$$C(\tau) = C_{\text{phonon}}(\tau) + C_{\text{roton}}(\tau) \, ,$$

$$\frac{\partial \gamma(\tau)}{\partial \tau} = \frac{1}{\rho} \frac{\partial}{\partial \tau} \left[\rho_n(\tau) \right] \tag{3}$$

$$= \frac{1}{\rho} \frac{\partial}{\partial \tau} \left[\rho_{n\,\text{phonon}}(\tau) + \rho_{n\,\text{roton}}(\tau) \right] \, ,$$

where to a good approximation

$$C_{\text{phonon}}(\tau) = 2\pi^2 k^4 \tau^3 / 15 \rho \hbar^3 u^3 \, ,$$

$$\rho_{n\,\text{phonon}}(\tau) = 2\pi^2 k^4 \tau^4 / 45 \hbar^3 u^5 \, ,$$

$$C_{\text{roton}} = \frac{2\mu^{1/2} p_0^2 \Delta^2}{(2\pi)^{3/2} \rho \hbar^3 k^{1/2} \tau^{3/2}} \tag{4}$$

$$\times \left[1 + \frac{k\tau}{\Delta} + \frac{3}{4}\left(\frac{k\tau}{\Delta}\right)^2 \right] e^{-\Delta/k\tau} \, ,$$

$$\rho_{n\,\text{roton}} = \frac{2\mu^{1/2} p_0^4}{3(2\pi)^{3/2}(k\tau)^{1/2}\hbar^3} e^{-\Delta/k\tau} \, ,$$

where Δ, p_0, μ are the usual excitation spectrum

parameters and u is the speed of sound. Putting these quantities into Eq. (2) and remembering that $\tau = \frac{4}{3} T$, we obtain the line labeled τ in Fig. 1 which is the same as the theoretical core radii determined from Pollock's theory presented in Ref. 1. The vortex-core radii determined from the phonon excitations alone are shown as the dashed line in Fig. 1. It can be seen that whereas rotons contribute little to bulk fluid thermodynamic properties below 0.5 °K, they begin to influence the vortex-core region in Pollock's theory as low as 0.35 °K.

One might argue that the thermodynamic quantities C and ρ_n ought to be calculated at the bulk temperature T rather than the "effective" temperature τ. In our opinion, this runs counter to the philosophy of the model but, in any event, this approach leads to the curve labeled T in Fig. 1. Although closer to the experimental data, it still is in gross disagreement with it.

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Shorter Route to the Mazenko Memory Function*

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The memory function associated with the phase-space density correlation function has previously been calculated in the low-density limit by Mazenko. In this paper a simple, classical method of arriving at his primary result is pointed out. The application to self-correlations is also noted.

A considerable amount of attention has recently been devoted to the classical correlation function,

$$S(\vec{r} - \vec{r}', \vec{p}\,\vec{p}', t - t') = \langle f(\vec{r}\,\vec{p}\,t) f(\vec{r}'\,\vec{p}'\,t') \rangle$$
$$- \langle f(\vec{r}\,\vec{p}\,t) \rangle \langle f(\vec{r}'\,\vec{p}'\,t') \rangle \, , \tag{1}$$

where $f(\vec{r}\,\vec{p}\,t)$ is the density in phase space,

$$f(\vec{r}\,\vec{p}\,t) = \sum_i \delta(\vec{r} - \vec{r}_i(t)) \delta(\vec{p} - \vec{p}_i(t)) \, , \tag{2}$$

and the sum extends over all particles in the system. In order to determine S without the occurrence of unphysical secular effects, one developes ap-

proximations for its memory function φ, which is the kernel in the Langevin-like equation,

$$\left(\frac{\partial}{\partial t} + \frac{\vec{p}}{m} \cdot \vec{\nabla} \right) S(\vec{r}, \vec{p}\,\vec{p}', t) = \int_0^t d\bar{t} \int d^3\bar{r}\, d^3\bar{p}$$
$$\times \varphi(\vec{r} - \bar{r}, \vec{p}\,\bar{p}, t - \bar{t}\,) S(\bar{r}, \bar{p}\,\vec{p}', \bar{t}\,) \, . \tag{3}$$

The fact that S satisfies an equation of this form[1] is well known. At least two useful approximations to φ have appeared in the recent literature: a weak-coupling expansion by Akcasu and Duderstadt[2]

and Forster and Martin,[3] and an expansion to lowest order in the density by Mazenko.[4]

The work of Mazenko has received particular attention because it constitutes a generalization of the linearized Boltzmann collision kernel to arbitrary wavelengths and frequencies. However, his calculation is a formidably difficult one. Because of the usefulness of his result, it seems of interest that the result can also be obtained by a much shorter method. It is hoped that such a derivation might serve to make his calculation more accessible.

