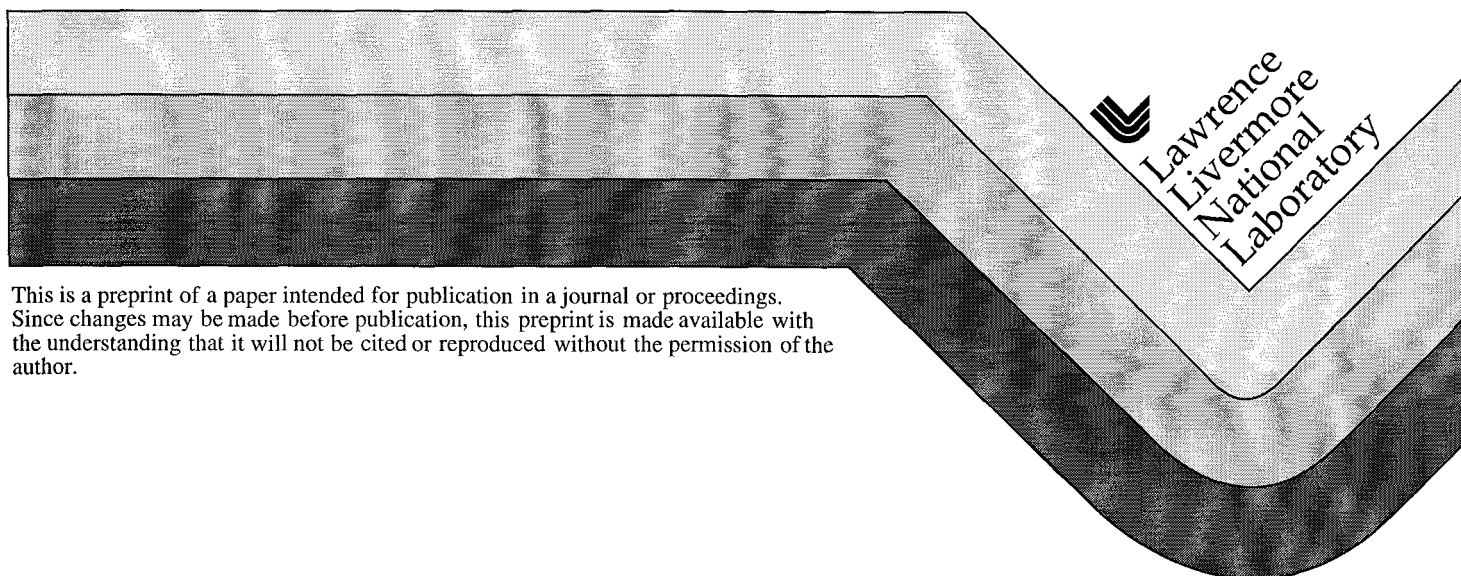


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HUGONIOTS OF AEROGELS INVOLVING CARBON AND RESORCINOL FORMALDEHYDE

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Abstract. Recently, a first-order phase transition is predicted in liquid carbon using atomistic simulation and Brenner's bond order potential. There are also experimental data suggesting a possibility for a first-order phase transition. In light of this, a thermochemical equilibrium code (CHEQ) is used to provide guidance to experiments to find a liquid-liquid phase change in carbon foam and carbon-rich aerogel, resorcinol formaldehyde. Isotherms and Hugoniot were computed based on the previous analysis by van Thiel and Ree. The present calculations predict the liquid-liquid-graphite triple point to be at 5000 K and 5.2 GPa and its critical point to be at 6000 K and 8.8 GPa. The present Hugoniot calculations suggest that the liquid-liquid phase transition may be detected by performing a shock experiment with initial density of approximately 0.15 gm/cm³.

INTRODUCTION

A possible presence of a first-order liquid-liquid phase transition in carbon is investigated with a thermochemical equilibrium code (CHEQ)¹ which fits theoretical free energy models for the three phases (diamond, graphite, and liquid) to experiments. In 1997 Togaya³ showed that the slope of pressure-temperature graphite-melting line is discontinuous at the temperature maximum and hence suggested a possible existence of a liquid-liquid phase change in carbon. In 1999 Glosli and Ree² predicted a first-order phase transition in liquid carbon using atomistic simulation and Brenner's bond order potential. This phase change is associated with density and structural changes. The low-density liquid is predominantly *sp* bonded with little *sp*³ character. The high density liquid is mostly *sp*³ bonded with little *sp* character. Using the CHEQ code¹, we computed the carbon phase diagram, and Hugoniot, which could provide possible experimental conditions where such a liquid-liquid phase transition could be observed.

DESCRIPTION OF CARBON MODEL

A carbon model in CHEQ is developed by van Thiel and Ree⁵⁻⁷. The solid phase is modeled by Grüneisen model. The corresponding liquid phase is modeled with Grover's "scaling" model.⁸ A modified Lindermann model is used in the scaling theory to predict the melting properties. The liquid carbon consists of a mixture of expanded graphitic and diamond-like forms.

