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particle production in cosmological models has several advantages. It takes the back reaction of the produced particles into account. Regularization can be accomplished in the action itself rather than in quantities of a more complicated tensorial character such as the stress-energy tensor. Finally, it lends itself naturally, as here, to approximation schemes which can be clearly related to the basic quantum-mechanical law for amplitudes, Eq. (1). It would be of great interest to apply this method to more general and more physically realistic cosmological models including anisotropies.

[1]For reviews of the large literature on this subject, see L. Parker, in Proceedings of the Second Latin American Symposium on Relativity and Gravitation, Caracas, Venezuela, 1975 (to be published); V. N. Lukash, I. D. Novikov, A. A. Starobinsky, and Ya. B. Zeldovich, Nuovo Cimento, 35B, 293 (1976). For a more recent work specifically on graviton production in homogeneous isotropic cosmologies, see B. L. Hu, to be published.

[2]For a review of the functional-integral formulation of field theory and of the effective potential, see E. Abers and B. W. Lee, Phys. Rep. 9C, 1 (1973).

[3]See, e.g., E. M. Lifshitz and I. M. Khalatnikov, Advan. Phys. 12, 185 (1963).

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Picosecond Dephasing of Coherently Excited Vibrations in Liquid N₂-Ar Mixtures

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Vibrational-dephasing times have been measured in mixtures of liquid N_2 and Ar. The correlation time of the molecular motion initiating the dephasing process is calculated to be 2.2 and 4.6 ps in pure N_2 and pure Ar, respectively. These rather long correlation times suggest that the dephasing results from the average force field determined by the number of nearest-neighbor molecules.

Recently it has been shown that after a coherent excitation of molecular vibrations by stimulated Raman scattering (SRS), the dephasing of the vibrations can be probed directly by measuring the intensity of the coherent anti-Stokes Raman scattering as a function of the delay between excitation and probe pulse.[1,2] By this method the vibrational-dephasing time has been obtained for a number of pure liquids.[2-4]

The dephasing of the coherent excited ensemble is the result of a modulation of the vibrational transition frequencies by stochastic perturbations which arise from the intermolecular interactions of the excited molecules with their individual surroundings. The modulation itself is determined by the dynamics of the molecular motions in the liquid.

Several descriptions have been developed to relate the dephasing time to a vibrational correlation function.[2,5-7] Recently, Rothschild[7] gave an analysis in terms of molecular-dynamics (M.D.) calculations for liquid nitrogen, a Lennard-Jones liquid for which the thermodynamical properties are reasonably understood by M.D. calculations. Using the results of M.D. calculations for calculating the mean-square frequency displacement, a correlation time τ_c can be calculated in case of a fast modulation of the oscillator frequencies. By comparison with the M.D. calculations it may then be determined which type of molecular motion is responsible for the vibrational dephasing.

In order to investigate the influence of the molecular environment upon the dephasing of nitrogen, the dephasing times were measured in liquid

mixtures of nitrogen and argon. Argon as a sol-
vent has the advantage that it cannot trap the vi-
brational excitation of the nitrogen molecules.
Moreover, detailed M.D. calculations of argon
are present in literature,[8] which allows a compar-
ison of the dynamics in pure nitrogen with that in
pure argon.

The liquid mixture were prepared by succes-
sive condensation of nitrogen and argon gas of
highest purity in a calibrated sample cell. The
mole fraction of Ar in the mixtures was varied
between 0 and 0.96.

For the coherent excitation of the molecular
vibrations via SRS, the second harmonic of a
mode-locked neodymium-glass laser was used.
The fundamental (1060 nm) was used as a probe
pulse. Values for the pulse duration of 6–8 ps
were obtained from two photon fluorescence mea-
surements. The same pulse duration is observed
from the anti-Stokes Raman signal measured for
cyclohexane (Fig. 1) and for ethanol from which
it is known[1] that the dephasing time is 0.26 ps.
The decay of the Raman signal therefore follows
the laser pulse, which in turn gives the time-res-
olution limit of the picosecond SRS method. The
apparatus is similar to the experimental system
used by Von der Linde, Kaisen, and Laubereau.[1]
A single pulse is selected from the front of a
pulse train of the mode-locked laser operating in
the TEM$_{00}$ mode. Two etalons in the oscillator
cavity assure the pulse to be nearly transform
limited which is, as has been pointed out by Lau-
bereau,[3] essential for obtaining meaningful exper-
imental results.

After amplification and frequency doubling, the
infrared and the green pulse are separated and
their intensities are monitored by means of pho-
todiodes. The infrared pulse travels through a
variable delay system before it probes the phase
coherence of the molecular vibrations generating
a coherent anti-Stokes light pulse at 850 nm under
phase matching conditions. The intensity of the
latter is measured by a GaAs photomultiplier at-
tached to a grating monochromator.