In this paper a short cut for obtaining the Mazenko memory function is pointed out. Roughly speaking, it consists of expanding each term in (3) and reading off the coefficients in the expansion of φ. More about the method is said below. Before proceeding, we should emphasize that Mazenko has accomplished much more than a derivation of the memory function. He has also shown, among other things, that it satisfies certain sum rules, that it reduces to the linearized Boltzmann collision kernel in the appropriate limit, and that it is consistent with the conservation laws.[5] The present discussion does not add to these important topics.

The general procedure is as follows. Fourier and Laplace transforms are applied to (3), according to

$$S(\vec{\mathbb{k}}, \vec{\mathbb{p}}\vec{\mathbb{p}}', t) = \int d^3 r\, e^{-i\vec{\mathbb{k}}\cdot\vec{r}}\, S(\vec{r}, \vec{\mathbb{p}}\vec{\mathbb{p}}', t) ,$$
$$S(\vec{\mathbb{k}}, \vec{\mathbb{p}}\vec{\mathbb{p}}', z) = i \int_0^\infty dt\, e^{izt}\, S(\vec{\mathbb{k}}, \vec{\mathbb{p}}\vec{\mathbb{p}}', t) , \tag{4}$$

to give

$$\left(z - \frac{\vec{\mathbb{p}}\cdot\vec{\mathbb{k}}}{m} \right) S(\vec{\mathbb{k}}, \vec{\mathbb{p}}\vec{\mathbb{p}}', z) + S(\vec{\mathbb{k}}, \vec{\mathbb{p}}\vec{\mathbb{p}}', t=0)$$
$$= \int d^3\bar{p}\, \varphi(\vec{\mathbb{k}}, \vec{\mathbb{p}}\vec{\mathbb{p}}, z)\, S(\vec{\mathbb{k}}, \vec{\mathbb{p}}\vec{\mathbb{p}}', z) . \tag{5}$$

Therefore the memory function is given by

$$\varphi(\vec{\mathbb{k}}, \vec{\mathbb{p}}\vec{\mathbb{p}}', z) = \int d^3\bar{p} \left[\left(z - \frac{\vec{\mathbb{p}}\cdot\vec{\mathbb{k}}}{m} \right) S(\vec{\mathbb{k}}, \vec{\mathbb{p}}\vec{\mathbb{p}}, z) \right.$$
$$\left. + S(\vec{\mathbb{k}}, \vec{\mathbb{p}}\vec{\mathbb{p}}, t=0) \right] S^{-1}(\vec{\mathbb{k}}, \vec{\mathbb{p}}\vec{\mathbb{p}}', z) , \tag{6}$$

where S^{-1} is the matrix inverse of S with respect to the momentum variables

$$\int d^3\bar{p}\, S(\vec{\mathbb{k}}, \vec{\mathbb{p}}\vec{\mathbb{p}}, z)\, S^{-1}(\vec{\mathbb{k}}, \vec{\mathbb{p}}\vec{\mathbb{p}}', z) = \delta(\vec{\mathbb{p}} - \vec{\mathbb{p}}') . \tag{7}$$

The inverse can be shown to exist. The expansion of φ in a small parameter is obtained merely by expanding S in that parameter and inserting the result into (6). We expand S^{-1} by means of the identity $(S_0 + S_1)^{-1} = S_0^{-1} - S_0^{-1} S_1 (S_0 + S_1)^{-1}$. For most small parameters, including the density, this expansion of S is to be used only for the purpose of finding φ; it is not physical except at very short times. If the notation seems confusing, the reader will note that this procedure is equivalent to expanding S and solving (5) in each order for φ. For simplicity, the present calculation is set up along the latter line.