Gibbs free energy of carbon liquid mixture is given by:

$$G_{liq} = xG_d + (1-x)G_g + Rt\{x \ln x + (1-x) \ln(1-x) + A(P, x)\}, \quad (1)$$

with

$$A(P, x) = \left[\frac{A_0}{1 + (P/P_0)^{1.5}} \right] x(1-x),$$

where x is the atom fraction of diamond liquid, t is the temperature, R is the gas constant, and the

Gibbs free energies of G_g and G_d are given in Ref. [5]. The two logarithmic terms are the entropy of mixing and $A(P,x)$ is the strain energy between diamond-like sites and graphitic sites. The functional form of $A(P,x)$ allows a decrease in strain energy as the graphitic sites are compressed and lose their specific symmetry. These coefficient of $A(P,x)$, A_o , affects the location of the triple and critical points of liquid-liquid phase transition. We have tried a range of value for A_o from 2.0 to 2.8 and selected $A_o = 2.4$ for our simulation. When A_o is 2.0, liquid-liquid phase transition disappears.

HUGONIOTS OF CARBON AEROGELS

Hugoniots of carbon foams are computed for initial densities ranging from 0.1 to 1.0 gm/cm^3 . Fig. 1 shows the phase diagram and Hugoniots for carbon foam. The critical temperature of liquid-liquid phase transition is located at 6000 K with 8.8 GPa of pressure. The liquid-liquid-graphite triple point is located at 5000 K and pressure of 5.2 GPa. The only Hugoniot that undergoes the liquid-liquid phase transition is the one with initial density of 0.15 gm/cm^3 . This Hugoniot tracks along the graphite-liquid phase transition line, branches out to the liquid-liquid phase transition line, and exits to the liquid phase. The phase diagram is constructed from tracing the phase changes in a series of isotherm calculations by the CHEQ code. The discontinuities in the Hugoniots correspond to the phase transitions.

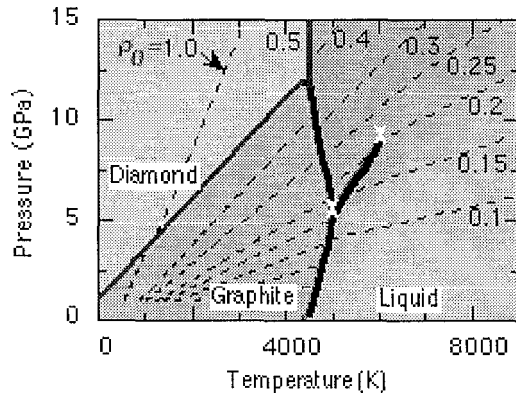


FIGURE 1. Hugoniots of carbon foams with various initial densities. The liquid-liquid-graphite triple point and its critical point are denoted with X. — represents the phase boundary. ---- represents the shock Hugoniots. (ρ_o is in gm/cm^3)

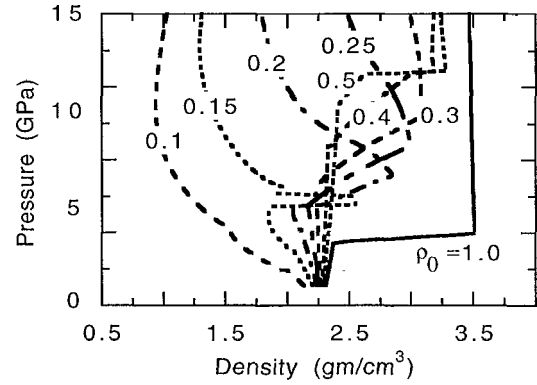


FIGURE 2. Pressure-density curves for carbon foam with initial densities ranging from 0.1 to 1.0 gm/cm^3 . These curves correspond to Hugoniots in Fig. 1. (ρ_o is in gm/cm^3)

Two more figures for carbon foam are obtained from the CHEQ calculations. Fig. 2 shows the pressure-density relations. Under shock compression the carbon can undergo an enormous volume change. This, in turn, produces a large gain in energy and, therefore, high temperature. The sharp horizontal region in the Hugoniot at $\rho_o = 0.15 \text{ gm/cm}^3$ is the signature for liquid-liquid phase transition in carbon foam. The sharp horizontal regions for $\rho_o = 0.15$ and 1.0 gm/cm^3 are the signatures for the liquid-liquid and graphite-diamond phase transition, respectively.

The corresponding shock velocity vs. particle velocity is shown in Fig. 3.

