) \quad (2)$$

TABLE 2. Calculated effects of electrostatic interactions on  $\text{CF}_4$  pairs in energy-minimizing contact at representative geometries for two point-charge models of bond dipoles

Pair geometry <sup>a</sup>	Contact points	Degeneracy	Energy ( $\text{kJ mol}^{-1}$ ) ( $\text{C}_2\text{F}_8$ )			Population at 145 K		
			Van der Waals	Electrostatic		Van der Waals	Atom-atom	Atom-bond
				Atom-atom <sup>b</sup>	Atom-bond <sup>c</sup>			
1 VF staggered	3	8	-2.46	-0.58	-1.90	0.021	0.038	0.106
2 VF eclipsed	3	8	-2.46	-0.55	-1.80	0.021	0.037	0.097
3 VF tipped forward	5	24	-3.98	-0.15	-0.41	0.227	0.284	0.325
4 VF tipped back	5	12	-4.32	0.10	0.32	0.151	0.153	0.118
5 VF tipped twice	6	24	-4.52	0.24	0.72	0.356	0.321	0.199
6 FF staggered	6	4	-5.09	0.83	2.18	0.095	0.053	0.016
7 FF eclipsed	3	4	-4.57	1.03	2.69	0.062	0.029	0.007
8 VV staggered	1	4	-1.04	0.22	0.63	0.003	0.003	0.002
9 VV eclipsed	1	4	-1.04	0.22	0.64	0.003	0.003	0.002
10 straddled	4	6	-3.56	-0.44	-1.31	0.040	0.064	0.121
11 edges	2	6	-2.72	0.42	1.20	0.020	0.016	0.008

<sup>a</sup>VF is vertex-to-face, FF is face-to-face, VV is vertex-to-vertex.

<sup>b</sup>Bond dipoles represented by point charges at centers of C and F atoms.

<sup>c</sup>Point charges at F nucleus and center of C-F bond.

Sources of uncertainty in  $\bar{E}_{es}$  and  $\Delta T_b$  include omitted pair geometries, representation of charge distribution in the C–F bond and many-body effects in the liquid. Omitted pair geometries of likely significance for the liquid are close to included geometries; we expect their energies to be similar also. We address the problem of charge distribution by using two quite different representations: the atom–atom and atom–bond models. Many-body effects on boiling points with and without electrostatic interactions should largely cancel because  $\Delta T_b$  is the differential result of replacing one tetrahedral force yield with another.

## Results

Table 2 reports van der Waals and electrostatic contributions to the CF<sub>4</sub> interaction energy for the 11 pair geometries. Van der Waals contributions dominate the interaction energies. The electrostatic energy for each geometry is approximately three times as large with the atom–bond model as with the atom–atom model. This table also reports pair populations for all three energy models. Only a few populations change more than twofold due to electrostatic interactions, and only with the atom–bond model.

Table 3 shows that the average electrostatic energy  $\bar{E}_{es}$  is positive from hedgehog repulsion;  $\bar{E}_{es}$  is so small, however, that it lowers the boiling point by 7 K or less. The magnitude of  $\bar{E}_{es}$  is larger with the atom–atom model than with the atom–bond model; this is the reverse of the  $E_{es}$  results for individual pair geometries.

The optimized value of the fluorine van der Waals radius depends somewhat on the energy model and the pair geometry. When the model omits electrostatic energy, this radius is  $1.67 \pm 0.01$  Å for the first six geometries in Table 2 and  $1.61 \pm 0.02$  Å for the remaining five geometries. When electrostatic energy is calculated, the radius changes by no more than 0.04 Å for the atom–atom model but by up to 0.12 Å for the atom–bond model. As one would expect, the radius increases when the electrostatic energy is positive (repulsive), but decreases when this energy is negative. The change in radius is roughly proportional to the electrostatic energy.

These values of the van der Waals radius are larger than the 1.35 Å of Pauling [5] and the 1.47 Å of Bondi

[6]. The present radii are contact radii. As Bondi emphasizes, his van der Waals radii were selected to reproduce molecular volumes and therefore may not be suitable for contact distances. Volume radii are smaller than contact radii because projecting atoms on the surface of a molecule can penetrate into crevices on adjacent molecules.

## Discussion

Table 2 shows that the electrostatic energy  $E_{es}$  is both positive and large only for face-to-face geometries. The energy  $E_{es}$  is smaller for vertex-to-face geometries because the vertex fluorine atom is close to the other molecule's oppositely charged carbon atom (or bond centers). The energy  $E_{es}$  is even negative for three of the vertex-to-face cases, in disagreement with hedgehog expectations. This electrostatic stabilization is most pronounced for the two untipped geometries, in which attraction between colinear C–F bonds dominates the  $E_{es}$  values.