It is convenient to work in the grand canonical ensemble, where a density expansion is first formulated as an expansion in the fugacity $\zeta = e^{\beta\mu}$. We actually find the first term in the fugacity expansion of φ. Since ζ goes to zero linearly with the density, this term is also the leading term in the density expansion. (The same program is followed by Mazenko.) A function F of the particle coordinates has the average

$$\langle F \rangle = \Xi^{-1} (\beta\zeta V) \sum_{N=0}^\infty \frac{\zeta^N}{N!\, h^{3N}} \int d1 \cdots dN\, e^{-\beta H_N (1\cdots N)}$$
$$\times F(1 \cdots N) , \tag{8}$$

where $1 = (\vec{r}_1, \vec{p}_1)$, etc., H_N is the Hamiltonian of the N-particle system, and h is Planck's constant; Ξ is the grand partition function, and the limit $V \to \infty$ is understood as the final step in the averaging process. Restricting attention to a two-body potential $v(r)$ of range r_0, we can eliminate the fugacity in terms of the density by the familiar cluster expansion[6]

$$n = y[1 + y \int d^3 r f(r) + O(y r_0^3)^2] , \tag{9}$$

where $y = \zeta (2\pi m/\beta h^2)^{3/2}$ (called the activity) and $f(r) = e^{-\beta v(r)} - 1$. Inversion of (9) gives the activity in terms of the density,

$$y = n[1 - n \int d^3 r f(r) + O(n r_0^3)^2] . \tag{10}$$

It is trivial to work out the first few terms in the expansion of S in powers of ζ, or equivalently of y. They can be written as

$$S = y S_1 + y^2 S_2 + O(y^3) , \tag{11a}$$

$$S_1(\vec{r}, \vec{\mathbb{p}}\vec{\mathbb{p}}', t) = \delta\left(\vec{r} - \frac{\vec{\mathbb{p}}}{m} t \right) \Phi(p) \delta(\vec{\mathbb{p}} - \vec{\mathbb{p}}') , \tag{11b}$$

$$S_2(\vec{r}, \vec{\mathbb{p}}\vec{\mathbb{p}}', t) = \frac{1}{2!} \int d1\, d2\, \Phi(p_1) \Phi(p_2) \left[e^{-\beta v(r_1 - r_2)} \left(e^{itL(12)} \sum_{i=1}^2 \delta(x - x_i) \right) \sum_{j=1}^2 \delta(x' - x_j) \right.$$
$$\left. - \sum_{i=1}^2 [e^{itL_0(12)} \delta(x - x_i)] \delta(x' - x_i) \right] - \Phi(p) \Phi(p') . \tag{11c}$$

In these expressions, Φ is the Maxwellian

$$\Phi(p) = \left(\frac{\beta}{2\pi m}\right)^{3/2} e^{-\beta p^2/2m} , \qquad (12)$$

the two-body streaming operators are

$$iL_0(12) = \frac{\vec{p}_1}{m} \cdot \vec{\nabla}_1 + \frac{\vec{p}_2}{m} \cdot \vec{\nabla}_2 ,$$

$$iL_1(12) = -\vec{\nabla}_1 v(r_1 - r_2) \cdot \left(\frac{\partial}{\partial \vec{p}_1} - \frac{\partial}{\partial \vec{p}_2}\right) ,$$

$$iL(12) = iL_0(12) + iL_1(12) , \qquad (13)$$

and $x = (\vec{r}, \vec{p})$, $x' = (0, \vec{p}')$. Note that the symmetries[3] of S persist to each order of the expansion.

