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A THEORETICAL EQUATION OF STATE FOR DETONATION PRODUCTS WITH CHEMICAL EQUILIBRIUM COMPOSITION OF THE SURFACE OF SMALL CARBON CLUSTERS

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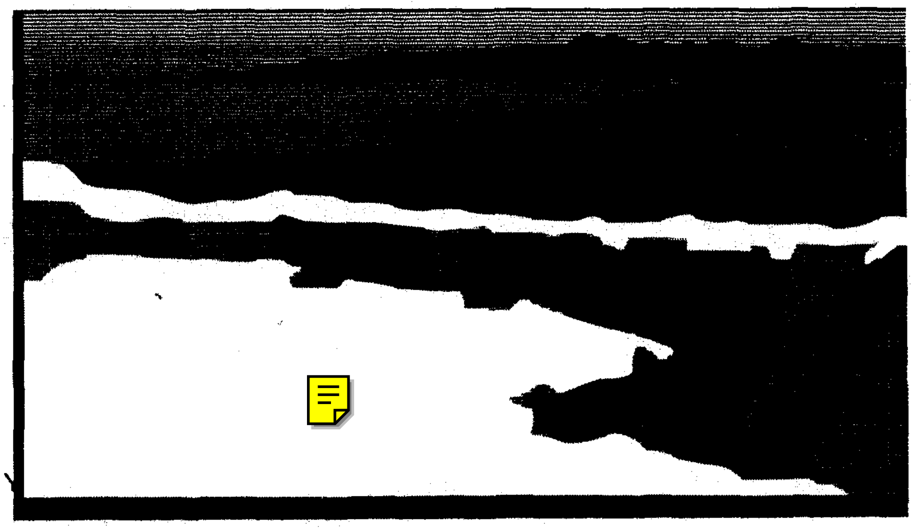

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A THEORETICAL EQUATION OF STATE FOR DETONATION PRODUCTS WITH CHEMICAL EQUILIBRIUM COMPOSITION OF THE SURFACE OF SMALL CARBON CLUSTERS *

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Abstract. A theoretical equation of state for detonation products is described and compared with various data. A perturbation theory approach is used for the mixture of molecular fluids that is based on Monte Carlo simulations. The solid carbon is characterized as small clusters rather than as a bulk material. The free energy of the clusters is modeled as primarily additive contributions such as vibrational modes, bond strengths, and effective volumes. Up to 30% of the atoms in a diamond cluster are on the surface with dangling bonds capped by various groups composed of C, H, N, and O from the background fluid. A counting term similar to ideal entropy of mixing is also found for the surface composition. Competition between the U, TS, and PV terms in the Gibbs free energy leads to dramatic shifts in the surface composition in some regions. This in turn leads to shifts in the background fluid mixture composition and anomalous behavior in the total EOS. This behavior in PBX 9502 is in good agreement with recent data on release isentropes from overdriven states(1).

INTRODUCTION

The detonation products of a high explosive form a very nonideal and complicated mixture under extreme conditions ($P \approx 30$ GPa and $T \approx 3000$ K). An accurate theoretical treatment must not only handle well the extreme conditions for a single molecular fluid, but also the mixture of species and the thermodynamic chemical equilibrium composition of the products. In addition, the solid carbon is in the form of small clusters with a large fraction of atoms on the surrface. In the diamond phase, the spherical clusters range from 20 - 50 Å in diameter with 20 - 30 % of the atoms on the surface with energetically unfavorable dangling bonds.

In this work, we provide for a variety of dangling bond cap groups in chemical equilibrium. The background fluid treatment is given by a fluid perturbation theory tied to benchmark simuation methods.

CARBON CLUSTERS

In this section we focus on the treatment of diamond clusters. A more detailed description can be found in a separate paper(2). (Graphite has no dangling bonds except at the edges and is treated as a bulk graphite EOS with a small shift in the heat of formation to include restructuring at the edges.) A spherical diamond cluster has dangling bonds exposed over the entire surface. It is energetically unfavorable to restructure the diamond surface(3). Figure 1 shows a slice through the z=0.5 (lattice constant) plane for a 23 Å cluster. A mirror plane is indicated as a dashed line. Surface atoms with single and double dangling bonds (denoted 1 and 2) are shown in the upper left. Examples of possible surface groups are shown in the corresponding mirror sites in the lower right. Nonsurface atoms, denoted 'core carbon atoms', are indicated by a circle and the origin is given by a plus. Also note that the tetrahedral bonds are all out of the plane and none of the atoms in a plane are bonded to each other.

For a given radius cluster, the number and type of surface groups in the truncated lattice and the number of core atoms without dangling bonds are counted. Figure 2 shows the ratio of surface to core atoms as a function of the number of core atoms for discrete possible clusters. The line shows an analytic fit that is

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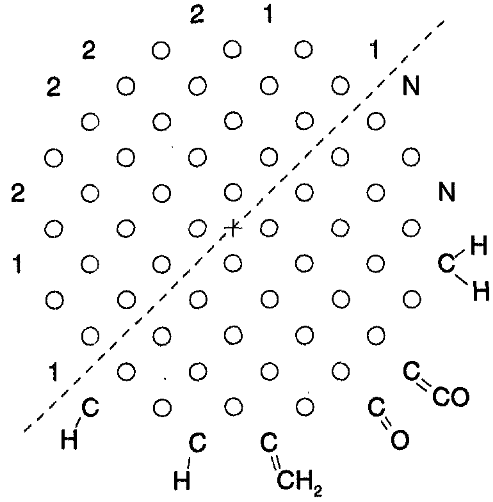

FIGURE 1. The z=0.5 plane of a 23 Å cluster. A mirror plane is indicated as a dashed line. Surface atoms with single (1) and double (2) dangling bonds in the upper left. Examples of surface groups in the corresponding mirror sites in the lower right.

dominated by the geometric surface to volume ratio of a sphere. The relative fraction of single dangling bond sites is nearly constant at about 0.65 over a wide range of cluster size.