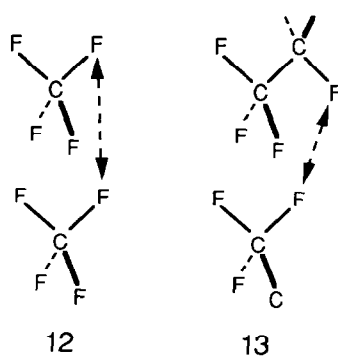
Compared to the atom–atom model, the atom–bond model doubles the charge on each fluorine atom and brings the midpoints of opposing dipoles closer together. This explains why positive values of  $E_{es}$  are much larger with the atom–bond model than the atom–atom model. Surprisingly, negative  $E_{es}$  values are also three times as large with the atom–bond model. For vertex-to-face geometries, this is because the center of the vertex atom is closer to centers of the C–F bonds of the face atoms than to the center of their carbon atom.

The average electrostatic energy  $\bar{E}_{es}$  is much smaller than the  $E_{es}$  values of the face-to-face and edges geometries. These large positive  $E_{es}$  values are offset by the large negative  $E_{es}$  values for the untipped vertex-to-face and straddled geometries. This alone does not explain the smallness of  $\bar{E}_{es}$ , since omitting the latter three geometries increases  $\bar{E}_{es}$  by only 0.22 kJ mol<sup>-1</sup> (atom–atom model) or 0.32 kJ mol<sup>-1</sup> (atom–bond model). The main reason for the small effect of face-to-face geometries on  $\bar{E}_{es}$  values is their low population. Table 2 shows that this has two causes: the low relative degeneracy of these geometries; and, ironically, their high  $E_{es}$  values, which reduce their Boltzmann factors markedly.

Although  $\bar{E}_{es}$  is small for CF<sub>4</sub>, we expect hedgehog repulsion to be more important for all other perfluoroalkanes. The first reason involves the straddled geometry (10, 12 and 13).

TABLE 3. Average interaction energies for CF<sub>4</sub> pairs and estimated contribution of the hedgehog effect to the boiling point

Bond-dipole model	$E_{total}$ (kJ mol <sup>-1</sup> )	$E_{electrostatic}$ (kJ mol <sup>-1</sup> )	$\Delta T_b$ (K)
Atom–atom	–4.04	0.20	–7
Atom–bond	–4.19	0.05	–2



No straddled geometry in other perfluoroalkanes could have an  $E_{es}$  value as negative as in CF<sub>4</sub>. In the straddled CF<sub>4</sub> geometry, **10** and **12**, four pairs of coplanar CF bond dipoles attract. In the straddled geometry for larger perfluoroalkanes, **13**, at least one of these bonds in each molecule is replaced by an essentially nonpolar C–C bond. Moreover, the designated pair of fluorine atoms in **13** is closer than the pair in **12**, and hence is higher in electrostatic energy. In C<sub>3</sub>F<sub>8</sub> and larger fluoroalkanes, the designated pair in some straddled geometries cannot avoid touching.

The second reason involves vertex-to-face geometries. CPK space-filling molecular models show that the entire surface of any perfluoroalkane consists of triangular faces. (In contrast, alkanes with three or more carbons have some rectangular faces, which perfluoroalkanes lack because of severe distortions due to crowding.) These models also show that carbon atoms below most faces of perfluoroalkanes are less accessible than in CF<sub>4</sub> to fluorine atoms from adjacent molecules. This relative inaccessibility raises the electrostatic energy of each vertex-to-face geometry. The vertex atom still touches the three fluorine atoms of the face but is farther than in CF<sub>4</sub> from the positive carbon atom (or, with the atom–bond model for bond dipoles, the positive centers of the C–F bonds).

The only type of perfluorocarbon face at which carbon is as accessible as in CF<sub>4</sub> is a face belonging solely to a CF<sub>3</sub> group (one face per CF<sub>3</sub> group). These are 1/4 of the faces in C<sub>2</sub>F<sub>6</sub>, 1/12 in C<sub>6</sub>F<sub>14</sub> and none in cyclic perfluorocarbons (Table 1).