We find the fugacity expansion of φ by taking

$$\varphi = \varphi_0 + y\,\varphi_1 + O(y^2) \qquad (14)$$

and matching powers of y in (5). It is obvious that $\varphi_0 = 0$, since S_1 evolves by free streaming. Thus we find for φ_1,

$$\varphi_1(\vec{k}, \vec{p}\vec{p}', z)\Phi(p') = -\left(z - \frac{\vec{p}' \cdot \vec{k}}{m}\right)\left[\left(z - \frac{\vec{p} \cdot \vec{k}}{m}\right)\right.$$

$$\left. \times S_2(\vec{k}, \vec{p}\vec{p}', z) + S_2(\vec{k}, \vec{p}\vec{p}', t=0)\right] . \qquad (15)$$

For further reduction it is convenient to note that $S_2(\vec{r}, \vec{p}\vec{p}', t)$ satisfies

$$\left(\frac{\partial}{\partial t} + \frac{\vec{p}}{m} \cdot \vec{\nabla}\right)\left(\frac{\partial}{\partial t} + \frac{\vec{p}'}{m} \cdot \vec{\nabla}\right) S_2(\vec{r}, \vec{p}\vec{p}', t)$$

$$= -\frac{1}{2!} \int d1\, d2\, \Phi(p_1)\Phi(p_2)\, e^{-\beta v(r_1 - r_2)}$$

$$\times \left(e^{itL(12)} iL_1(12) \sum_{i=1}^{2} \delta(x - x_i)\right)$$

$$\times iL_1(12) \sum_{j=1}^{2} \delta(x' - x_j) . \qquad (16)$$

The transform of this equation, in conjunction with (15), leads to

$$\varphi_1(\vec{k}, \vec{p}\vec{p}', z)\Phi(p') = \left[i\left(\frac{\partial}{\partial t} + i\frac{\vec{p} \cdot \vec{k}}{m}\right) S_2(\vec{k}, \vec{p}\vec{p}', t)\right]_{t=0}$$

$$+ i\int_0^\infty dt\, e^{izt} \int d^3r\, e^{-i\vec{k}\cdot\vec{r}}$$

$$\times [\text{right-hand side of (16)}] . \qquad (17)$$

This shows that φ_1 breaks up into a static part (independent of z) and a "collisional" part: $\varphi_1 = \varphi_1^{(s)} + \varphi_1^{(c)}$. They are given by, respectively, the first and second terms on the right-hand side.

The static part is readily reduced to

$$\varphi_1^{(s)}(\vec{k}\vec{p}) = -\frac{\vec{p} \cdot \vec{k}}{m} f(k)\,\Phi(p) . \qquad (18)$$

To zero order in the fugacity, the direct correlation function is given by $c(r) = f(r)$, and so (18) contains the Fourier transform of c. Therefore, at low density, $\varphi^{(s)} = -n\vec{p} \cdot \vec{k}c(k)\Phi(p)/m$, the factor of n coming from the expansion parameter in (14). This also happens to be the general expression,[7,8] obtained most easily by a large-z expansion of (5).

The collisional part of φ_1 can be reduced by the change of variables,

$$\vec{p}_1 + \vec{p}_2 = 2\vec{\alpha}, \quad \vec{p}_1 - \vec{p}_2 = 2\vec{p} ,$$

$$\vec{r}_1 + \vec{r}_2 = 2\vec{R}, \quad \vec{r}_1 - \vec{r}_2 = \vec{r} , \qquad (19)$$

and integration over $\vec{r}$, $\vec{R}$, and t. The result is

$$\varphi_1^{(c)}(\vec{k}, \vec{p}\vec{p}', z)\Phi(p') = \frac{\partial}{\partial p_i}\frac{\partial}{\partial p_j}\int d^3\alpha\, d^3\bar{p}\, d^3\vec{r}\left(\frac{\beta}{\pi m}\right)^3 e^{-\beta\alpha^2/m - \beta\bar{p}^2/m} g(\vec{r})\nabla_j v(\vec{r})\left[e^{(i\vec{k}\cdot\vec{r})/2}\delta(\vec{p}' - \vec{\alpha} - \vec{p})\right.$$

$$\left. - e^{-(i\vec{k}\cdot\vec{r})/2}\delta(\vec{p}' - \vec{\alpha} + \vec{p})\right]\left[z - \frac{\vec{\alpha} \cdot \vec{k}}{m} - i\left(2\frac{\vec{p}}{m} \cdot \vec{\nabla} - \vec{\nabla}v(\vec{r}) \cdot \frac{\partial}{\partial\vec{p}}\right)\right]^{-1} \nabla_i v(\vec{r}) e^{-(i\vec{k}\cdot\vec{r})/2}\delta(\vec{p} - \vec{\alpha} - \vec{p}) . \qquad (20)$$

When the factor of n in the expansion parameter is taken into account, this agrees with the Mazenko expression.