In order to determine the equilibrium composition of the surface, it is necessary to determine the Gibbs free energy of the cluster with arbitrary surface composition. Figure 3 shows a diagram of a small part of the surface. Each surface group has an additive contribution to the free energy. An Einstein model is used for the vibrational frequencies in surface group. These modes are assumed to couple weakly to the core and are estimated from similar small molecules where possible. The heat of formation of each surface group is determined by additive bond strengths. The effective volume is estimated from the geometry of similar groups in small molecules. An effective standoff distance from the geometric surface is chosen to take into account that the occupied volume (i.e. volume excluded from the molecular fluid) is not identical to the geometric volume. Notice that a substitutional N atom would occupy a small volume that will become significant in the PV term at high pressure.

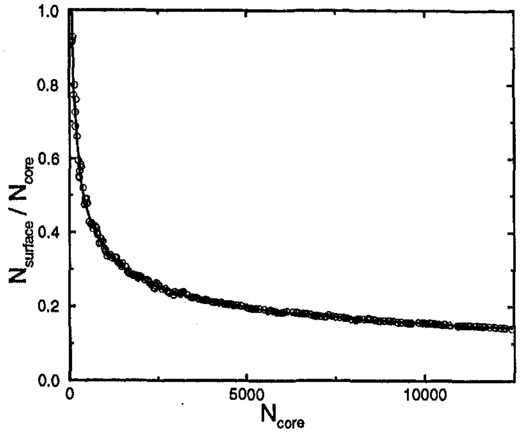

FIGURE 2. Ratio of surface sites to core atoms versus the number of core atoms in a cluster

The surface free energy has an entropy contributions due to the counting of possible ways to occupy a set of surface sites with a given composition. This contribution to the Helmholtz free energy for single bond sites is given by

$$\frac{A^{(1)}}{NkT} = \sum_{i}{}' x_i^{(1)} ln(x_i^{(1)}/x^{(1)}) \tag{4}$$

where $x_i(1)$ is the concentration (mol) of surface groups of type i and $x^{(1)}$ is the total concentration of single dangling bond sites (and similarly for the double bond sites).

Finally, the core contributions are taken from a bulk diamond model incorporating a Debye model of vibrations and a measured cold curve. A related model by van Thiel and Ree(4) implemented similar characterization of the surface groups with a fixed choice of surface composition.

FLUID MIXTURE

Benchmark simulation methods are used to test the various approximations used to evaluate the fluid mixture EOS. Accurate fluid perturbation theories

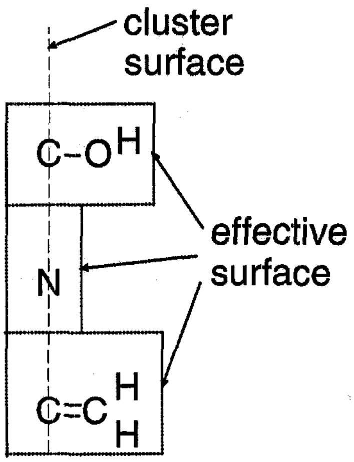

FIGURE 3. Diagram of the effective surface and occupied volume (box) of additive surface groups

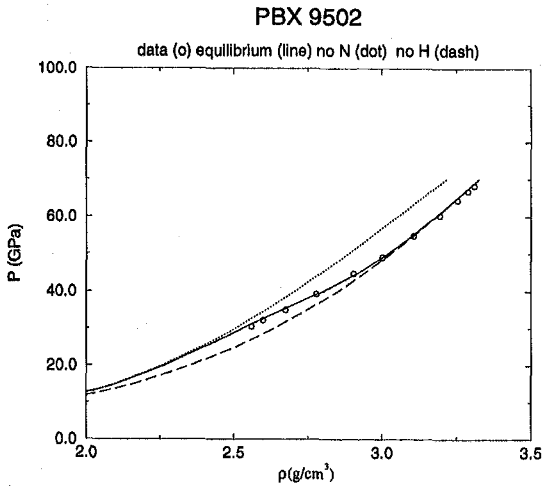

FIGURE 4. PBX 9502 isentrope from a high pressure overdriven state. Data (O), Theory: equilibrium (line), substitutional N (dash), H cap (dot).

and other approximations are used for spherical potentials, nonspherical potentials, nonideal mixing, and chemical equilibrium composition. Details are given elsewhere(2) because of space limitation.

The parameters in this method were least squares fit over a limited set of data and with terms added to limit the variation of the constants where an estimate could be made of the value and uncertainty. The slope change in the overdriven Hugoniot of PBX 9502 had a strong influence(2) on the final set of parameters. Further refinement is planned with a much larger data set, in particular using more of the new types of measurements such as sound speeds(5) and temperatures(6).

RESULTS

Vorthman et al.(1) have measured the release isentrope in PBX 9502 from overdriven states. The anomalous behavior of the data at high pressure is shown in Fig. 4. The present theory is in very good agreement with the data and provides a possible mechanism for the anomalous behavior. At high pressure, the single dangling bond surface C atoms are replaced by a substitutional N atom with no dangling bonds. The PV term gives preference for the small volume occupied by this surface group. At low pressure, the lower energy of a H cap on the dangling bond dominates. The transition in surface chemistry is spread over 20 GPa in pressure and 0.5 g/cm^3 in density. The theory reproduces the rapid slope change around 50 GPa. In the transition region, the slope of the isentrope is very nearly constant. That implies the sound speed is also nearly constant over that region. Figure 5 shows the rapid variation in surface composition that produces the unusual EOS.

There is also a very large effect due to the graphite diamond transition. Figure 6 shows good agreement between theory and experiment(7) for a series of detonation velocity versus density for TNT, 25/75 TNT/RDX, 50/50 TNT/RDX, and RDX. The detonation velocities are dominated by the graphite diamond transition. Although the transition region is rather small (1 - 2 GPA), Fig. 7 shows that the minimum shock velocity is sometimes determined by the location of the equilibrium transition rather than the minimum of either phase.