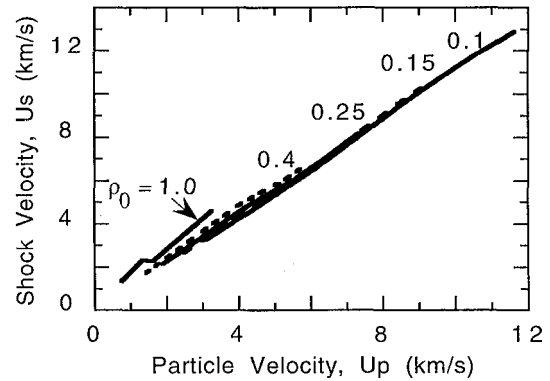


FIGURE 3. Shock velocity vs. particle velocity for shocking carbon foam. These curves correspond to Hugoniots in Fig. 1. (ρ_o is in gm/cm^3)

HUGONIOTS OF RESORCINOL FORMALDEHYDE

Resorcinol formaldehyde is a carbon-rich organics. Our calculation uses its aerogel with composition $C_1H_{0.93}O_{0.35}$ or, by weight %'s of 64.8% carbon, 5.0% hydrogen, 30.0% oxygen. Composition is measured by dynamic flash combustion by Hrubesh. The initial density for resorcinol formaldehyde is about 0.2 gm/cm^3 . The heat of combustion of resorcinol formaldehyde is also measured to be $5326 \pm 27 \text{ cal/mol}$ from combustion calorimetry experiments by Schmidt. The corresponding heat of formation for resorcinol formaldehyde is -216.48 kcal/mol . CHEQ calculations are carried out to obtain the shock Hugoniots and pressure-density relations. The parameter, A_o , is also chosen to be 2.4. Phase diagram is identical to that of carbon foam, since only carbon undergoes the phase transition for the ranges of interest. But the Hugoniots in Fig. 4 have slightly higher slope from that of pure carbon foam. Hugoniot curve for the initial density of 0.15 gm/cm^3 briefly traces the liquid-liquid phase transition of carbon, as shown in the case of carbon foam.

Fig. 5 shows the pressure-density curves for resorcinol formaldehyde. For low-density aerogel (0.15 gm/cm^3), the density goes down initially due to high heat release from the compression.

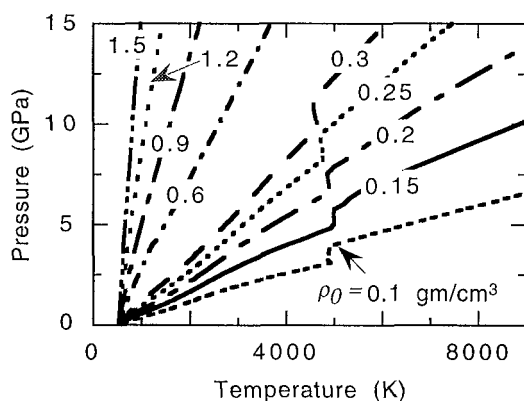


FIGURE 4. Shock Hugoniots of resorcinol formaldehyde for initial densities ranging from 0.1 to 1.5 gm/cm^3 . The Hugoniot for the initial density of 1.5 gm/cm^3 undergoes the liquid-liquid phase transition. The discontinuities in Hugoniots represent the presence of the carbon phase transition.

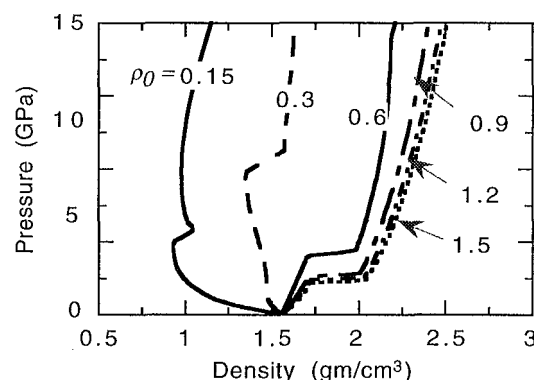


FIGURE 5. Pressure-density curves for resorcinol formaldehyde with initial densities ranging from 0.15 to 1.5 gm/cm^3 .

The discontinuity shown in $\rho_o = 0.15 \text{ gm/cm}^3$ represents graphite-liquid, and liquid-liquid phase transition. The discontinuity shown in $\rho_o = 0.3 \text{ gm/cm}^3$ represents the graphite-liquid phase transition. The pressure-density curves for $\rho_o = 0.6$ - 1.5 gm/cm^3 undergo the graphite-diamond phase change at the discontinuities.

DISCUSSIONS

Carbon foam and carbon-rich aerogel, resorcinol formaldehyde are investigated for a possible presence of the first order phase transition in liquid carbon. CHEQ calculations predict that the shock Hugoniot experiments for an initial density of 0.15 gm/cm^3 has the best chance for observing the liquid-liquid phase transition.

The critical temperature for the liquid-liquid phase transition sensitively depends on the parameter A_o of $A(P, x)$ term in the liquid Gibbs free energy expression. At $A_o = 2.4$, the critical point is located at 6000 K and 8.8 GPa . The liquid-liquid-graphite triple point is located at 5000 K and 5.2 GPa .

The parameter A_o is chosen somewhat arbitrary between the values of 2.0 to 2.8. However we currently do not have any experimental evidence to determine A_o accurately. Therefore, the exact location of the critical temperature for liquid-liquid phase change is still unknown. Experimental effort to determine the liquid-liquid phase transition could clarify this situation.

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