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# Photoacoustic detection of the spinodal decay of carbon

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**The equivalence of the amplitudes of the thermoacoustic pressure and recoil pressure in a graphite surface layer laser vaporised during an irradiation pulse corresponds to reaching the critical point of carbon.**

Transition into the critical state has been considered in optothermodynamics since the early 1970s within the context of the problem of strong heating and compression of compounds under the action of laser irradiation; this problem had been defined and studied in the area of inertial laser thermonuclear synthesis.[1] A transition of this type has been realised experimentally for readily boiling liquids (methanol, ethanol) heated with laser irradiation of millisecond duration; the instant at which the critical state was reached was detected by the effect of liquid opalescence in the critical state[2,3] observed with resolution on the laser pulse time scale. Calculation of the energy deposited and photoacoustic pressure measurements at the instant of reaching the critical point made it possible to estimate the pressure of the substance in the critical state and the enthalpy of its formation. However, the necessity of using high-power and shorter irradiation pulses for heating, melting and evaporation of the compounds, the locality of heating and the opaqueness of the most of materials studied creates a real problem in studies of solids when the observation of the critical state is made by optical or photoacoustic methods; thus far, this problem has not been solved.

In the present work, we studied the evaporation of polycrystalline graphite (PCG) by simultaneous photoacoustic monitoring of both components of the acoustic signal [thermoacoustic and evaporative (recoil) pressure]. The resolution of these components, which is impossible in real time due to diffraction and dissipation of the high-frequency component of the Fourier spectrum of the acoustic signal in the lamellar structure of graphite, was achieved by suppressing the thermoacoustic wave of rarefaction (formed upon reflection of the thermoacoustic wave of compression from the free surface of the target) by the recoil pressure wave of compression. The photoacoustic study was performed on a set-up[4] that enabled measurement of the mean crater depth during a pulse (*X*) as well as the thermoacoustic and recoil pressures. A portion of irradiation of the second harmonics of a pulse Nd:YAG laser [pulse energy 5 mJ in the $TEM_{00}$ mode (stability 6%), pulse length (FWHM) 25 ns, pulse repetition rate 12.5 Hz] was fed to a photodiode and a pyroelectric in order to synchronise the system of recording and control of laser irradiation energy at each pulse. After reducing the main irradiation to a required magnitude and focusing, it was directed to a target normally to the surface. Absorption of irradiation in the graphite target created a surface source of ultrasonic waves, which were recorded at the rear side of the target in the idle mode by means of a 'thick' piezoelectric sensor and an oscilloscope.

According to the optothermodynamics theory,[5] during the evaporation of a material under the action of laser irradiation of nanosecond duration, there exists thermal equilibrium on the surface due to compensation of the flux of irradiation energy onto the surface from the environment by a reverse flux of energy transferred by the material removed by the thermal mechanism. However, equilibrium of mass transfer and mechanical equilibrium on the surface does not exist, since mass transfer is unidirectional.

In this case, the first compression wave of the material, which corresponds to the thermoacoustic pressure $P_{ta}$, is created by a change in the internal pressure of the condensed phase due to changes of its density and temperature and is accompanied by a rarefaction wave appearing upon reflection of the compression wave from the free surface of the target. The

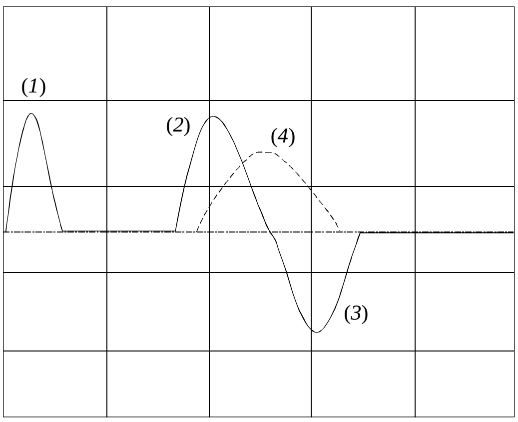


**Figure 1** Shape of the acoustic signal: (*1*) synchronisation pulse; (*2*) thermoacoustic pulse of compression; (*3*) thermoacoustic pulse of rarefaction; (*4*) evaporation pulse of compression.

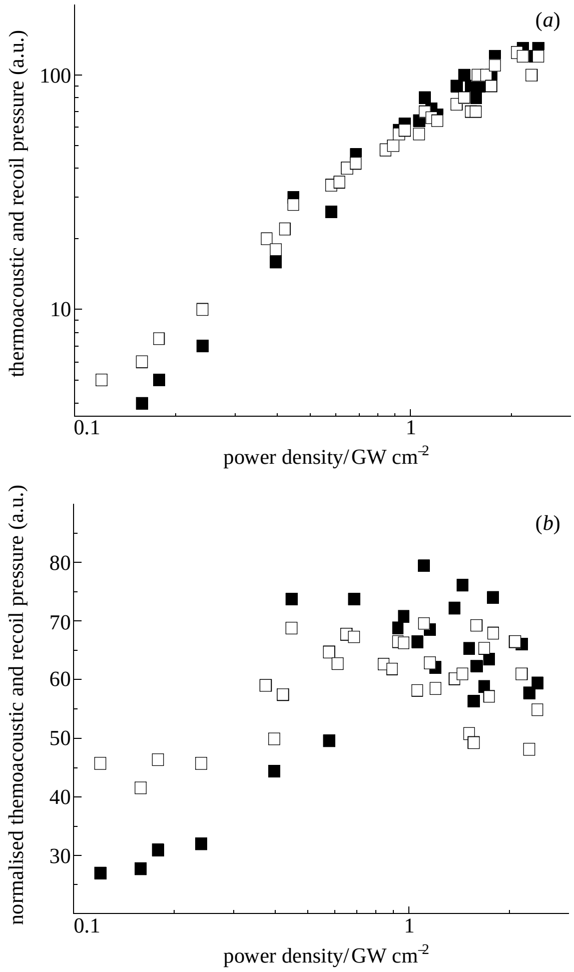


**Figure 2** (*a*) Dependences of $P_{ta}(I_0)$ and $P_{rec}(I_0)$ (light and dark squares) for PCG. (*b*) Dependences of normalised values $P_{ta}/I_0$ and $P_{rec}/I_0$.