CONCLUSIONS

The chemical equilibrium treatment of surface chemistry on diamond clusters was started based on the premise that there was too large a fraction of atoms on the surface to treat the carbon as a pure bulk material. The calculations demonstrate that there can

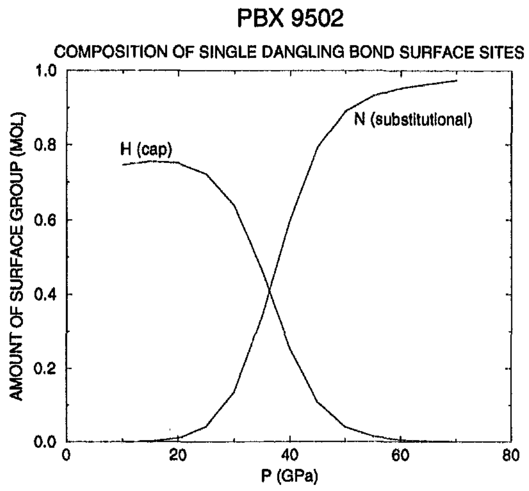

FIGURE 5. Composition of single dangling bond surface sites. Moles of surface group per formula weight versus pressure on the isentrope shown in Fig. 6.

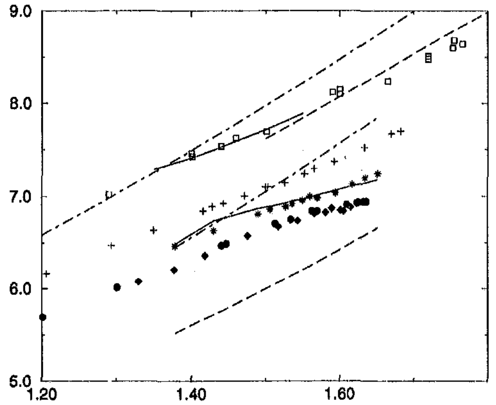

FIGURE 6. Detonation velocity versus density for TNT, 25/75 TNT/RDX, 50/50 TNT/RDX and RDX. Theory: equilibrium (line), graphite only (chain dash), and diamond clusters only (dash).

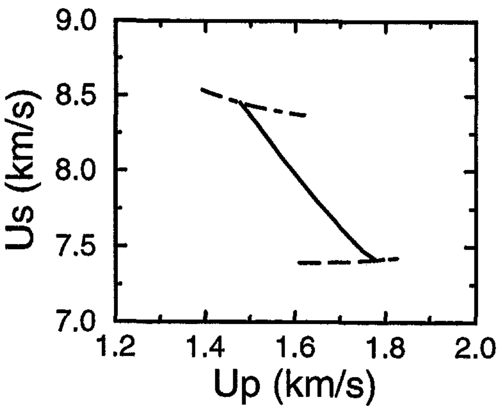

FIGURE 7. Shock velocity versus particle velocity at two values of initial density of RDX in the transition region. Equilibrium (line), graphite only (chain dash), and diamond only (dash). CJ state for equilibrium (O), graphite only (+), and diamond only (*)

be regions with a large shift in the chemical composition on the surface and that the consequences of these shifts are within the range of sensitivity of experiments. These preliminary results suggest that fitting an EOS theory to detonation velocity data is not as straightforward as it seems. Significant portions of the data could be strongly influenced by transition regions in the chemical composition.

REFERENCES

1. J. E. Vorthman, W. W. Anderson, J. N. Fritz, R. S. Hixson, and M. S. Shaw - this conference.
2. M. S. Shaw, "A Theoretica Equation of State for Detonation Products", Eleventh Symposium (International) on Detonation, to be published.
3. N. W. Winter and F. H. Ree, "Stability of the Graphite and Diamond Phases of Finite Carbon Clusters", Eleventh Symposium (International) on Detonation, to be published.
4. M. van Thiel and F. H. Ree, "Nonequilibrium Effects of Slow Diffusion Controlled Reactions on the Properties of Explosives", Ninth Symposium (International) on Detonation, pp.743-750 (1989).
5. Schmidt, S. C., Moore, D. S., and Shaw, M. S., *J. Chem. Phys.* **107**, 325 (1997).
6. Fritz, J. N.,Hixson, R. S., Shaw, M. S., Morris, C. E., and McQueen, R. G., *J. Appl. Phys.* **80**, 6129 (1996).
7. Dremin, A. N., Pershin, S. V., Pyaternev, S. V., and Tsaplin, D. N., *Fizika Goreniya i Vzryva* **25**, 141 (1989).

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1999 TOPICAL CONFERENCE
ON SHOCK COMPRESSION OF CONDENSED MATTER
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OVERVIEW

DETONATION PRODUCTS

- Unreacted:

  $C_aH_bN_cO_d$ + binder

- Products:

  dense fluid mixture

    CO_2, N_2, H_2O, CO, + minor species

  carbon clusters ≈ 1000 atoms ≈ 20 Å

    graphite-like

    diamond-like

APPROACH

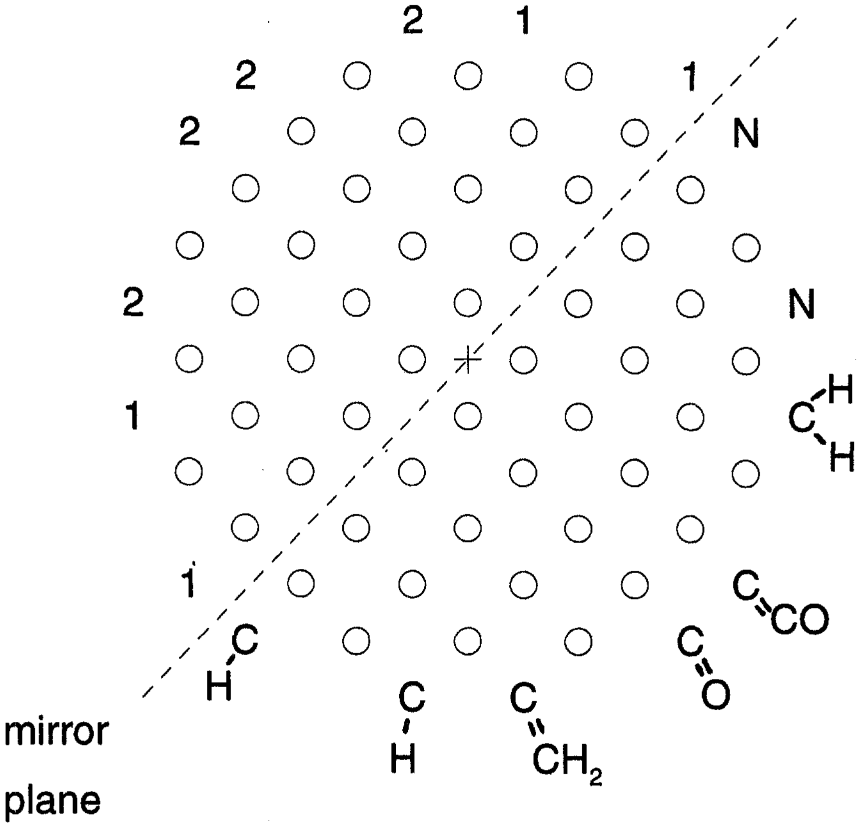
- Characterize Cluster Surface
- Chemical Equilibrium of Surface
- Simulation Methods
- Perturbation Theory
- Constrained Fit