Unfortunately, the reproducibility of the pico-
second SRS experiments becomes unsatisfactory
for mole fractions beyond 0.65. For this region
the linewidths of the incoherently scattered Ra-
man bands were measured with a 1.5-m Jobin-
Yvon monochromator with a holographic grating
(2400 g/mm) used in double passage (measured
resolution 350.000). The Raman signal was gen-
erated by the 514-nm line of a single-frequency
continuous-wave argon-ion laser.

A typical decay curve of the anti-Stokes probe
scattering signal is shown in Fig. 2. The intensi-
ty of the coherent anti-Stokes Raman signal,[9] de-
creases exponentially with the time interval be-
tween the green and the infrared pulse. The de-
phasing time is obtained from the exponential
slope. The points in this figure are the average
of ten individual measurements.

Figure 3 shows the influence of the argon con-
centration upon the vibrational-dephasing time
for argon concentrations up to 65 mol% Raman
linewidth measurements were carried out in the
whole concentration range. The dephasing time
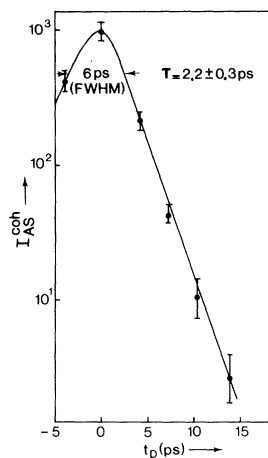τ_d has been calculated from the linewidth $\Delta\sigma$ (full

FIG. 1. Anti-Stokes Raman signal I_{AS}^{coh} for cyclo-
hexane as a function of the delay time t_D, showing the
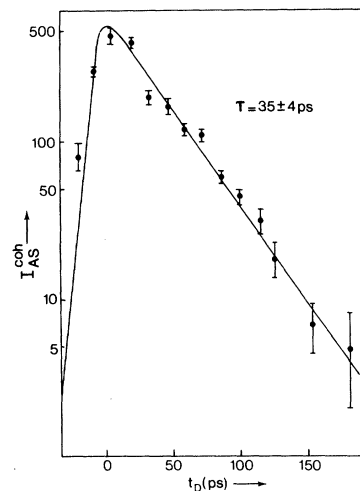time resolution of the experimental setup.

FIG. 2. Semilog plot of the coherently scattered anti-
Stokes Raman signal I_{AS}^{coh} vs the delay time t_D. X_{Ar}
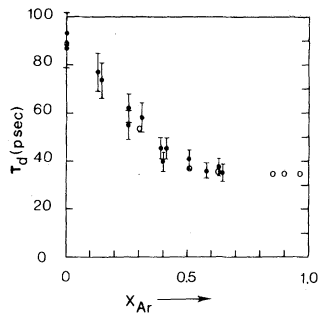= 0.64.

FIG. 3. Vibration-dephasing time τ_d of N_2 in liquid N_2-Ar mixtures as a function of the mole fraction of argon X_{Ar}. Solid circles are from coherent anti-Stokes Raman measurements. Open circles are from isotropic spontaneous Stokes Raman linewidths. The inaccuracy in the determination of the mole fraction is ± 0.03.

width at half-maximum) of the Raman line which has a Lorentzian shape:

$$\tau_d^{-1} = 2\pi c \Delta \sigma. \tag{1}$$

The obtained values varied from 0.058 ± 0.006 cm cm^{-1} in pure N_2 to 0.15 ± 0.01 cm^{-1} in N_2 with 96% Ar. It can be seen in Fig. 3 that the results of both methods fit very well. This means that the Raman linewidth is determined by vibrational-dephasing processes only.

The energy relaxation time in pure liquid nitrogen has been established recently to be 1 s.[10] Thus energy relaxation will not contribute to the measured dephasing times.

Phase relaxation can also occur by transfer of the vibrational excitation to neighboring molecules in the vibrational ground state. This process will be slowed down when argon is substituted for nitrogen. Actually an increase in the dephasing rate has been observed with increasing argon concentration. On the other hand, this does not prove that V-V transfer will not contribute to the actual dephasing rate. However, an estimate of the energy transfer rate has been made[7] which shows that the time scale of this process is a few orders of magnitude larger than that of the experimentally observed dephasing rates. Therefore, in the following the experimental results are analyzed only in terms of stochastic secular perturbations of the surrounding molecules.