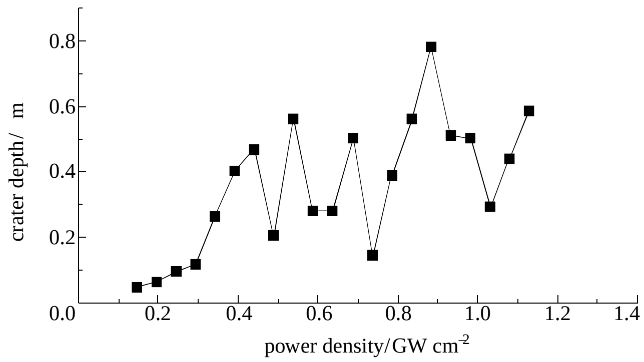


**Figure 3** Dependence of mean crater depth per irradiation pulse, $X(I_0)$ for PCG.

experimentally recorded bipolar pulse of thermoacoustic pressure in the liquid corresponds to the existence of both waves upon laser generation of sound on a free surface (Figure 1) and is described for a thermally 'thick' absorbing layer by the following expression:[6]

$$P_{ta}(t) = \rho_l C_l V_{vib}(t) = \frac{A(Y)\beta}{\alpha C_p} I_0 \frac{df}{dt} \qquad (1)$$

where $V_{vib}$ is the vibrational velocity; $\rho_l$ and $C_l$ are the liquid density and sound speed for the liquid; $\alpha$ is the coefficient of optical absorption; $\beta$ and $C_p$ are coefficients of thermal expansion and isobaric specific heat of liquid carbon; $A(Y)$ is the absorbance of a melted film at a given thickness $Y$; $I_0$ is the amplitude of normal distribution of laser power density over the surface; and $df/dt$ is the derivative of the time profile of a laser pulse (in our case, a Gaussian shape).

In turn, the gasodynamic recoil pressure of products of target evaporation in a near-surface Knudsen layer, $P_{rec}$, creates a compression wave on the target surface (Figure 1), whose pressure equals one half of the saturated vapour pressure under static evaporation conditions at the same instantaneous surface temperature[5]

$$P_{rec}(t) = \rho_{vap}(t)[V_{vap}(t)]^2 = \rho_s V_{evap}(t) V_{vap}(t) = 0.5 P_{sat}[T(t)] \qquad (2)$$

where $V_{vap}$ and $\rho_{vap}$ are the velocity and the density of the vapour; $\rho_s$ is the density of the graphite target; and the movement rate of the evaporation frontier in it, $V_{evap}$, equals[7]

$$V_{evap}(t) \cong \frac{A(Y)I(t)V_m}{{}_{evap}H(p, T) + H(P_{tr}, T_{tr} \rightarrow P, T)} \qquad (3),$$

where ${}_{evap}H(P, T)$ is the heat of evaporation, and $P_{tr}$ and $T_{tr}$ are parameters of the triple point of carbon.

In qualitative respects, the above expressions describe well the linear behaviour of experimental dependences $X(I_0)$, $P_{ta}(I_0)$ and $P_{rec}(I_0)$ in the region from 0.15 to 0.3 GW cm$^{-2}$ (Figures 2,3) corresponding to the subcritical region of the carbon evaporation curve.[7]

At power density $I_0 > 0.3$ GW cm$^{-2}$, an abrupt increase in efficiency of acoustic generation by the thermoacoustic and evaporation mechanisms is observed, while the recoil pressure increases considerably faster and becomes the same as the thermoacoustic pressure at 0.3–0.4 GW cm$^{-2}$ (Figure 2), completely suppressing the thermoacoustic rarefaction wave. Previously, an analogous effect has been observed in low temperature boiling liquids[8] and has been related to surface optical breakdown.

We relate this fact to the following: at a certain moment during a laser pulse whose maximum power density is within 0.3–0. 4 GW cm$^{-2}$, the thermodynamic state of the carbon melt surface layer becomes unstable at the intersecting spinodal curve of carbon. The latter implies hydrodynamic expansion of material of the target into the environment instead of its evaporation. Therefore in this case thermoacoustic compression pressure is the stagnation internal pressure of the carbon melt before expansion and recoil pressure is the gasodynamic external pressure during expansion. Their amplitudes under these conditions become equal in accordance with the known Bernoulli equation.

The non-linear increase in the velocity of movement of the evaporation frontier above 0.3 GW cm$^{-2}$ observed for experimentally measured parameters of crater depth ($X$) and recoil pressure of destruction products $P_{rec}$ (Figures 2,3) correlates with the formation and spinodal decay of the labile state of carbon, and it can thus be explained by the abrupt decrease in the thermal effect of removal of target material in the vicinity of the spinodal curve on the state diagram.

Thus, the new photoacoustic technique for identifying the spinodal decay of carbon upon laser evaporation of graphite based on $P_{ta}/P_{rec}$, as suggested in this paper, makes it possible to study near-critical phenomena for refractory and opaque materials upon local laser heating of the target.

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