CROSS SECTION OF A SMALL DIAMOND CLUSTER

CORE ATOMS: O = 0 DANGLING BONDS

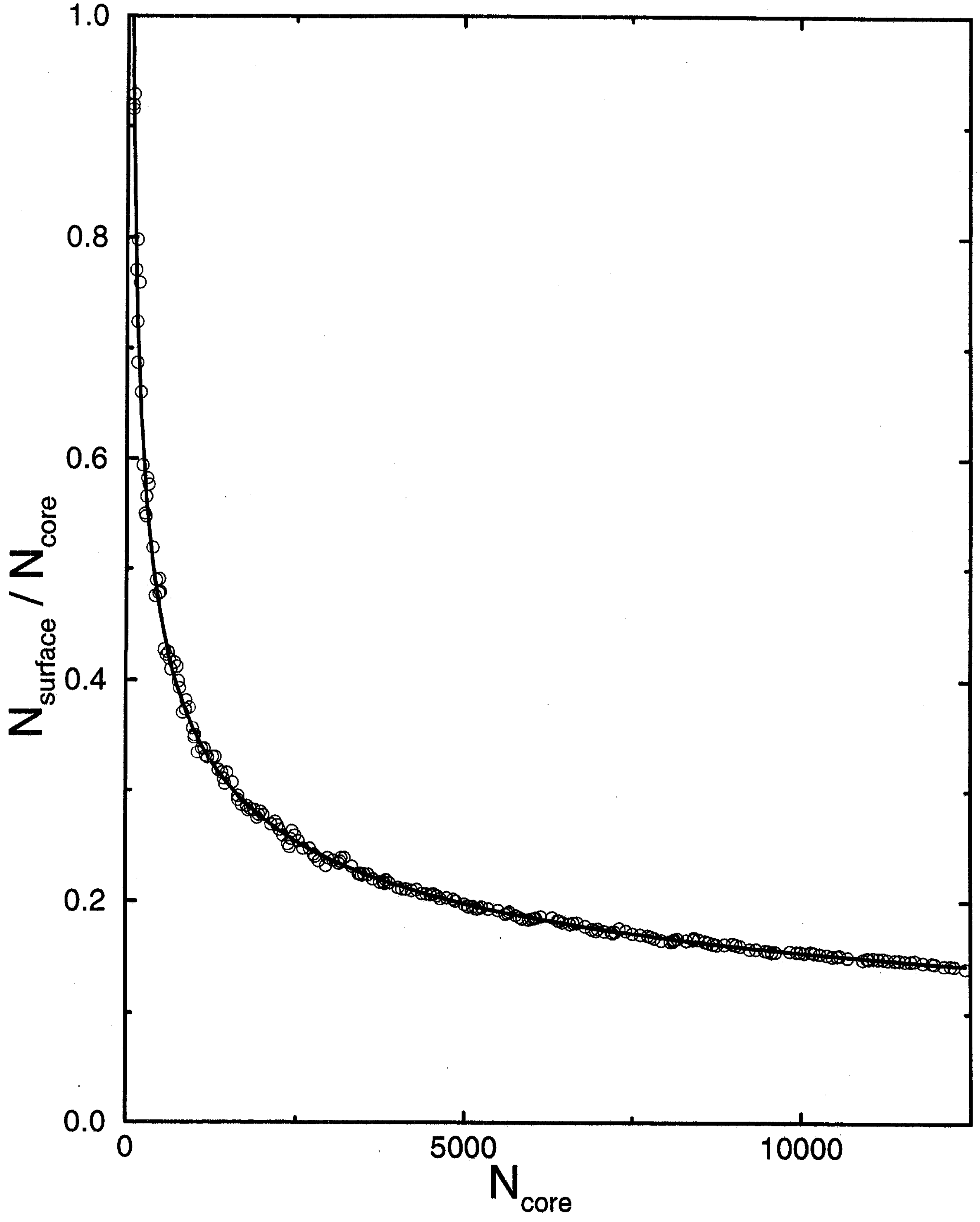
SURFACE ATOMS: 1 = 1 DANGLING BOND

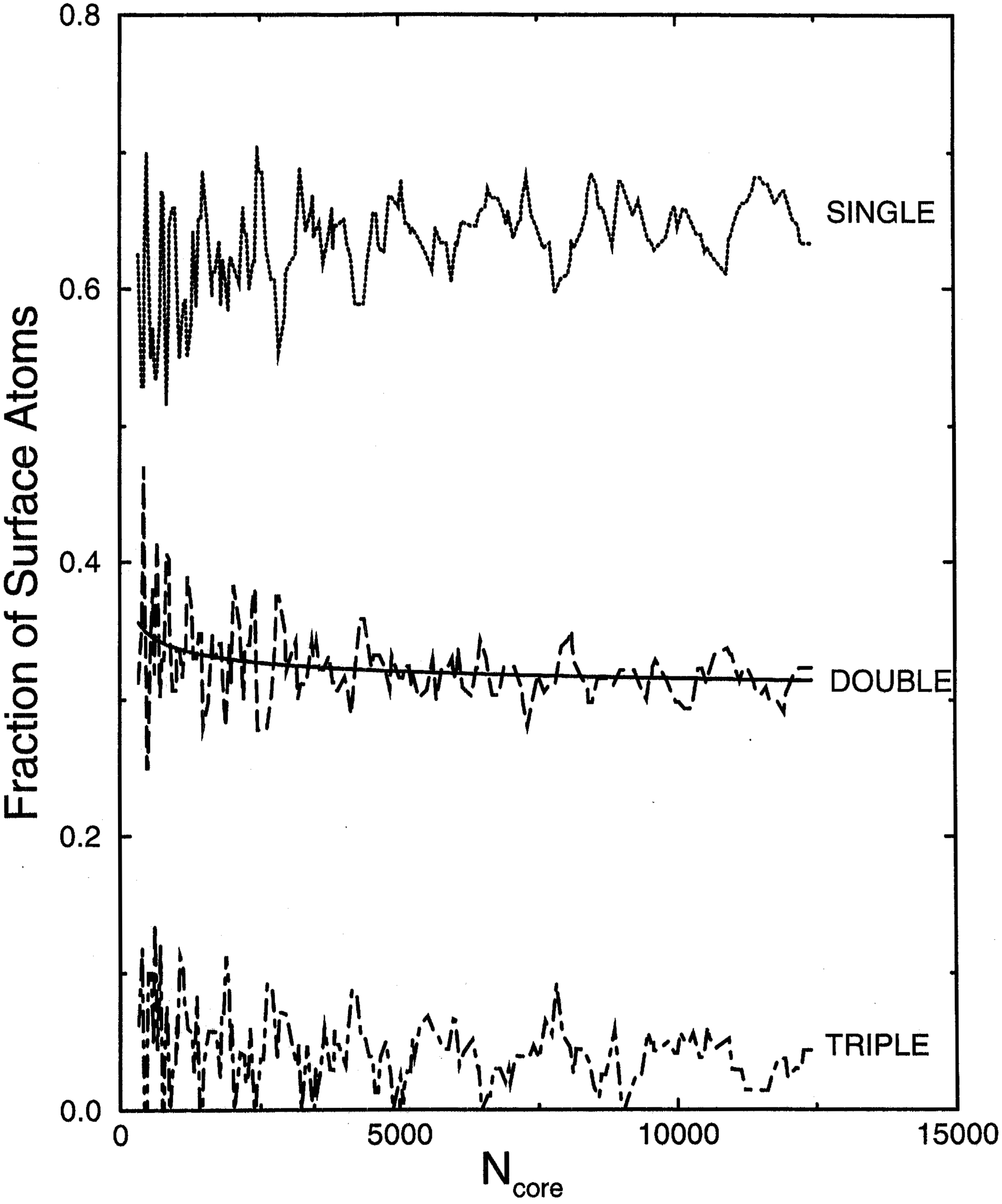
2 = 2 DANGLING BONDS

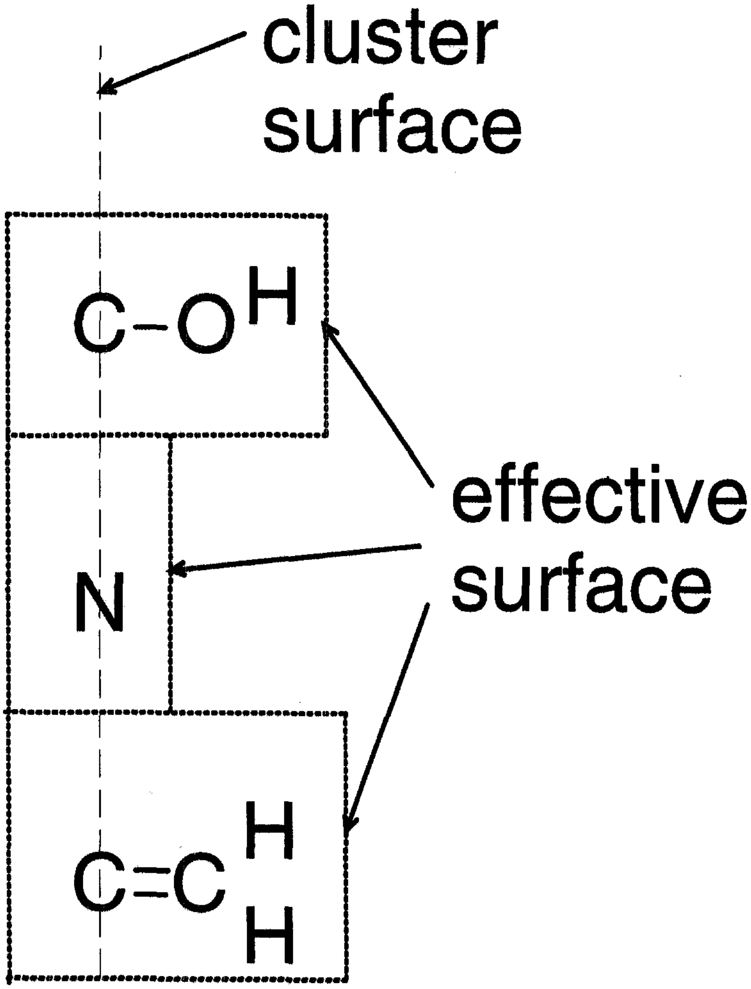


EXAMPLES OF SURFACE GROUPS

note: N without dangling bonds
can substitute for a surface C
with one dangling bond