In the fast modulation limit (following from the Lorentzian shape of the spontaneous Raman band[11,12]), the vibrational correlation function obtains the form[13]

$$\varphi = \exp[-\langle \{\omega(0)\}^2 \rangle \tau_c t]. \tag{2}$$

TABLE I. Measured vibrational-dephasing times τ_d. Calculated mean-square frequency displacement of the transition frequency $\langle \{\omega(0)\}^2 \rangle$ and modulation correlation time τ_c of N_2 in pure N_2 and pure argon.

	$\langle \{\omega(0)\}^2 \rangle$ (rad/sec)^2	τ_d (psec)	τ_c (psec)
Pure N_2	2.50×10^{21}	87	2.2
Pure Ar	3.12×10^{21}	35	4.6

In this, $\langle \{\omega(0)\}^2 \rangle$ is the mean-square frequency displacement of the transition frequencies due to the intermolecular perturbations and τ_c is the correlation time of the molecular motions determining the dephasing rate

$$\tau_d = [2\langle \{\omega(0)\}^2 \rangle \tau_c]^{-1}. \tag{3}$$

$\langle \{\omega(0)\}^2 \rangle$ can be obtained from an expression given by Bratos and Marechal,[14] describing the frequency shift of an anharmonic oscillator in terms of the intermolecular potential with respect to the normal coordinate of the oscillator (and not the center-of-mass separation as has been done in Ref. 7). The averaging over the ensemble was performed by using the atomic pair-correlation function obtained from M.D. calculations.[8,15] In the case of N_2 in Ar, the atomic pair-correlation function was shifted over $\sigma_{N-Ar} - \sigma_{Ar-Ar} = 0.045$ Å.

To obtain an estimate of τ_c from (3), $\langle \{\omega(0)\}^2 \rangle$ was only calculated for perturbing nitrogen molecules having their molecular axis perpendicular to the axis of the reference molecule and passing through its center of gravity. Table I gives the calculated correlation times for pure liquid nitrogen and argon. The first feature emerging from Table I is that the correlation times of the molecular motions determining the dephasing are an order of magnitude larger than the correlation times for rotational reorientation, which are about 10^{-13} s.[8,15,16]

From M.D. calculations[16] it follows that the autocorrelation of the fluctuations of the number of nearest-neighbor molecules indicates that a persistant clustering is present on a time scale of 10^{-12}-10^{-11} s. Also from a calculation of the cross-correlation factor between two molecules,[17] it was found that the correlation of motion of the reference molecule and its nearest neighbors (in contrast with more-distant neighbors) was remarkably strong on a time scale of 10^{-12}-10^{-11} s. Moreover, in the calculations of $\langle \{\omega(0)\}^2 \rangle$ it was found that the contribution of the second solvent layer was only a few percent of the effect from

the perturbation from the first solvent layer.
These calculations then suggest that the vibration-
al dephasing is mainly determined by the average
force field that the excited molecules experience
from the fluctuating number of nearest neighbors.
Also in agreement with this picture is the increse
in the correlation time (Table I) with increasing
molecular interaction.[17]

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Colliding Impulsive Gravitational Waves

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We formulate the problem of colliding plane gravitational waves with two polarizations
as the harmonic mappings of Riemannian manifolds and construct an exact solution of the
vacuum Einstein field equations describing the interaction of colliding impulsive gravita-
tional waves which in the limit of collinear polarization reduces to the solution of Khan
and Penrose.

In this Letter we adopt an approach to the Ein-
stein field equations of gravitation which is based
on the theory of Eells and Sampson of harmonic
mappings of Riemannian manifolds.[1] We had
earlier pointed out the connection between these
problems[2,3] and it seems worthwile to remark
that the theory of harmonic mappings of Riemann-
ian manifolds is also applicable to a wide variety
of problems in other branches of physics. In
particular, we can readily recognize the Nambu
string, solitons, nonlinear σ model, and the
Heisenberg ferromanget in the expression of
Eells and Sampson for their invariant functionals
of the mapping. The formulation of a problem in
terms of harmonic mappings provides us with a
powerful formalism for the discussion of a num-

ber of questions ranging from the construction
of exact solutions to considerations of topology
related to the index of the mapping, and its ad-
vantage lies in the direct geometrical insight it
brings into the problem. We shall now present a
new exact solution of the vacuum Einstein equa-
tions which is of physical interest and which was
obtained by the use of these techniques.

Penrose[4] has introduced the notion of impulsive
gravitational waves where space-time is flat
everywhere except along a hypersurface with the
Riemann tensor suffering a δ-function discontinui-
ty at this surface. Here we shall be concerned
with the case where the discontinuity surface is a
null plane and the impulsive wave is then a famili-
ar p-p wave.[5] For purely impulsive gravitational