Increases in electrostatic energies of vertex-to-face and straddled geometries would raise the average electrostatic energy, not only directly but indirectly. These geometries account for 90% of the CF<sub>4</sub> population with the atom–atom model and 97% with the atom–bond model. Increases in their energies decrease their populations by decreasing their Boltzmann factors. Decreases in populations of these geometries cause increases in populations of other geometries, notably face-to-face and edges, for which electrostatic energies are large but populations in CF<sub>4</sub> are small.

Trends in boiling points correlate well with the qualitative changes in vertex-to-face and straddled geom-

etries. Table 1 presents values of  $\Delta T_b$  defined as the boiling point of a perfluoroalkane minus that of the corresponding alkane. Consider first how  $\Delta T_b$  decreases as the number of carbons in the straight-chain compounds increases. The biggest decrease by far is 23 °C in going from CX<sub>4</sub> to C<sub>2</sub>X<sub>6</sub>. For the perfluoroalkanes, this corresponds to going from a carbon relatively accessible at all four faces to a carbon accessible at only 1/4 of the faces. Continuing along this homologous series,  $\Delta T_b$  decreases in smaller steps, as does the fraction of faces with accessible carbons. In addition, increasing fractions of straddled interactions are like **13** instead of **12**, and increasing fractions have two C–C bonds on one or both central carbons. All these trends with increasing weight correspond to increasing importance of hedgehog repulsion.

Table 1 also shows that trends in  $\Delta T_b$  among isomers (and cyclic near-isomers) correlate with the number of CF<sub>3</sub> groups in the direction expected from the discussion of carbon accessibility.

Hedgehog repulsion should also be significant in perhaloalkanes whose surface atoms are any mixture of halogens. The C–Cl and C–Br bond dipole moments are estimated to be 6% and 2% larger, respectively, than the C–F moment, versus 10% smaller for C–I [3]. The van der Waals radii of Cl, Br and I are approximately 22, 29 and 43% larger than that of F [6]. These larger atoms would enhance hedgehog repulsion by making carbon less accessible even in the tetrahalides. On the other hand, the increase in distance between negative centers on atoms from adjacent molecules would tend to reduce hedgehog repulsion. In any event, replacing F with Cl, Br or I greatly increases the van der Waals attraction and hence decreases the magnitude of  $\bar{E}_{es}/\bar{E}_{vdw}$ .

We expect hedgehog repulsion to be much smaller for alkanes than for perfluoroalkanes. The magnitude of the C–H bond dipole moment is only 0.4 D [3]. Therefore the interaction energy between two C–H dipoles is only 1/12 the energy of two C–F dipoles at the same separation. This difference is partly offset by the fact that C–H bond dipoles can get closer than C–F bond dipoles. The definitive difference is the fact that the accessibility of carbon atoms in vertex-to-face geometries is far greater in alkanes, even large ones, than in perfluoroalkanes.

We do not expect hedgehog repulsion to be important for perfluorosilanes, even though SiF<sub>4</sub> boils only 26 K higher than SiH<sub>4</sub>, and Si<sub>2</sub>F<sub>6</sub> boils 4 K lower than Si<sub>2</sub>H<sub>6</sub>. Silicon atoms are larger than carbon, and scale models show that they are accessible to fluorine atoms at all faces of SiF<sub>4</sub> and Si<sub>2</sub>F<sub>6</sub>. Chlorine atoms are better than fluorine at blocking access to silicon, yet scale models of SiCl<sub>4</sub> are ambiguous as to whether hedgehog repulsion should be important in this compound.

Octahedral molecular hexafluorides are notable for their volatility. Hedgehog repulsion may be more important for some of them than for  $\text{CF}_4$ . The electronegativities of carbon, sulfur and selenium are similar, and that of tellurium is somewhat lower [7]. This suggests that the bonds in  $\text{SF}_6$ ,  $\text{SeF}_6$  and  $\text{TeF}_6$  should be approximately as polar as C–F bonds. Although the central atoms of these three hexafluorides are larger than carbon, fewer atoms surround carbon. Molecular models show that a fluorine atom from a second molecule can get closer to the center of carbon than to sulfur, selenium or tellurium. In addition, attraction between colinear bond dipoles is impossible with octahedral molecules, whereas it helps make  $E_{\text{cs}}$  particularly negative for the untipped vertex-to-face geometries of  $\text{CF}_4$ .

Numerous heavy metals form volatile octahedral hexafluorides. These metal atoms are considerably larger than sulfur but are much less electronegative and

probably have larger bond dipole moments. The opposing effects of central-atom radius and bond-dipole moment prevent us from predicting whether hedgehog repulsion is significant for the metal hexafluorides.

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