1.0
0.8
0.6
0.4
0.2
0.0
$N_{surface} / N_{core}$
0
5000
10000
N_{core}


0.8
0.6
0.4
0.2
0.0
0
5000
10000
15000
Fraction of Surface Atoms
N_{core}
SINGLE
DOUBLE
TRIPLE

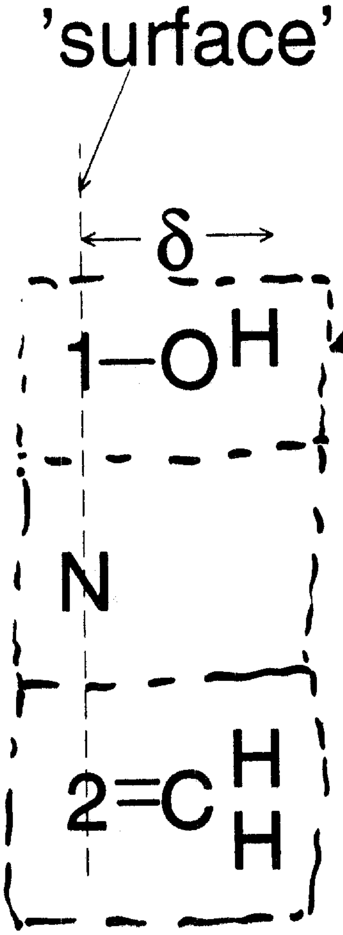

cluster surface
C–OH
N
C=C H H
effective surface

$$G(x_1, \ldots, x_n, P, T)$$

core

Debye

+ cold curve



surface

additive units

Einstein

frequencies from small molecules