In conclusion, it seems worthwhile to point out the corresponding memory function for the self-correlation function,

$$S_s(\vec{r}, \vec{p}\vec{p}', t) = \langle \sum_i \delta(\vec{r} - \vec{r}_i(t))\, \delta(\vec{p} - \vec{p}_i(t))$$

$$\times \delta(\vec{r}_i(0))\, \delta(\vec{p}' - \vec{p}_i(0))\rangle . \qquad (21)$$

The quantity S_s satisfies a Langevin equation like (3), with memory kernel φ_s. The preceding method applies equally well to self-correlations. We obtain φ_s merely by ignoring dynamical correlations between different particles in the collisional part of φ. There is no static contribution. Thus to lowest order in the density, φ_s/n is given by the right-hand side of (20) with the term $e^{-(i\vec{k}\cdot\vec{r})/2}$ $\times \delta(\vec{p}' - \vec{\alpha} + \vec{p})$ removed. This kernel is a wavelength- and frequency-dependent generalization of the kernel in the neutron transport equation.

The application of the present method to higher orders in the density is being studied. A quantum-mechanical discussion is also possible, but special

care must be used to handle the momentum variables.

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Computation of Pressure Effects of Inert-Gas Mixtures on Atomic Line Shapes[*]

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Recent line-shape experiments on the absorption series of cesium pressurized by various concentration ratios of argon and helium provide an opportunity to study the additivity of perturber interactions. Calculations which assume additivity and which assume additive adiabatic collisions agree well with the reported data. The results suggest that a systematic study of such experiments using accurate digitized data can furnish criteria for the valid applications of the additivity approximation.

A variety of approximations are invoked in order to compute the pressure effects of neutral perturbing atoms on atomic spectra. One of the most common is that the effects of various perturbers add as scalars, an assumption that is not generally correct. On the other hand, the principal features of line structure can be explained for a variety of experiments by calculations which employ the approximation.[1] The criteria for applying other common approximations are well established, e.g., the impact approximation,[2] and the classical-path approximations.[3] These criteria appear as inequalities and there is rarely any experimental evidence to indicate whether the inequality should read "very much greater than" or "about equal to." In order to obtain realistic reliable comparisons with experiment, it is important to establish how sensitive line-shape theories are to the assumptions of additivity. Viewed differently, it would be very interesting if line-shape studies could be used as a probe of the phenomena of nonadditivity. The purpose of this paper is to indicate some requirements that the additivity assumption imposes on the computed spectra and to relate these requirements to recent experimental work of Ch'en and Garrett[4] which was focused on these questions.

The experiments studied the effect of various mixtures of inert gases on the absorption spectrum of the principal series of cesium. For example, Fig. 1 of Ref. 4 displays three absorption contours of the fourth doublet of cesium, all measured at 251 °C: The first corresponds to the case when 110.5 lb/in.^{2} of pure argon is used to pressurize a small amount of cesium, the second is for 110.5 lb/in.^{2} of helium, and the third is for 221 lb/in.^{2} of a mixture of argon and helium in equal concentrations. (It is this experiment that we shall focus on in the sequel.) In general, their results indicate that the shifts of the lines in the pure cases add algebraically to yield the shift in the mixed case and that the sum of the widths in the pure cases is about $\frac{3}{4}$ of the width of the line in the mixed case.

If, in fact, the effects of helium and argon are independent, the resultant line should be a convolution of the lines in the pure cases. That such a convolution produces qualitative agreement with the experimental results can be seen clearly by considering two idealized shapes:

$$F_1(\omega) = e^{-(\omega - d)^2/2\sigma^2}$$

and

$$F_2(\omega) = e^{-(\omega + d)^2/2\sigma^2} .$$

The resultant shape is proportional to $e^{-\omega^2/4\sigma^2}$, which is a line centered at $\omega = 0$ (the sum of the shifts) and which has a width that is 0.71 times the sum of the original widths.

The line shape is computed by taking the Fourier transform of the correlation function $C(t)$,