Energy

bond strengths

ΔH_f

Volume

geometry $A\delta$

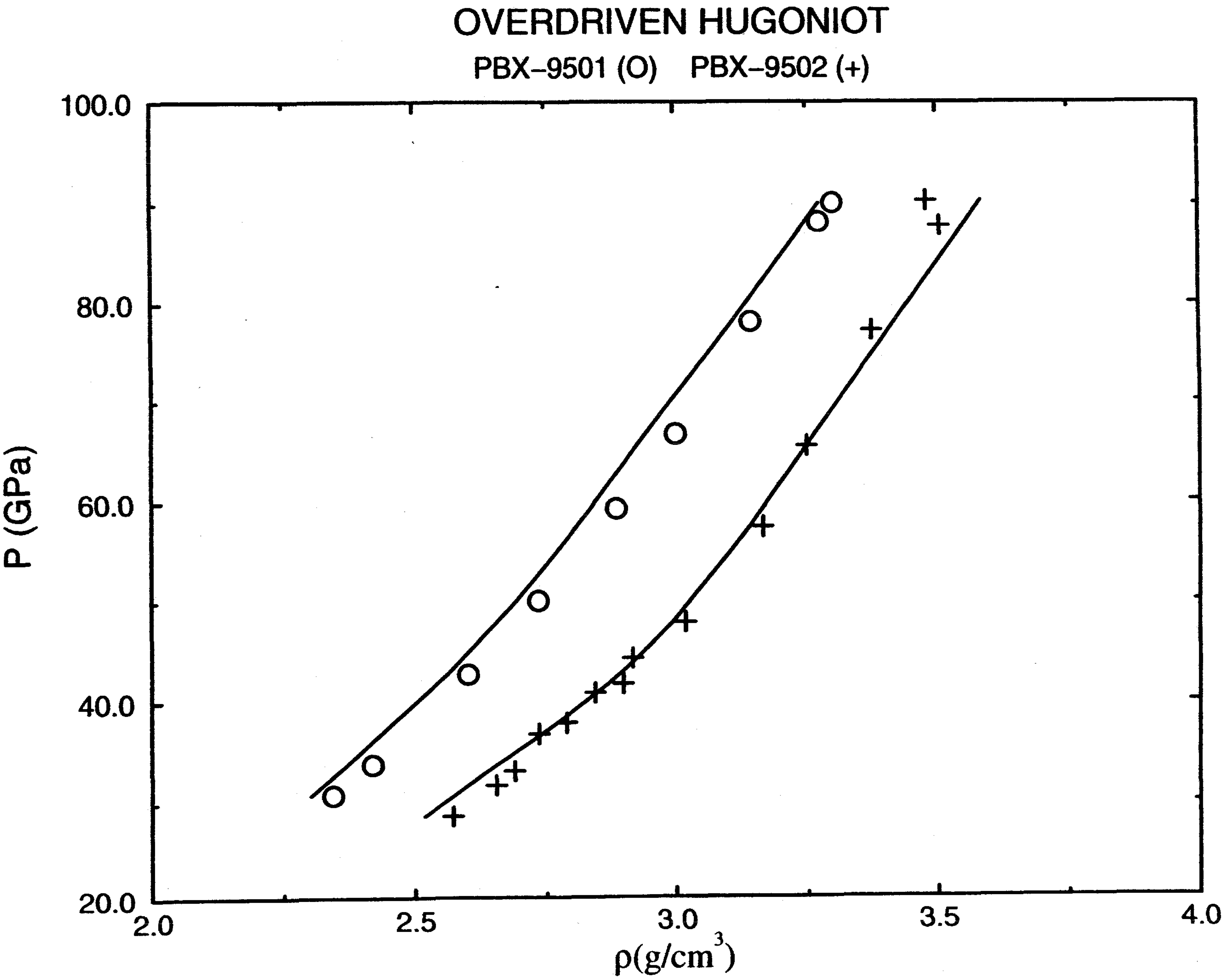
scaled cold curve

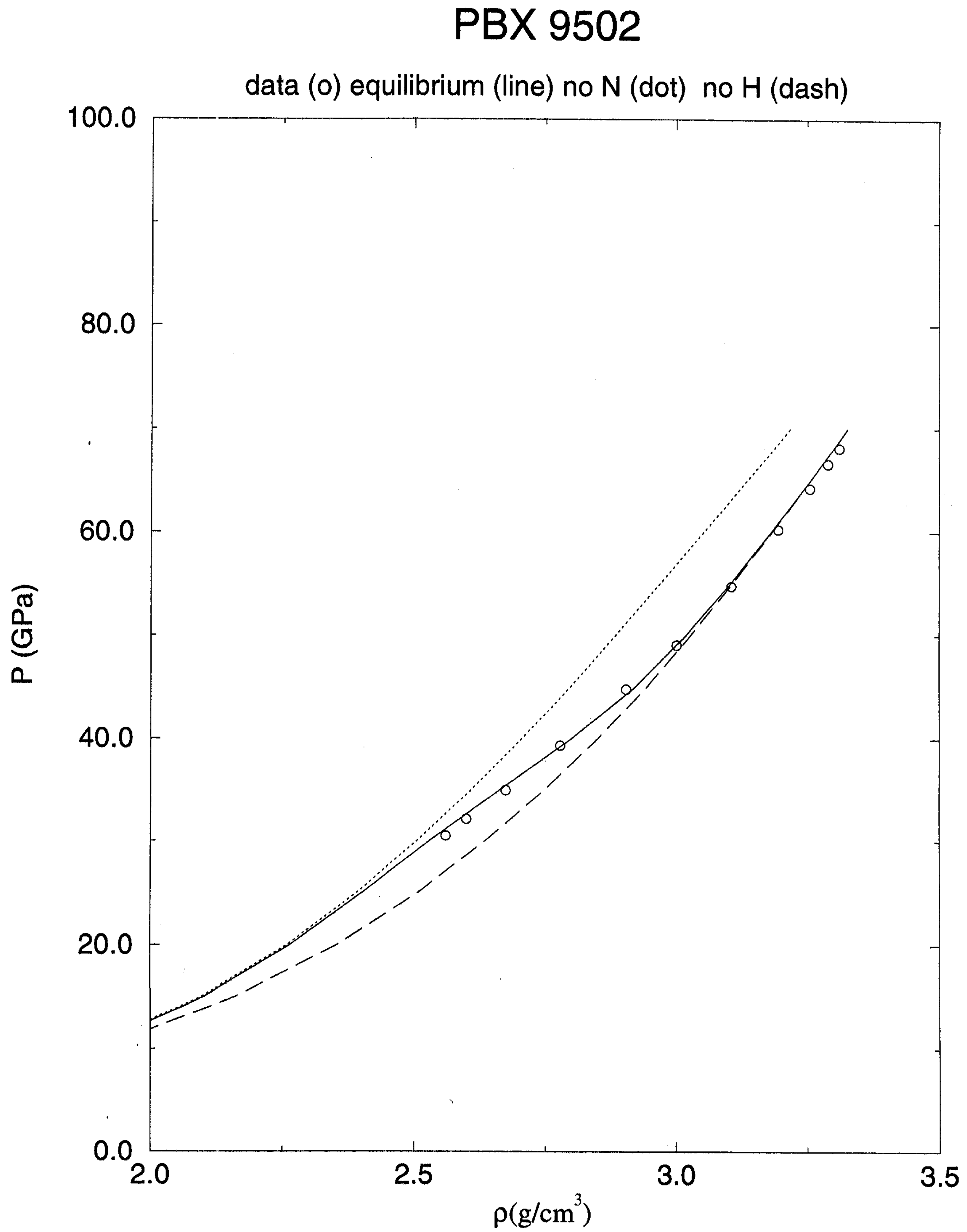
Entropy

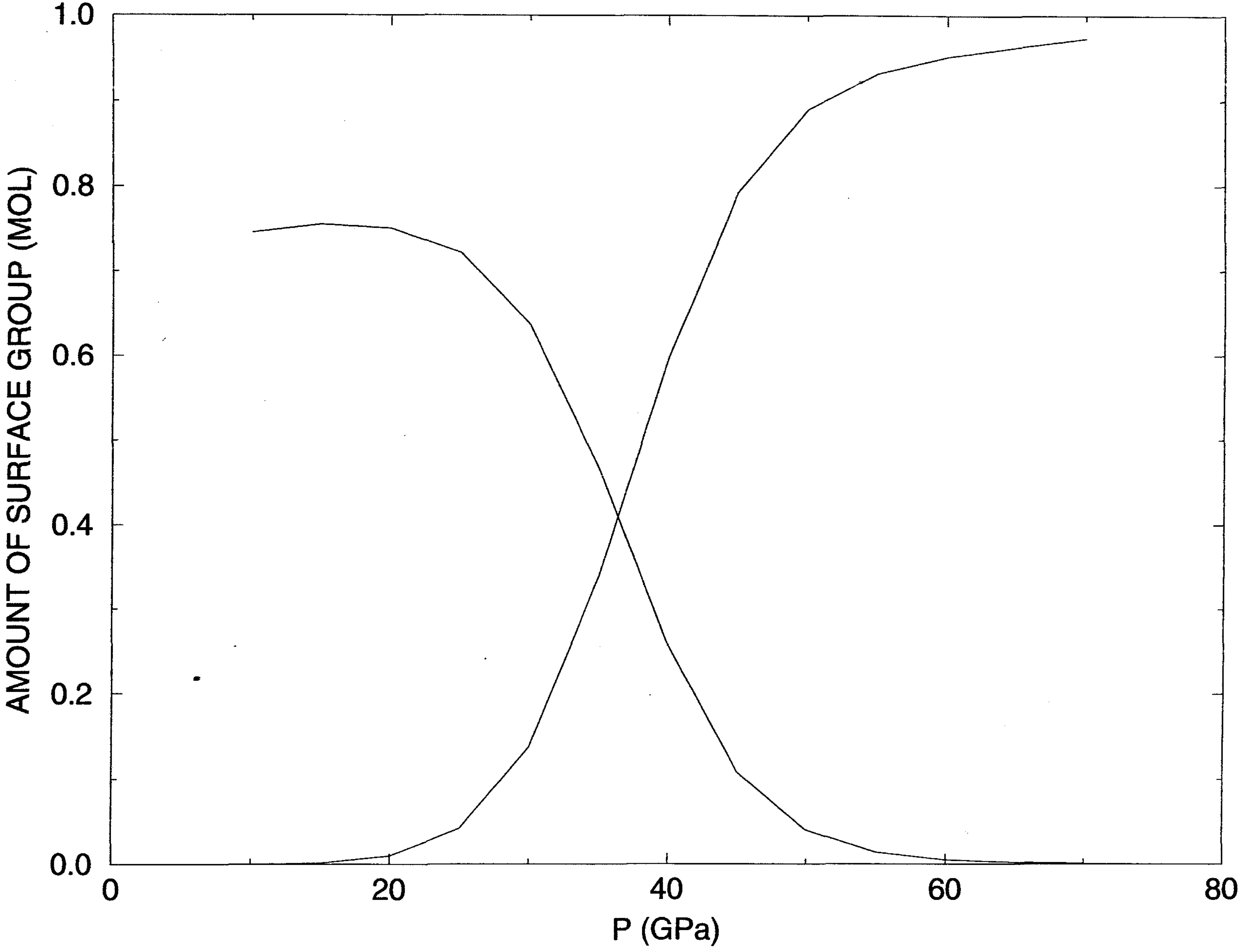
counting

$x_i \ln\left(\frac{x_i}{\bar{x}_s}\right)$

$$\bar{x}_s = \Sigma' x_i = f_s x_c$$

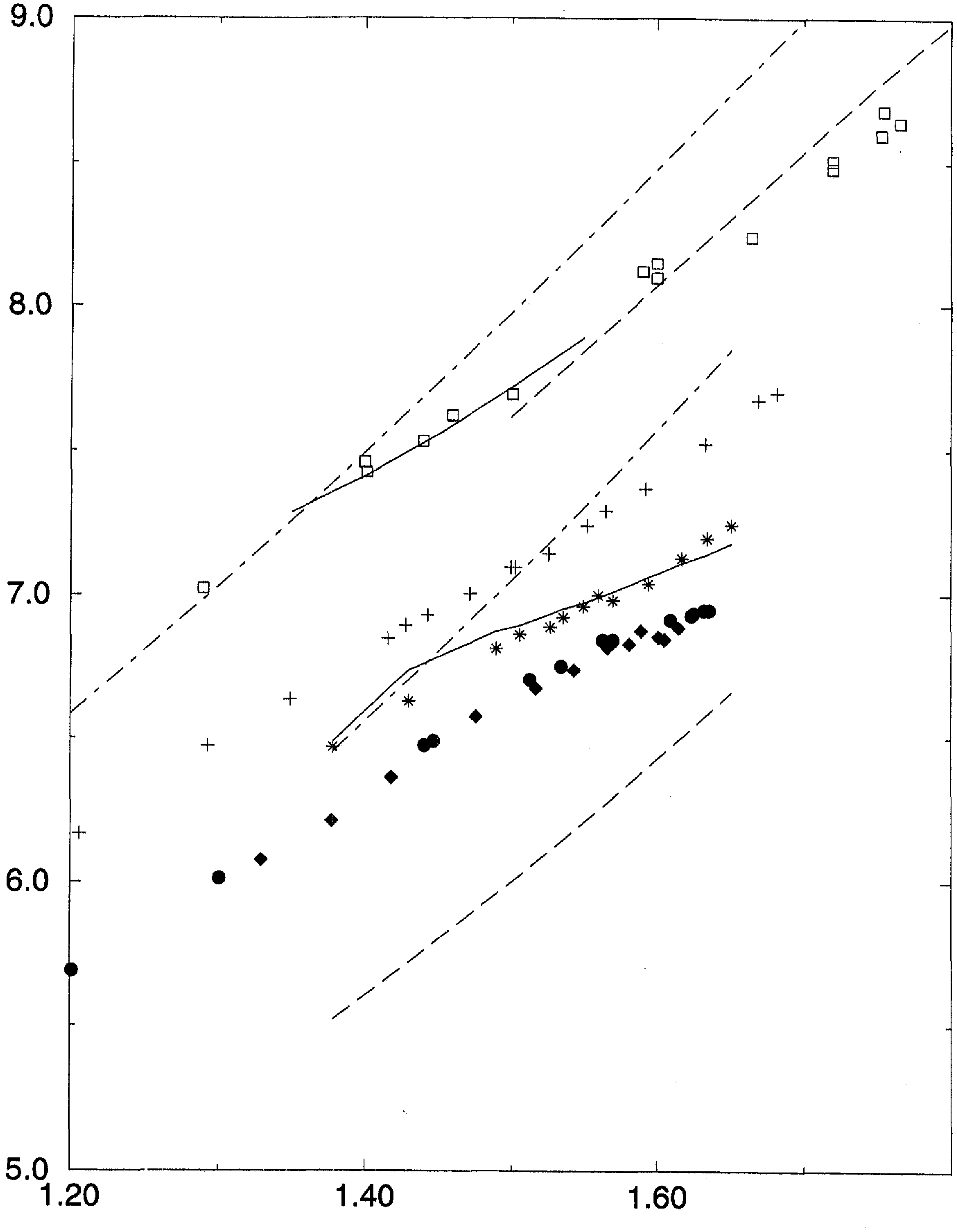

OVERDRIVEN HUGONIOT
PBX-9501 (O) PBX-9502 (+)
P (GPa)
100.0
80.0
60.0
40.0
20.0
2.0
2.5
3.0
3.5
4.0
ρ(g/cm³)


PBX 9502
data (o) equilibrium (line) no N (dot) no H (dash)
P (GPa)
100.0
80.0
60.0
40.0
20.0
0.0
2.0
2.5
3.0
3.5
ρ(g/cm³)



PBX 9502

COMPOSITION OF SINGLE DANGLING BOND SURFACE SITES


9.0
8.0
7.0
6.0
5.0
1.20
1.40
1.60

50/50 RDX/TNT

Equilibrium (line) Diamond (dash) Graphite (chain)